3.1 Introduction

Thermal properties of materials are extremely important for heat transfer applications. Nanofluids and nanomaterials have been a topic of great interest during the last decade primarily due to the initial reports of anomalous thermal conductivity enhancement (i.e. beyond Maxwell’s limits) in nanofluids with a small percentage of nanoparticles. Several recent studies in stable nanofluids show thermal conductivity enhancement within Maxwell’s limits. The reasons for the reported anomalous enhancement in thermal conductivity in nanofluids are still a topic of debate. After considering various mechanisms responsible for the observed enhancement in $k$, one of the most probable aspects considered in the recent years is the effective conduction of heat through percolating aggregating nanoparticle paths. However, many researchers still believe that the micro-nano convection could be another plausible cause for thermal conductivity enhancement. Another grey area in the understanding of thermal property variations in nanofluids is the role of interfacial resistance and the morphology of suspended nanoparticles in fluids. The former aspect is extremely important because most of the suspensions are stabilized using surface active species or surfactant. Though the mechanism of stabilization of nanoparticles by surfactants is quite well understood, their precise role on the interfacial thermal resistance, on thermal and rheological properties of nanofluids is still unclear. Therefore, a systematic study to understand the effect of interfacial resistance on thermal conductivity of liquids and suspensions is warranted, which is one of the key issues addressed in this study.
Nanofluids are thermodynamically unstable systems. However, they can be made kinetically stable with the aid of suitable surface active species. Unlike molecular fluids, production of well stabilized nanofluids is a difficult task. For the production of stable nanofluids, one has to produce fairly monodisperse nanoparticles and functionalize them with a suitable stabilizing moiety to prevent interparticle attractions. Owing to the large surface area to volume ratio of fine nanomaterials, the dispersed particles (even with stabilizing entities) have a tendency to aggregate because of van der Waals attraction. Even with the best available production route, it is difficult to produce nanoparticles with polydispersity less than 5%. However, to unravel the exact mechanism of heat conduction in nanofluids, model systems with high degree of monodispersity and well controlled morphology is necessary. To resolve the problem of high polydispersity of nanoparticles, model systems of micellar fluids with remarkable monodispersity, along with other nanofluids are chosen for the present study.

Though there are several studies on viscosity of nanofluids, a proper understanding of the role of $\eta$ on $k$ enhancement is still missing that is a very important aspect for thermal engineering. The particle concentration, particle-particle interactions, agglomeration and clustering of suspended entities play a major role in the reduced viscosity ($\eta/\eta_0$) where, $\eta_0$ is the viscosity of the basefluid.\textsuperscript{282} The rheological properties of nanofluids are strongly related to the conformation of suspended particles in the basefluids. Agglomeration in nanofluids is an undesirable effect that is difficult to control. Since agglomeration issue is practically negligible in micellar systems due to electrostatic or steric forces, it is one of the best model systems to study the role of viscosity on thermal and related properties.
The questions that are addressed in this study are the following (a) Do the $k$ enhancements in ‘soft’ and ‘hard’ nanofluids follow the effective medium theory? (b) What is the role of initial thermal conductivity, morphology and number density of suspended particles on thermal conductivity enhancement? (c) Do surface active moieties at nanoparticle interfaces enhance or reduce the $k$ of nanofluids? (d) What is the role of the aspect ratio of particles and their orientation with respect to heat flow direction on $k$ enhancement? For these studies, model soft systems of micelles in the size range of 2.5 to 7 nm with different head group charges and commercially obtained water based alumina, silica and non-aqueous kerosene based iron oxide nanofluids with particle size in the range of 12 to 15 nm were used. Through these systematic studies, the effect of surface active species on thermal conductivity, rheology, density, contact angle and refractive index are studied.

3.2 Materials and Methods

3.2.1 Materials

SDS, CTAB, NP9 and NP10 were used in this study. The critical micellar concentrations (CMC) for SDS, CTAB, NP9 and NP10 are $8\times10^{-3}$ M, $9\times10^{-4}$ M, $6\times10^{-5}$ M and $7\times10^{-5}$ M, respectively. The reported micellar diameter of SDS, CTAB, NP9 and NP10 are approximately 3.7, 5.0, 6.3 and 6.8 nm, respectively. The average aggregation number of micelles for SDS, CTAB, NP9 and NP10 are 64, 95, 350 and 144, respectively. For the studies, 16 vol% stock solutions of SDS, CTAB, NP9 and NP10 surfactants were prepared using milli-Q water with a resistivity value of 18.2 MΩ cm, from which different concentrations were prepared.

Water based γ-Al$_2$O$_3$, SiO$_2$ nanofluids and oil based Fe$_3$O$_4$ nanofluid were used to study the effect of adsorbed surfactant layer on thermal conductivity. Fe$_3$O$_4$ nanoparticles were
prepared by chemical coprecipitation technique.\textsuperscript{207, 252} The details of the materials used for this study are discussed in Chapter 2.

