Chapter VI

Study of Temperature Dependent Thermal Conductivity and Viscosity of Aqueous and Non-Aqueous Magnetite Nanofluids

6.1 Introduction
6.2 Effect of Temperature on Thermal Conductivity of Nanofluids
6.3 Effect of Temperature on Particle Size Distribution of Nanofluids
6.4 Effect of Temperature on Viscosity of Nanofluids
6.5 Conclusions
Chapter VI

Study of Temperature Dependent Thermal Conductivity and Viscosity of Aqueous and Non-Aqueous Nanofluids

6.1 Introduction

Among various issues pertaining to heat transport in nanofluids, one of the area lacking consensus is the exact dependence of temperature on k of nanofluids. Some of the studies show an enhancement in k ratio (k/k\textsubscript{f}) with temperature while others reports invariant k/k\textsubscript{f} with rise in temperature. Also, a decrease in k/k\textsubscript{f} with temperature is reported in some cases. Contradictory temperature dependent k results are reported both for metal and metal oxide nanofluids even in the same base fluids. Most of the studies in water based alumina (Al\textsubscript{2}O\textsubscript{3}) nanofluids show an enhancement in k/k\textsubscript{f} with temperature. An enhancement in k/k\textsubscript{f} with temperature is also reported in EG based Al\textsubscript{2}O\textsubscript{3} nanofluids. A few reports show temperature independent thermal conductivity for water, EG and hexadecane based Al\textsubscript{2}O\textsubscript{3} nanofluids where the k of nanofluids simply follows that of the base fluids. An enhancement in k/k\textsubscript{f} and a constant k/k\textsubscript{f} ratio are reported in water based CuO nanofluids with increase in temperature. Similarly, both an enhancement and a constant k/k\textsubscript{f} with increase in temperature is reported for water based titania (TiO\textsubscript{2}) nanofluids. Among other metal oxide nanofluid studied, kerosene and transformer oil based Fe\textsubscript{3}O\textsubscript{4} nanofluids showed least temperature effect on k. Studies in metal nanofluids show an increase in k/k\textsubscript{f} with temperature for kerosene and water based Ag nanofluids. Toluene based gold (Au)
nanofluids also show an increase in $k/k_f$ with temperature.\[^{38}\] However, a constant $k/k_f$ was reported for Au in toluene and Au in water nanofluids with increase in temperature.\[^{62, 110}\] Studies show enhancement in $k/k_f$ with temperature for water and EG based carbon nanotube (CNT) nanofluids.\[^{100-103}\] Multi Walled CNTs (MWCNTs) dispersed in EG showed a temperature independent $k/k_f$.\[^{113}\] Among the other nanofluids studied, TiO$_2$ nanotubes in water, diamond nanoparticles in water, aluminum (Al) nanoparticles in engine oil, amorphous carbonic nanoparticles in water and tin oxide (SnO$_2$) nanoparticles in water have shown enhancement in $k/k_f$ with temperature.\[^{87, 90, 96, 98, 99}\] However, for silicon carbide (SiC) in water, zinc oxide (ZnO) in EG, graphene oxide nanosheets dispersed in water, EG, propyl glycol and liquid paraffin, the $k/k_f$ was found to be independent of temperature.\[^{35, 63, 109}\] Interestingly barium titinate (Bi$_2$Te$_3$) nanorods exhibits a decrease in $k/k_f$ with increase in temperature in both perfluron-heaxane and hexadecane based fluids.\[^{116}\] These conflicting reports warrant a systematic study on temperature dependent $k$ in stable aqueous and non-aqueous nanofluids. This is the main motivations behind the present study.

Another important and intriguing question that remained unanswered in the domain of thermal properties of nanofluids is the effect of temperature on nanoparticle clustering and viscosity. DLS and $\eta$ measurements are the two widely accepted tools to probe effect of aggregation in nanofluids.\[^{58, 62, 63, 128, 136, 147, 148, 150-152, 155-160, 275}\] The purpose of this systematic study is to obtain insight into the exact dependence of temperature on $k$, particle agglomeration, and $\eta$ in well tailored ‘stable’ nanofluids.
6.2 Effect of Temperature on Thermal Conductivity of Nanofluids

Stable oil based nanofluids for the present study is prepared by dispersing oleic acid coated magnetite nanoparticles in kerosene and hexadecane. TMAOH coated magnetite nanoparticles are used for preparation of stable water based nanofluids. Figures 6.1 show the variation of $k$ as a function of temperature for kerosene based $\text{Fe}_3\text{O}_4$ nanofluids.