3.2.2 Methods

The thermal conductivity of the samples was measured by using a hot wire probe as per the procedure described in Chapter 2. Viscosity, FTIR, Contact angle and thermogravimetric analysis were carried out. DMA 35 portable densitometer from Anton Paar (Germany) was used for density measurements. Refractive index measurements were done using a Rudolph digital refractometer with peltier based temperature controller. Small angle X-ray scattering (SAXS) studies for nanofluids were carried out using Rigaku Ultima IV instrument. It uses Cu K$_\alpha$ (\(\lambda = 1.5418 \, \text{Å}\)) as X-ray source. The scattering intensity \(I(q)\) was measured as a function of the scattering vector \(q = \frac{4\pi \sin \theta}{\lambda}\). The scattering intensity plot was fitted with the spherical model equation, \(I(q) = |\Delta \rho|^2 \left\{ \frac{4\pi}{q^3} \left[ \sin \left( \frac{qd}{2} \right) - \frac{qd}{2} \cos \left( \frac{qd}{2} \right) \right] \right\}^2\) where, \(\Delta \rho\) is the difference in electron density of particle and the suspended medium. The most probable particle size was obtained from the distance distribution function.

3.3 Results and Discussion

3.3.1 DLS, SAXS, FTIR and TGA Analysis

Fig. 3.1 shows the hydrodynamic diameter of the water-based and kerosene based nanofluids. The average hydrodynamic sizes are found to be 13, 15 and 12.5 nm for \(\gamma\)-Al$_2$O$_3$, SiO$_2$ and Fe$_3$O$_4$ nanoparticles, respectively. The size distribution is found to be narrow for all the three nanofluids.
Figure 3.1: Hydrodynamic size distribution of water based uncoated γ- Al₂O₃, SiO₂ and oleic acid coated kerosene based Fe₃O₄ nanofluids.

Fig. 3.2(a) shows the X-ray scattering intensity as a function of scattering vector and Fig. 3.2(b) shows the particle size distribution obtained from the best fit on SAXS data for water based γ- Al₂O₃ and SiO₂ nanofluids and kerosene based Fe₃O₄ nanofluids. The most probable particle size is found to be 10.74 nm for γ- Al₂O₃ nanoparticle, 14.7 nm for SiO₂ nanoparticles and 11.66 nm for Fe₃O₄ nanoparticles. The average hydrodynamic diameter measured by DLS was slightly higher than that obtained from the SAXS results.
Figure 3.2: (a) The X-ray scattering intensity as a function of scattering vector and (b) the particle size distribution obtained from the best fit on SAXS data for water based γ-Al₂O₃ and SiO₂ nanofluids and kerosene based Fe₃O₄ nanofluid.

The thermogravimetric curves for γ-Al₂O₃ and SiO₂ nanofluids and Fe₃O₄ nanoparticles are shown in Fig. 3.3. The thermogravimetric curves for water based γ-Al₂O₃ and SiO₂ nanofluids (Fig. 3.3 (a&b)) show a single step weight loss at ≈ 103 °C (~75 wt%) and ≈ 105 °C (~71 wt%), respectively, corresponding to the loss of most of the water. Thereafter, a gradual decrease in weight is observed till 600 °C in both the cases. The gradual decrease in weight observed beyond 100 °C (till 600 °C) was about ~ 4 wt% and 6 wt%, respectively for γ-Al₂O₃ and SiO₂ nanofluids. The decrease in weight observed beyond 100 °C in the cases of γ-Al₂O₃ may be due to the dehydroxylation of the alumina surface.²⁹¹
Figure 3.3: The thermogravimetric curves for water based (a) γ-Al₂O₃ (b) SiO₂ nanofluids and (c) Fe₃O₄ nanoparticles.

The weight loss observed in γ-Al₂O₃ in the temperature range of 100-600 °C was similar to that observed by Costa et al. A similar trend in the thermogram was also observed in SiO₂ nanofluids. The TGA curve for the Fe₃O₄ nanoparticles shows a two-step weight loss between 199 to 310 °C (~ 4 wt% ) and between 310 to 400 °C (~12 wt% ) (Fig. 3.3(c)). The first step should be due to the removal of loosely bound or free surfactant and the second step should be due to the removal of strongly bound surfactant molecules.
The FTIR spectrum for Al₂O₃, SiO₂ and Fe₃O₄ nanofluids are shown in Fig. 3.4. Fig. 3.4 (a) corresponds to the FTIR spectrum of water based γ-Al₂O₃ nanofluid. The transmittance band at 746 cm⁻¹ corresponds to the stretching vibration of Al-O.²⁹² The spectrum shows characteristic peaks at 1074 and 1155 cm⁻¹ which corresponds to the Al-O-Al symmetric bending and stretching vibrations and Al-O-Al asymmetric bending modes, respectively.²⁹² The transmittance band at 1637 and 3290 (3575) cm⁻¹ corresponds to bending²⁰¹ and stretching modes of water, respectively. Fig. 3.4 (b) corresponds to the FTIR spectrum of SiO₂ nanofluid. The rocking, symmetric and asymmetric stretching of Si-O-Si are observed at
The FTIR spectrum of oleic acid coated iron oxide nanoparticles dispersed in kerosene is shown in Fig. 3.4 (c). The spectrum shows characteristic peaks at 2921, 2858, 2358, 1728, 1458, 1375, 1274, 632 and 570 cm$^{-1}$. The symmetric and asymmetric stretching mode of the methylene group of the oleic acid appears at 2858 and 2921 cm$^{-1}$, respectively. The peak at 1458 cm$^{-1}$ corresponds to the asymmetric stretching of the carboxylate (COO$^-$) group. The peak at 570 cm$^{-1}$ is attributed to the stretching of bonds between octahedral and tetrahedral metal ions to oxide ions while the one at 1728 cm$^{-1}$ is due to the presence of free oleic acid molecules. The rest of the peaks are attributed to the vibrations in kerosene. In all the three cases, a peak is noticed around 2360 cm$^{-1}$ that corresponds to asymmetric stretching mode of carbon dioxide.

### 3.3.2 Effect of Number Density of Dispersed Particle on Thermal Conductivity

Fig. 3.5 shows the variation of $k/k_f$ and the percentage of decrease in thermal conductivity as a function of surfactant concentration for SDS, CTAB, NP9 and NP10 in water. It should be noted that the surfactants are amphiphilic molecules with hydrophilic and hydrophobic parts. The surfactant molecules exist as unimers at concentrations below CMC and form spherical micelles above CMC. The driving forces for micelle formation are the hydrophobic force and entropy. The forces opposing micelle formation are concentration gradient, thermal motion and electrostatic repulsion between ionic polar heads (applicable to CTAB and SDS only). In all the four systems, the $k/k_f$ is found to decrease with increase in surfactant concentration. The micellar system is a disordered system. As the surfactant concentration increases the number of micelles in the system increases, leading to an increase in the degree of disorder, which has resulted in a decrease in $k/k_f$ with increase in surfactant concentration.
Figure 3.5: The variation of thermal conductivity as a function of volume fraction for SDS, CTAB, NP9 and NP10 along with the theoretical fit (The CMC values of surfactants are shown by arrows of respective symbol colors). Inset shows the schematic representation of micelles and the possible thermal resistive contributions from different moieties (head group, tail and water molecules). $R_0$, $R_H$, $R_T$ represents the resistance offered by water molecules, head group and tail, respectively.

Similar results were reported by Anderson, who observed that an increase in the disorder of the system can decrease the thermal conductivity. Muller suggested that the strength of the interatomic binding force is related to the thermal conductivity. The greater the strength of this binding force, the higher the thermal conductivity. The higher interatomic binding force in metals results in higher thermal conductivity. The binding force is weak in the case
of micellar systems due to its disordered structures leading to a lower thermal conductivity.

The number density for the micellar system is given by, \( n = \frac{6\varphi}{\pi d^3} \).

The experimental data are fitted with Maxwell model as shown by the solid line in Fig. 3.5. It can be seen that the experimental data show large deviations from effective medium theory at low volume fractions of micelles, especially for CTAB and NP9. At lower volume fraction, the number of micelles in the system is less and therefore, the interfacial thermal resistance is also less. As the volume fraction increases, the number of micelles in the system increases, which leads to higher interfacial thermal resistance. The lower interfacial thermal resistance at lower concentration might be a probable reason for the observed large deviation from theoretical fit at lower volume fractions. For volume fractions above 0.06, the experimental data fit quite well with the effective medium theory.

In general, the interfacial thermal resistance reduces the effective thermal conductivity. When \( \alpha \to \infty \), \( k/k_f \) reduces to \( (1-3\varphi/2) \), where the effective thermal conductivity becomes smaller than that of the base fluid. A negative interfacial thermal resistance means an interfacial thermal gradient that is lower than that of the bulk region. A positive \( R_k \) leads to a decrease in the effective thermal conductivity. Simulation studies in the nanofluids showed that a positive Kapitza, due to a weak solid-fluid interaction, can lead to a negligible or negative thermal conductivity enhancement.\(^{23, 296}\) The non-equilibrium molecular dynamics simulations show that the thermal conductivity of a well-dispersed nanofluid can be enhanced beyond the Maxwell limit through a percolating amorphous like fluid structure at the cluster interface, due to the strong cluster-fluid interaction.\(^{246}\) Our experimental data suggest that the interfacial resistance in the presence of surfactant is positive but far from infinity. The
Chapter III

interfacial thickness as given by Yan $^{113}$ is 

$$h = \frac{1}{\sqrt{3}} \left( \frac{4M_f}{\rho_f N_a} \right)^{\frac{1}{3}}$$

where, $M_f$ and $\rho_f$ are the molecular weight and density, respectively of the surrounding fluid medium around a nanocluster and $N_a$ is Avogadro’s number. Using the above expression, the calculated values of the interfacial thickness for water, SDS, CTAB, NP9 and NP10 are found to be 2.84, 71.5, 77, 90.9 and 93.7 nm, respectively. The observed larger reduction of thermal conductivity, especially at lower surfactant concentrations in NP9 and NP10, followed by CTAB and SDS are consistent with the theoretical values of interfacial thickness.