![Image](image.png)

Fig. 6.1: The variation of thermal conductivity with temperature for kerosene based $\text{Fe}_3\text{O}_4$ nanofluids with $\phi = 0, 0.008, 0.027, 0.05, 0.078$ and $0.095$.

Here, the base fluid $k$ includes the surfactant contribution. $k$ experiments are performed with base fluid alone and with the exact amount of surfactant that is adsorbed onto the nanoparticles. In order to take into consideration of the contribution of surfactant present in the base fluid $k$, the surfactant and base fluid $k$ is used as $k_f$. Present experiments show no observable changes in the $k$ values upon the addition of surfactant. The $\phi$ equal to zero corresponds to the base fluid $k$ (i.e., $k_f$). Over the temperature range of 25 to 50 °C, the absolute $k$ of kerosene based nanofluids and the base fluid decreases with the increase in temperature. A similar trend of decrease in $k$ with
the increase in temperature is observed in kerosene-based silver nanofluids.\textsuperscript{[312]} Interestingly, $k/k_f$ (Fig. 6.2) remains constant with an increase in temperature for kerosene based nanofluids.

![Graph](image)

**Fig. 6.2:** The variation of thermal conductivity ratio with temperature for kerosene based $\text{Fe}_3\text{O}_4$ nanofluids with $\phi$ = 0.008, 0.027, 0.05, 0.078 and 0.095.

Figures 6.3 (a) and (b) shows the variation of $k$ and its ratio as a function of temperature for hexadecane based $\text{Fe}_3\text{O}_4$ nanofluids. Over the 25 to 50 °C, the $k$ of hexadecane based nanofluids decreases with the increase in temperature [Fig. 6.3(a)]. But, again the $k/k_f$ remains invariant with the rise in temperature [Fig. 6.3(b)]. Figures 6.4 (a) and (b) shows the variation of $k$ and its ratio as a function of temperature for water based $\text{Fe}_3\text{O}_4$ nanofluids. Over 25 to 50 °C, the $k$ of water based nanofluids increases with increase in temperature [Fig. 6.4(a)]. Such an increase in $k$ with temperature was reported earlier in water based nanofluids.\textsuperscript{[92, 101, 114]} Interestingly, the thermal conductivity ratio remains invariant with the rise in temperature for water based nanofluids [Fig. 6.4(b)].
Fig. 6.3 (a): The variation of thermal conductivity with temperature for hexadecane based Fe$_3$O$_4$ nanofluids with $\phi=0$, 0.0165 and 0.0608. (b): The variation of thermal conductivity ratio with temperature for the above nanofluids.

Fig. 6.4 (a): The variation of thermal conductivity with temperature for water based Fe$_3$O$_4$ nanofluids with $\phi=0.0102$ (b): The variation of thermal conductivity ratio with temperature for the above nanofluids.
Why does the temperature-dependent $k$ show a different trend in water and oil-based nanofluids? The relationship for the $k$ in terms of fundamental properties of the liquid is $k = 2R\nu\Delta^{-2}$ where $R$ is the gas constant, $\nu$ is the velocity of sound in the liquid and $\Delta$ is the mean distance of separation of the centers of the molecules.\textsuperscript{[315]} The conductivity of water is three to four times as high as that of the ordinary organic liquids because of its low compressibility and the fact that the centers of the molecules in water are closer together than in the ordinary liquid. The above formula gives the right sign for the temperature coefficient of conductivity at atmospheric pressure, both for ordinary liquids and water. For the ordinary liquid, both $\nu$ and $\Delta^{-2}$ decrease with rising temperature, so that the conductivity is expected to decrease with rising temperature, as it actually does, whereas for water $\nu$ increases with rising temperature (both the isothermal compressibility and the thermal expansion of water vary abnormally with temperature) at a rate more than that is sufficient to compensate for the decrease of $\Delta^{-2}$, so that on the whole the conductivity should increase. This perhaps explains the different trend in temperature dependence observed between aqueous and nonaqueous nanofluids.