According to kinetic theory, the thermal conductivity is defined as,

$$k = \frac{1}{3} \sum_{\text{pol}} C V \Lambda_{\text{eff}} d\omega$$

where, $C$, $v$, $\omega$, $\Lambda_{\text{eff}}$ are the heat capacity, group velocity, frequency and the effective mean free path over all phonon polarizations, respectively. The thermal conductivity reduction in solids originates from scattering from the grain boundaries where the mean free path is a function of the average grain size and phonon frequency. Further, it also depends on the grain boundary structure and the impurity atoms at the boundary that affect the phonon transmission and reflection at each interface.$^{297-300}$ Very recently, it was reported that a substantial reduction in thermal conductivity in FeSb$_2$ occurs as the grain size decreases from micrometers to nanometers due to dominant scattering from smaller grains.$^{301}$ The porosity and phonon scattering at grain boundaries are found to be the dominant mechanisms for thermal conductivity reduction in nanocrystalline materials.$^{302}$ Isotopic doping $^{303-305}$ and a decrease in the phonon group velocity$^{306}$ can also cause reduction in thermal conductivity. In porous materials, thermal conduction through the solid phase, radiation across the pores and convection through the porous phase etc., contributes to the effective thermal conductivity.
The scattering of phonons by interaction with the surroundings or the presence of defects produced by the surfactant micelles in solutions can also lead to a decrease in thermal conductivity. Since phonons are scattered at surfaces and interfaces, a reduction in $k$ is anticipated with increase in the surface area-to-volume ratio. Experimental studies show that the excess SDS surfactants on the CNT surface can decrease the thermal conductivity enhancement of nanofluids due to an increase in the interfacial resistance. Assal et al. also reported a considerable decrease in thermal conductivity of water as the surfactant (CTAB) concentration increases.

It should be noted that the spherical micellar size of SDS is much smaller than that of CTAB, NP9 and NP10. Therefore, the total interfacial area ($\sim 1/r$ dependence) available for SDS is much larger than the other three. If the concept of phonon scattering at interfaces is invoked, $k$ should decrease with increase in the surface-to-volume ratio. However, the $k$ decrease was almost the same at high volume fraction for all the four surfactants. The average CTAB intermicellar spacing (IPS) reduces from 32 to 2.9 nm as the concentration is increased from $\phi = 0.002$ to 0.16 where the micellar number density increases from $2.41 \times 10^{22}$ to $2.43 \times 10^{24}$.

For NP9, the IPS reduces from 36 to 3.7 nm as the concentration is increased from $\phi = 0.002$ to 0.16 where the micellar number density increases from $1.58 \times 10^{22}$ to $1.21 \times 10^{24}$. For NP10, the IPS reduces from 41 to 4.2 nm as the concentration is increased from $\phi = 0.002$ to 0.16 where the micellar number density increases from $1.11 \times 10^{22}$ to $8.54 \times 10^{23}$. For SDS, the IPS reduces from 20 to 2 nm as the concentration is increased from $\phi = 0.002$ to 0.16 where the micellar number density increases from $8.64 \times 10^{22}$ to $6.1 \times 10^{24}$. Among all the four surfactant micelles, SDS seems to have the highest number density and lowest IPS. Therefore, SDS is expected to have the maximum thermal conductivity enhancement.
compared to the other surfactant. But from the experimental results it is clear that the thermal conductivity enhancement for non-ionic and cationic surfactant is more when compared to that of SDS for the same volume fraction. This may be due to the fact that the number of micelles present in the system for the same surfactant concentration is more in the case of non-ionic and cationic surfactants when compared to that of SDS, since the CMC for SDS is $8 \times 10^{-3}$ M, where as for CTAB, NP9 and NP10 the CMC are $9 \times 10^{-4}$ M $6 \times 10^{-5}$ M and $7 \times 10^{-5}$ M, respectively. Therefore the number of holes (disorder) in the systems studied follow the trend, NP10 $\approx$ NP9 $>$ CTAB $>$ SDS for the same volume fraction. Hence the decrease in thermal conductivity should be more for non ionic surfactant followed by cationic and anionic system, which was consistent with our experimental results.

3.3.3 Effect of Concentration of Dispersed Phase on Interfacial Tension

To study the effect of interfacial tension, the contact angle measurements were carried out for all the four surfactant solutions on a stainless steel substrate. Steel substrate is chosen as the hotwire probe used has a stainless steel body. Fig. 3.6 (a) shows the variation of contact angle as a function of concentration of surfactant solutions. As the surfactant concentration increases, the contact angle is found to decrease for all the four surfactant solutions.

It is known that the addition of surfactant to water reduces its surface tension or interfacial tension and causes it to spread on a substrate.\textsuperscript{308} The relationship between interfacial tension and contact angle is given by \textsuperscript{265} $\gamma^{sl} = \gamma^{sv} - \gamma^{lv} \cos \theta$. $\gamma^{lv}$ is calculated using the following formula\textsuperscript{309}

$$\cos \theta = -1 + \sqrt[\gamma^{sv}]{\gamma^{lv} e^{-0.000124 (\gamma^{lv} - \gamma^{nv})^2}}$$

(3.1)
On conversion of the solid to liquid surface tension using the above equations, the solid-liquid interfacial tension for SDS at $\phi = 0.002$ is $1.625 \text{ mJ/m}^2$, which reduces to $0.225 \text{ mJ/m}^2$ at $\phi = 0.09$.

**Figure 3.6:** (a) Contact angle as a function of volume fraction, (b) The reduced viscosity as a function of volume fraction along with the theoretical fits using Einstein, Batchelor and Krieger & Dougherty models (The CMC values of each surfactant are shown by arrows of respective symbol colors), (c) density and (d) refractive index as functions of surfactant concentration for SDS, CTAB, NP9 and NP10.
Similarly the interfacial tension of CTAB, NP9 and NP10 solutions decreased from 2.734 to 0.228 mJ/m$^2$, 0.913 to 0.074 mJ/m$^2$ and 1.98 to 0.06 mJ/m$^2$, respectively as the surfactant concentration decreases from $\phi = 0.02$ to 0.09. From our contact angle measurements, the calculated value of $\gamma_{sl}$ of water is 72.7 mJ/m$^2$ which is in good agreement with the reported value of 72.75 mJ/m.$^2$ The reported value of $\gamma_{sl}$ for CTAB on mica substrate is $1.5 \pm 1$ at one CMC concentration.$^{312}$ This clearly shows that the presence of surfactant micelles makes the fluid more hydrophilic. Theoretical studies show that $R_k$ attains a relatively larger value only when the liquid is more hydrophobic to the solid surface.$^{296, 313}$ Studies show that the orientation of adsorbed moieties of non-ionic surfactants changes with surfactant concentrations that results in changes in the free energy of adsorption.$^{314}$ An early study shows that the thermal conductivity of zinc-sulphide is increased when large particles of highly conducting diamond are added, but $k$ lowered when submicron size particles of diamond is added, which was attributed to the change in the interfacial thermal resistance at larger surface to volume ratio.$^{315}$ According to Debye model \[ R_{BD} = \frac{4}{\rho C_p v \eta} \] where $R_{BD}$ is the phonon boundary resistance. Therefore, thermal conductivity of the dispersion is \[ K_m = \frac{1}{3} \rho Cv l \] where ‘$l$’ is the phonon mean free path. The Kapitza radius, $a_k$ ($\sim l/q$) depends on the probability of phonon crossing at the interface. When particle size is less than the Kapitza radius, the effective conductivity of the dispersion is lowered by the particles.

3.3.4 Effect of Concentration of Dispersed Phase on Viscosity Enhancement

Fig. 3.6 (b) shows the reduced viscosity as a function of surfactant concentration for SDS, CTAB, NP9 and NP10. In all the four systems, the viscosity increase was nominal up to 0.05
The percentage of enhancement in viscosity at \( \varphi = 0.002 \) was 7, 13, 3 and 40\% for SDS, CTAB, NP9 and NP10, respectively. Further increase in the concentration of the surfactant leads to a dramatic enhancement in reduced viscosity for all the four surfactants. The reduced viscosity values at \( \varphi = 0.08 \) for SDS, CTAB, NP9 and NP10 are 1.95, 2.65, 27.59 and 13.03, respectively. What is the reason for the observed sharp increase in viscosity above a certain surfactant concentration? The large increase in the viscosity above 0.08 volume fraction of surfactant solutions can be understood in terms of the structural changes of the micelles. It is known that upon increasing the surfactant concentration well beyond CMC, the motion of charged micelles are inhibited by their crowding, and the hydrated spherical micelles are deformed to rod-shaped micelles, resulting in an increase in viscosity.\(^{289}\) A sphere to rod transition in SDS solution occurs at a concentration of 0.25 mole/litre (\( \sim \varphi = 0.07 \)) at a temperature of 27 °C.\(^{316}\) The reported value of the aggregation number of SDS spherical micelle is 60 and for rod shaped micelles [formed above \( \varphi = 0.07 \) with a semi minor axis 17 Å (b=c) and semi major axis 35.8 Å] is approximately 106.\(^{317}\) In the case of CTAB, the sphere to rod transition occurs at a concentration above \( \varphi = 0.075 \).\(^{289, \ 318}\) The dramatic increase in the viscosity observed in SDS and CTAB micellar solution above \( \varphi = 0.08 \) confirms the formation of rod shaped micelles that are randomly packed. Such a sharp increase in the viscosity of the surfactant solution due to the formation of rod-like micelles was reported earlier.\(^{317, \ 319, \ 320}\) A similar dramatic increase in viscosity due to rod shaped micelles is observed for NP9 and NP10 systems, above \( \varphi = 0.07 \). In general, the viscosity data follows Einstein model at dilute concentrations, where it assumes that the particles are rigid, uncharged, without attractive forces and are small enough so that the dilatational perturbation of the flow is unbounded to decay to zero.\(^{321}\) A particle moves at the velocity of
the streamline in line with the particle centre in such a suspension. The Einstein equation describes the dependence of viscosity increase with concentration of particles in the simplest case of dilute suspensions \( (\leq 0.01) \) as \( \frac{\eta}{\eta_0} = 1 + 2.5\varphi \). For \( \varphi \geq 0.01 \), hydrodynamic interactions between particles become important as the disturbance of the fluid around one particle interacting with those around other particles. The viscosity in such a case is given by Batchelor equation \( \frac{\eta}{\eta_0} = 1 + 2.5\varphi + 6.5\varphi^2 \). For \( \varphi \geq 0.1 \), the 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

\[
\frac{\eta}{\eta_0} = \left(1 - \frac{\varphi}{\varphi_m}\right)^{-[\eta]_{\varphi_m}},
\]

where, \([\eta] \) is the intrinsic viscosity, which is 2.5 for hard spheres and \( \varphi_m \) is the maximum packing fraction. For randomly mono-dispersed spheres, the maximum close packing fraction is approximately 0.64.