These results suggest that the $k$ of the nanofluids simply track the $k$ of the base fluid. A similar $k$ variation with increase in temperature was reported for both water and oil based nanofluids.\textsuperscript{[25, 35, 61-63, 108, 109, 111, 113, 313]} Many studies show an increase in $k/k_f$ with temperature for aqueous and nonaqueous nanofluids.\textsuperscript{[38, 49, 54, 72, 74, 87, 89-93, 96, 98-103, 115, 311, 312]} By taking into consideration the interfacial thermal resistance and the mixing of convection currents from multiple nanoparticles, the ratio $k/k_f$ according to microconvection model is\textsuperscript{[316]}

\[
\frac{k}{k_f} = \left(1 + Z\text{Re}^{0.333}\text{Pr}^{0.333}\frac{\phi^{1/3} + 2\beta\phi}{1 - \beta\phi}\right)^{-1}
\] (6.1)
where $\omega$ is a system-specific exponent. For aqueous suspensions, $\omega$ is found to have an optimal value of 2.5, $Z$ is constant with values as large as $4 \times 10^4$, $Re$ is the Reynolds number of the particle and $Pr$ the Prandtl number of the base fluid. The hypothesized microconvection effects appear through $Re = \nu_N d/\eta$, where $\nu_N$ is the convection velocity, $\eta$ is the viscosity and $d$ is the particle size. In the microconvection model, the convection velocity is taken to be the root-mean-square velocity ($\nu_N$) of the nanoparticle, defined as

$$\nu_N = \sqrt{\frac{18k_B T}{\pi \rho d^3}} \quad (6.2)$$

Where $k_B$ is the Boltzmann constant, $T$ the temperature, $\rho$ the density of particles, and $d$ size of nanoparticle. The $k/k_f$ results observed in our experiments is contrary to the semi-empherical convective model predictions,[316] but the results are in good agreement with the traditional Maxwell-Garnett model for composites.[317]

Figure 6.5 shows the variation of $k$ ratio with volume fraction at three different temperatures (25, 40 and 50 °C) for kerosene based Fe$_3$O$_4$ nanofluids. Maxwell fit is shown by the black dotted lines. The $k$ increases linearly and the data fit well with Maxwell model. According to kinetic theory, the enhancement in $k$ due to the Brownian movement of the particles is $\phi C_N \nu_N l_N/3$, where $C_N$ is the heat capacity per unit volume of the nanoparticles, $\nu_N$ root-mean-square velocity of Brownian particle and $l_N$ is the mean free path.

As nanoparticles start to form aggregates of larger size or chains, the convection velocity $\nu_N$ drops drastically due to the cube dependence of particle size and increases linearly with square root of $T$ and hence the $k$ is also expected to increase in the same manner irrespective of the fluid used. The present observation is in sharp contrast to the microconvection theory predictions of an
increase in thermal conductivity with a rise in temperature. These results once again reaffirm that microconvection has a less prominent role on thermal conductivity enhancement of nanofluids.

Fig. 6.5: The variation of thermal conductivity ratio with volume fraction at three different temperatures (25, 40, and 50 °C) for kerosene based Fe$_3$O$_4$ nanofluids. The Maxwell fit is shown by the dotted line.