The Einstein, Batchelor and Krieger-Dougherty (KD) fit on the experimental data points are shown in the Fig. 3.6 (b). The result shows that the enhancement in viscosity ratio with \( \varphi \) is much more than the values predicted by models at relatively large volume fractions. Since the number density increases with concentration, the interaction between the micelles at higher concentration becomes stronger, which has contributed to the observed deviation from the theoretical fit. It should be noted that the effectiveness of the nanofluid coolants depends on the flow modes (laminar or turbulent). Lower viscosity implies lower pumping power, which is advantageous from an industrial application standpoint. 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 $k$. Viscosity and thermal conductivity enhancements can be described by linear dependence on the particle volume fraction as 

$$\frac{k}{k_f} = 1 + C_k \phi$$ and $$\frac{\eta}{\eta_o} = 1 + C_\eta \phi$$ where $C_k$ and $C_\eta$ are constants. At low volume fractions, for the nanofluid to be beneficial for heat transfer applications, the ratio of coefficients ($C_\eta/C_k$) should be < 4.93. At 10 CMC (and 30 CMC), the ratio of viscosity to thermal conductivity increase for SDS, CTAB and NP9 are -6 (and -13), -3.7 (and -2.8) and 0.39 (and -0.26), respectively. These results suggest that the cationic and non ionic surfactants are better emulsifiers for optimal value of thermal to rheological property enhancements.

### 3.3.5 Effect of Surface Morphologies on Thermal Conductivity, Viscosity, Density and Refractive Index

The viscosity measurements clearly show that a morphological change (sphere to rod transition) occurs for all the surfactants above $\phi = 0.07$. It may be seen from Fig. 3.5 that the $k$ is reduced drastically after $\phi = 0.07$, which may be possibly due to the sphere to rod transition. Fig. 3.6 (c&d) shows the density and refractive index variation as a function of surfactant concentration for SDS, CTAB, NP9 and NP10. The morphological transitions in the surfactant solutions above $\phi = 0.08$ is also evident in the density and refractive index measurements. From Fig. 3.6 (c), it is seen that the density increases from 1.0013 to 1.0143 g/cm$^3$ as the concentration of SDS increases from $\phi = 0.002$ to 0.08. Similarly in the case of CTAB, the density increases from 0.9988 to 1.0005 g/cm$^3$ while in the case of NP9, it increases from 0.999 to 1.0076 g/cm$^3$ for an increase in $\phi$ from 0.002 to 0.08. For the same increase in volume fraction, the density of NP10 increases from 0.9989 to 1.0054 g/cm$^3$. The
large variation in the density of the surfactant solutions above 0.08 $\phi$ further corroborates the formation of rod shaped micelles. The refractive index (Fig. 3.6 (d)) of the solutions also shows a systematic increase with concentration of surfactants in all four cases. Again a dramatic increase in the refractive index is observed above 0.08 $\phi$. In the microconvection model, the convection velocity is taken to be the root-mean-square (rms) velocity of the nanoparticle. The root-mean-square velocity ($v_N$) of a Brownian particle can be defined as

$$v_N = \sqrt{\frac{18k_BT}{\pi\rho d^2}}.$$  

Considering the micellar size, the maximum convection velocity is expected in SDS (size ~2.5 nm) and the least in NP9 (size ~6.5 nm). Therefore, in terms of microconvection theory, the observed negative enhancement in $k$ with volume fractions is consistent. However, it is intriguing that the effective medium theory holds good even after the morphological transformation (spherical to cylindrical micelles). Studies show that the cylindrical structure with large aspect ratio enhances the thermal conductivity of nanofluids compared to the spherical ones.\textsuperscript{27, 147, 183} The aspect ratio of the suspended particles and the orientation of the particles with respect to the heat flow direction play a crucial role in $k$ enhancement. In the case of magnetic nanofluids, alignment of nanostructures along the field direction can cause dramatic enhancement in the thermal properties due to parallel mode of conduction.\textsuperscript{324} It should be noted that the aspect ratio, in the case of magnetic nanofluids, increases several orders of magnitude when they are subjected to a magnetic field. However, aspect ratio change in the case of surfactant micelles after transformation from spherical to cylindrical micelle is very small. In the case of SDS at 0.07 vol%, the semiminor and major axis are 1.7 nm and 3.58 nm, respectively.\textsuperscript{317} Probably, the small changes in the aspect ratio and the lower $k$ of the micelles have contributed to the observed good agreement between the
experimental data and EMT prediction. On the basis of these results, the possible thermal resistance contributions from different moieties of the micelles (head group, tail and water molecules) are schematically shown in the inset in Fig. 3.5. The maximum interfacial resistance is offered by the hydrophobic tail part and minimum by the fluid molecules.