According to microconvection models,\textsuperscript{[142]} the time required for a Brownian particle to travel its diameter $t_B$, is $3\pi\eta d^3/2k_BT$, where $\eta$ is the viscosity of base fluid, $d$ is the nanoparticle size, $T$ is the temperature and $k_B$ the Boltzmann constant. Their study with dye diffusion shows that Brownian motion of the particles does not contribute directly to the mass transport enhancement but it enhances the convection currents due to increase in the nanoscale stirring of the liquid. The Brownian models assume that the nanofluid $k$ is directly dependent on the self diffusion coefficient of nanoparticles. If micro-convection contributes to the enhanced $k$, the $k/k_f$ ratio would have increased with increase in temperature. A constant ratio of $k/k_f$ observed in the present experiments indicates a less important role of microconvection of $k$ enhancement. By a simple analysis Keblinski et al\textsuperscript{[140]} have proved that thermal diffusion is much faster than
nanoparticle Brownian motion; thus the movement of nanoparticles has a negligible effect on the effective k of the suspension. Molecular dynamics simulations in a model nanofluid have shown that Brownian motion of the particle does not affect the cooling process.\textsuperscript{[318]} Kinetic theory based analysis of heat flow in nanofluids demonstrates that the hydrodynamics effects associated with Brownian motion have only a minor effect on the k of the nanofluid.\textsuperscript{[319]} Moreover estimation of the k enhancement in nanofluids as a function of temperature from thermal diffusivity measurements on the nanofluids and base fluids at temperatures in the range of 25–75°C have shown that the k enhancement is independent of temperature.\textsuperscript{[65]}

The observed temperature independent k in the present study is consistent with effective medium theory (EMT). EMT is applicable to statistically homogeneous and low volume fraction liquid–solid suspensions with randomly dispersed and uniformly sized spherical particles. According to EMT, the effective k of nanofluids relies on the k of the spherical particle, the base fluid and the volume fraction of the solid particles. No temperature dependence of the k enhancement is considered by this model.

### 6.3 Effect of Temperature on Particle Size Distribution of Nanofluids

Figure 6.6 shows effect of temperature on average particle size of kerosene based nanofluid at different volume fractions of 0.00819, 0.027, 0.05, 0.078 and 0.095. The DLS measurements show no change in the size with rise in temperature (Inset of Fig 6.6), which indicates the absence of aggregation with temperature. Figure 6.7 shows the variation of average particle size with temperature for hexadecane based ferrofluids with φ = 0.0608. Inset shows the number percentage vs. size for the above nanofluid at 25, 35 and 50 °C. The average particle size does
not change with temperature for hexadecane based nanofluids also. Water based nanofluids (Fig. 6.8) also shows an invariant average particle size with temperature.

Fig. 6.6: The variation of average particle size with temperature for kerosene based Fe$_3$O$_4$ nanofluids with $\phi$= 0.00819, 0.027, 0.05, 0.078, and 0.095. Inset shows the number percentage vs size for nanofluids with $\phi$=0.00819 and 0.095 at 25, 35, and 50 °C.

The aggregation time constant is given as $t_p = (\pi r^3 W)/(k_B T \phi)$, where $W$ is the stability ratio, $r$ is the particle radius; $\phi$ is the volume fraction. For a stable system, $t_p$ tends to infinity. The stability ratio is assumed to be unity in the absence of a repulsive force and hydrodynamic interactions between the nanoparticles and it is greater than one in the presence of a repulsive forces. According to the above equation, aggregation time constant decreases with decrease in nanoparticle size and with increase in temperature.
Fig. 6.7: The variation of average particle size with temperature for hexadecane based Fe$_3$O$_4$ nanofluids having $\phi=0.0608$. Inset shows the number percentage vs size for the above nanofluid at 25, 35, and 50 °C.

Fig. 6.8: The variation of average particle size with temperature for water based Fe$_3$O$_4$ nanofluids having $\phi=0.0102$. Inset shows the number percentage vs size for the above nanofluid at 25, 35, and 50 °C.
With increasing temperature, Brownian motion increases and so aggregation time constant decreases, leading to a higher probability for particles to aggregate. Interestingly DLS studies show no sign of aggregation with temperature in our samples. This is also independently confirmed from static light scattering studies.\cite{320}

The present results show that the aggregation is essentially governed by surface chemistry of the nanoparticles and the stabilizing moieties used. Proper steric stabilization with a high potential barrier (>10k_BT) prevents the particles crossing the barrier. Further, the presence of surfactant monolayer leads to complete wetting of the particle by the liquid medium, which has a major role on the interfacial resistance. In such stable nanofluids, the aggregation is negligible at higher temperatures.

### 6.4 Effect of Temperature on Viscosity of Nanofluids

Figures 6.9 and 6.10 show the variation in $\eta$ of kerosene based Fe$_3$O$_4$ nanofluids and its ratio (with respect to base fluid) respectively for three different volume fractions of nanoparticles. Although the absolute $\eta$ decreases with increase in temperature in both the base fluids and the nanofluids, the $\eta$ ratio remains almost constant with increase in temperature, which is a clear indication for the absence of aggregation with temperature. A similar viscosity behavior with temperature was reported for other nanofluids also.\cite{163, 113, 144, 146} A constant viscosity ratio is also observed with increase in temperature in water and hexadecane based Fe$_3$O$_4$ nanofluids in our study.
Fig. 6.9: The variation of viscosity with temperature for kerosene based Fe$_3$O$_4$ nanofluids having \( \phi = 0, 0.027, 0.05, \) and \( 0.095 \).

Fig. 6.10: The variation of viscosity ratio with temperature for kerosene based Fe$_3$O$_4$ nanofluids with \( \phi = 0.027, 0.05, \) and \( 0.095 \).
Almost all the exiting theoretical formulas which are used for the determination of particle suspension viscosity was derived from Einstein analysis of infinitely dilute suspensions of hard spheres.\textsuperscript{[321]} In Einstein model, the particles are assumed to be rigid, uncharged and without attractive forces; they are small enough so that the dilatational perturbation of the flow is unbounded and is able to decay to zero. A particle moves at the velocity of the streamline with the particle centre in such a suspension. Einstein equation describes the dependence of viscosity increase with concentration of particles in the simplest case of dilute suspensions ($\phi \leq 0.01$) as

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi$$ \hspace{1cm} (6.3)

Where, $\eta$ is the nanofluid viscosity and $\eta_0$ the base fluid viscosity.

When $\phi \geq 0.01$, hydrodynamic interactions between particles become important as the disturbance of the fluid around one particle interacts with that around other particles. The viscosity in such a case is given by Batchelor equation\textsuperscript{[322]}

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi + 6.5\phi^2$$ \hspace{1cm} (6.4)

For $\phi \geq 0.1$, where multi-particle collisions become increasingly important, a semi-empirical relationship for the shear viscosity covering the full range of particle volume fraction was obtained by Krieger and Dougherty\textsuperscript{[323]}

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-\frac{1}{3}}$$ \hspace{1cm} (6.5)
where, $[\eta]$ is the intrinsic viscosity, which is 2.5 for hard spheres and $\phi_m$ is the maximum packing fraction. For randomly mono-dispersed spheres, the maximum close packing fraction is approximately 0.64. Figure 6.11 shows variation of viscosity ratio with volume fraction for kerosene based ferrofluids together with Einstein and Krieger-Dougherty (KD) fit.

![Figure 6.11: The variation of viscosity ratio with volume fraction for kerosene based Fe$_3$O$_4$ nanofluids at 25 °C together with the Einstein and Krieger-Dougherty (KD) fit.](image)

The results show that the enhancement in viscosity ratio with $\phi$ is much more than the values predicted by Einstein and K-D models. Some of the studies show a moderate viscosity enhancement\textsuperscript{[63, 87, 115, 143-145, 160]} while others reports a very high viscosity enhancement\textsuperscript{[98, 147, 153, 161, 163]} in nanofluids compared to Einstein model.

Functional dependence of the viscosity on the fluid temperature can be expressed by Arrhenius-type equation.\textsuperscript{[324]}

$$\eta = \eta_0 e^{E_r / k T}$$  \hspace{1cm} (6.6)
where $\eta$ is the viscosity from experimental tests, $\eta_\infty T$ is the viscosity at infinite temperature, $E_a$ is the activation energy to fluid flow, $R$ is the universal gas constant, and $T$ is the temperature in Kelvin. The activation energy and infinite temperature viscosity are parameters that reflect the behavior of fluids and can be extracted from experimental data through the logarithmic form of the Arrhenius equation.

We have also measured the viscosity of the nanofluid as a function of the shear rate ($10^-1000 \text{ s}^{-1}$) at different temperatures. Figures 6.12 and 6.13 shows variation of viscosity with shear rate at different temperatures for kerosene based $\text{Fe}_3\text{O}_4$ nanofluids with $\phi=0$ (base fluid), $\phi = 0.027$, $\phi = 0.050$ and $\phi = 0.095$.