3.3.6 Effect of Surfactant on $k$ Enhancement in Aqueous and Non Aqueous Metal Oxide Nanofluid

Aqueous Alumina Nanofluid: Fig. 3.7 shows the variation of $k/k_f$ as a function of $\varphi$ of Al$_2$O$_3$ nanofluids without surfactant and with surfactants CTAB and NP9 of 10, 70 CMC. The $k/k_f$ for pure surfactants of CTAB and NP9 of same volume fractions (10 and 70 CMC) are also shown in the Fig. 3.7 for comparison. The best fit using effective medium theory is shown by the solid line. Over all the experimental data fits fairly well with the EMT theory for various volume fractions of alumina nanofluids with and without surfactants, except a small deviation observed at higher volume fractions. The maximum thermal conductivity enhancement for nanofluids with a particle loading of 0.06 was $\sim$14.4 %. The most striking observation was that though the $k/k_f$ of the surfactant micellar solutions was lower than that of the basefluid, the $k/k_f$ of the nanofluids with the same amount of soft spheres (micelles) is dictated by the thermal conductivity of the nanofluids. This is a very promising result in terms of industrial applications of surfactant stabilized nanofluids. To verify these intriguing results, the experiments are repeated for other nanofluids. The schematic representation of the system containing charged Al$_2$O$_3$ nanoparticles and surfactant micelles is depicted in the inset of Fig. 3.7.
Figure 3.7: The variation of effective thermal conductivity as a function of alumina nanoparticle volume fraction without and with CTAB and NP9 along with the theoretical fit using (solid line) EMT. The inset in the figure shows the schematics of charged γ-Al₂O₃ in CTAB micellar solution.

**Aqueous Silica Nanofluid:** Fig. 3.8 shows the variation of $k/k_f$ as a function of $\phi$ of SiO₂ nanofluids without surfactant and with surfactants SDS and NP9 of 5, 10 and 70 CMC. The $k/k_f$ for pure surfactants of SDS and NP9 of the same volume fractions (5, 10 and 70 CMC) are also shown in the Fig. 3.8 for comparison. The best fit using effective medium theory is shown by the solid line. The experimental data fits fairly well with the EMT theory up to 0.04 $\phi$ of SiO₂ with and without surfactants and the fit was poor at higher volume fractions. The maximum thermal conductivity enhancement for nanofluids with a particle loading of 0.1 was ~12.6%.
Figure 3.8: The variation of effective thermal conductivity as a function of SiO$_2$ nanoparticle volume fraction without and with SDS and NP9 along with the theoretical fit (solid line) using EMT. The inset in the figure shows the schematics of charged SiO$_2$ in SDS micellar solution.

Again, the $k/k_f$ of the nanofluids with the same amount of soft spheres is dictated by the thermal conductivity of the nanofluids. The schematic representation of the system containing charged SiO$_2$ nanoparticles and surfactant micelles are depicted in the inset of Fig. 3.8.

Non-Aqueous Fe$_3$O$_4$ Nanofluid: Fig. 3.9 shows the variation of $k/k_f$ as a function of $\phi$ of Fe$_3$O$_4$ nanofluids coated with 10 % oleic acid and 5,10 wt % of oleic acid in basefluid (kerosene). The best fit using effective medium theory is shown by the solid line. The experimental data fits fairly well with the EMT theory, especially above 0.04 $\phi$ of Fe$_3$O$_4$. The maximum thermal conductivity enhancement for nanofluids with a particle loading of 0.08 $\phi$
was ~ 23.4 %. These results were consistent with the $k$ enhancement observed in magnetic nanofluids, without external magnetic field.\textsuperscript{11} On the contrary, very large enhancement in $k$ is observed under magnetic field due to a parallel mode of conduction. Again, the $k/k_f$ of the basefluid with the same amount of surfactant alone shows much lower value compared to the one with nanoparticles. The carboxylic acid group of oleic acid binds to the magnetite while the aliphatic chain extends out into the non-polar solvent thus providing steric hindrance between the particles. The charges at the carboxylate ion of oleic acid, de-localizes in between two oxygen atoms because of resonance effect.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The variation of effective thermal conductivity as a function of Fe$_3$O$_4$ nanoparticle volume fraction along with the theoretical fit (solid line) using EMT. The schematic in the figure shows the oleic acid coated Fe$_3$O$_4$ particle.}
\end{figure}

The surfactant coating thus prevents the agglomeration of particles against van der Waals and magnetic attractive interactions. Besides, it passivates the nanocrystals against further
oxidation. This once again confirms that the thermal conductivity of nanofluid is dictated by the thermal conductivity of the suspended particles. The schematic representation of the nanoparticles with adsorbed surfactant moieties is depicted in the inset of Fig. 3.9.

With and without surfactant, the $k/k_f$ enhancement was almost the same in the case of alumina, silica and iron oxide nanofluids. It can be seen that the value of $k/k_f$ enhancement with pure surfactant was negative, while it is positive at all concentrations of nanoparticles for all the three systems. In general the excess surfactant did not show a lowering of $k$ of the nanofluid, though the surfactant alone in base fluids showed a negative enhancement. For example, SiO$_2$ nanofluid of 0.08 $\varphi$ shows an enhancement of 13 % without any surfactant and an 18 % enhancement with SDS. This shows that the thermal conductivity of a nanofluid in presence of surfactant and nanoparticles simply follows the thermal conductivity of nanoparticles in the fluid and the addition of surfactant, even beyond optimal concentration would not lower the thermal conductivity of nanofluids significantly. Besides, the surfactant moieties on nanoparticles aid thermal conductivity enhancement and also improve the stability of nanofluids against agglomeration of suspended particles.

**Figure 3.10:** Schematic representation of nanofluids (a) ‘soft’ system with spherical and cylindrical micelles randomly arranged ($k_p<k_f$). (b) aligned cylindrical micelles ($k_p<k_f$). (c)
bare nanoparticle in basefluid ($k_p \gg k_f$) and (d) surfactant coated nanoparticle in base fluid ($k_p \gg k_f$).

**Fig. 3.10** shows the schematic representation of nanofluids drawn based on the experimental findings. (a) ‘soft’ micellar system with spherical and cylindrical micelles randomly arranged ($k_p < k_f$). This scenario arises when the surfactant concentration is above the critical micellar concentration. Because $k_p < k_f$, the system shows a $k/k_f < 1$ (b) Aligned cylindrical micelles at extremely large concentrations of surfactants ($C >> CMC$). Again, because $k_p < k_f$, the system shows a $k/k_f < 1$. (c) Bare nanoparticle in basefluid ($k_p \gg k_f$) where no surface active species are used. Due to agglomeration and subsequent settling, the heavy nanoparticles settles at the bottom of container.

**Table 3.1**: Thermal conductivity of bulk particle, base fluid, thermal conductivity ratio of nanofluid of different volume fraction and their corresponding % enhancement.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Material</th>
<th>$k$ of bulk particle (W/m.k)</th>
<th>Base fluid</th>
<th>$k$ of base fluid (W/m.k)</th>
<th>$k/k_f$ of Nanofluid</th>
<th>% enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Fe₃O₄</td>
<td>9.7</td>
<td>Kerosene</td>
<td>0.116</td>
<td>1.1 ($\phi=0.04$)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.18($\phi=0.06$)</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.23($\phi=0.07$)</td>
<td>23</td>
</tr>
<tr>
<td>2.</td>
<td>Al₂O₃</td>
<td>35</td>
<td>Water</td>
<td>0.6</td>
<td>1.09($\phi=0.02$)</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.10($\phi=0.04$)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.14($\phi=0.06$)</td>
<td>14</td>
</tr>
<tr>
<td>3.</td>
<td>SiO₂</td>
<td>1.4</td>
<td>Water</td>
<td>0.6</td>
<td>1.09($\phi=0.04$)</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.10($\phi=0.06$)</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.13($\phi=0.08$)</td>
<td>13</td>
</tr>
</tbody>
</table>

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Here, two different conduction pathways are possible- one though the nanoparticle pathway where the $k/k_f$ is high and the other through liquid pathway where the $k/k_f$ is low and (d) surfactant coated nanoparticle in base fluid ($k_p>>k_f$). Here, the surfactant moieties stabilize the nanoparticles thereby providing a stable suspension, where the $k/k_f$ enhancement will be modest or high. However, conduction through percolating nanoparticle paths can carry heat much more effectively.\textsuperscript{207} Thermal conductivity values of bulk particle, base fluid, nanofluids of different volume fractions and their respective percentage enhancement are listed in Table 3.1

3.4 Conclusions

The thermal properties of nanofluids containing soft spheres of surfactants with different head group charges and alkyl chain length are investigated. The contributions of interfacial resistance, density, viscosity and surface morphology of dispersed particles on thermal conductivity are also studied by using model soft systems of micelles in the size range of 2.5 to 7 nm. Our results show that the thermal conductivity variation of surfactant micelles with volume fraction fits well with the effective medium theory of poor thermal conductors. The long alkyl chain group of non-ionic surfactant micelles is found to be very poor thermal conductors at very low concentrations, with large interfacial tension compared to their anionic counterparts. Though a dramatic enhancement in viscosity is noticed at high concentrations, due to transformation of spherical micelles into cylindrical, the effective medium theory still holds good even after the morphological transformation. This may be probably due to the minor changes in the aspect ratio and poor $k$ of the micelles as such. The $k$ measurement in alumina, silicon dioxide and iron oxide nanofluids in presence of ionic and non ionic surfactants shows that the adsorbed surfactant does not influence the thermal
conductivity enhancement in nanofluids. Further, the stabilizing moieties on nanoparticles do not reduce the thermal properties of nanofluids but it enhances the dispersibility and stability of nanoparticles in the base fluids. These finding will have important implications for producing efficient nanofluids with superior heat transfer properties.