![Graph showing viscosity variation with shear rate at different temperatures](image)

Fig. 6.12: The variation of viscosity with shear rate at different temperatures for kerosene and kerosene based $\text{Fe}_3\text{O}_4$ nanofluids with $\phi = 0.027$.

Our results show that the viscosity is independent of shear rate from 25 to 50 °C, indicating that the nanofluids are stable and possess Newtonian nature. Such Newtonian nature of viscosity was reported for both metal and metal oxide based nanofluids.
Fig. 6.13: The variation of viscosity with shear rate at different temperature for kerosene based Fe₃O₄ nanofluids with φ= 0.05 and φ=0.095.

Figure 6.14 shows the variation of viscosity with shear rate at different temperatures for hexadecane and hexadecane based Fe₃O₄ nanofluids with φ=0 (base fluid) and φ=0.0608. The viscosity did not appreciably vary, indicating Newtonian behavior, over the shear rate and temperature studied.

The effectiveness of nanofluid coolants depend on the flow mode (laminar or turbulent), that can be estimated based on fluid dynamics equations. Lower viscosity implies lower pumping power that is advantageous from an industrial application point of view.

A quantitative expression derived for fully developed laminar flow that compares the relative coefficients of viscosity and k enhancement shows that the use of nanofluid will be beneficial if the increase in the viscosity is less than four times of the increase in k.¹⁴⁴
Viscosity and thermal conductivity enhancements can be described by linear dependence on the particle volume fraction in our studies.

\[
\frac{k}{k_f} = 1 + C_k \phi \quad (6.7)
\]

\[
\frac{\eta}{\eta_0} = 1 + C_\eta \phi \quad (6.8)
\]

where \(C_k\) and \(C_\eta\) are constants. At low volume fractions, for the nanofluid to be beneficial, the ratio of coefficients \((C_\eta/C_k)\) should be < 4 \[^{[144]}\]. The value of \(C_k\) and \(C_\eta\) was found to be 3 and 11 respectively for kerosene based nanofluid with \(\phi = 0.027\) at 25 °C in our study. Thus the calculated \(C_k/C_\eta\) ratio of 3.6 is within the expected regime for efficient nanofluid. The above value was lower than the ratio reported for SiC and Al₂O₃ nanofluids \[^{[63]}\]. However, \(C_k/C_\eta\) was
found to be 7.3 and 7.8 for kerosene based nanofluids with $\phi = 0.05$ and 0.095 respectively in our study, implying that either viscosity needs to be reduced or conversely the $k$ at the same particle loading has to be improved further for practical applications.

### 6.5 Conclusions

The $k$ of aqueous nanofluids increases with temperature while it shows a decrease in nonaqueous nanofluids. The ratio of thermal conductivity of both nanofluids with respect to base fluids ($k/k_p$) remains constant with an increase in temperature, irrespective of the nature of the base fluid. These results suggest that the $k$ of the nanofluids simply track the $k$ of the base fluid and the enhancement in nanofluids relative to base fluids is essentially temperature independent. This observation is in sharp contrast to microconvection theory predictions of an increase in $k$ with a rise in temperature. These results unambiguously confirm the less dominant role of microconvection on $k$ enhancement.

Although the absolute $\eta$ decreases with an increase in temperature in both the base fluids and the nanofluids, the viscosity ratio remains almost constant with an increase in temperature, which is a clear indication of the absence of aggregation of particles with temperature. The results confirm that nanofluid simply track temperature depend viscosity behavior of base fluid and observed variation in $\eta$ with increasing temperature comes from the base fluid rather than from behavior associated with the nanoparticles. DLS studies show no aggregation of particles with temperature in stable water and oil based nanofluids.

The present results show that the aggregation is essentially governed by surface chemistry of the nanoparticles and the stabilizing moieties used. Nanoparticle aggregation is
insignificant with the increase in temperature in properly functionalized nanofluids. Such nanofluids are ideal for practical applications because of their long-term stability.