Thermal conductivity and viscosity of water-in-oil nanoemulsions

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1. Introduction

Fluids such as air, water, ethylene glycol and mineral oils are typically used in applications like power generation, chemical production, automobiles, computing processes, air conditioning and refrigeration. However their heat transfer capability is limited by their very low thermal conductivity. These fluids have almost two orders of magnitude lower thermal conductivity compared to metals, resulting in low heat removal efficiencies. First attempts to improve the thermal conductivity involved dispersing micron-sized particles in these liquids. Ahuja [1] studied the heat transfer augmentation and rheology of slurries. The main challenge when using this approach lies in the preparation of stable suspensions, which do not sediment very quickly. The recent advantages in nanoparticles synthesis have enabled the development of stable suspension containing nanoparticles. This suspensions are also referred to as “nanofluids” [2]. Nanofluids contain particles that are significantly smaller than 100 nm in at least one dimension, and have bulk thermal conductivity significantly higher than the base liquids [2]. A number of studies have been performed on different properties of nanofluids see for example [2–6]. Although the scientific community has not yet come to an agreement, these studies seem to suggest that properly engineered nanofluids may provide advantages such as: (a) thermal conductivity than that predicted by currently available macroscopic models, (b) better stability than what achieved by suspension of millimeter or micrometer particles, and (c) little wall abrasion. Recently the use of properly formulated water-in-oil nanofluid has also been reported to provide a good candidate for heat transfer fluids with enhanced thermal conductivity [12].

In the present work, the concept of emulsifying water in oil by means of non-ionic surfactant is employed in order to investigate the effect on the thermal conductivity and on the viscosity of the base fluid. De-ionized (DI) water is emulsified into 99% pure n-decane with a constant amount of surfactant, a mixture of sorbitan monolurate (C_{24}H_{44}O_6 and C_{18}H_{34}O_6), by using an ultrasonic disruptor and a high shear mixer. At constant surfactant-to-oil ratio, the mean water droplet size is dependent on the water concentration: the higher the water concentration, the larger the water droplet size. Loadings of water nanodroplets up to 70 vol% are produced and tested. The existence of nanoeumulsion regions is confirmed with time multiple light scattering technique. The mean water droplet sizes is measured in the interval 20 and 120 nm for water loading below 20% in volume. An experimental investigation of the thermal conductivity and viscosity of nanofluids with a constant surfactant-to-oil ratio and with different water concentration is carried out. Our experimental data can be explained by means of existing theory. Water-in-oil nanofluids containing 12% volume of water nanodroplets of diameter 40 nm show an increase in effective thermal conductivity close to 22% while the...
viscosity increases just slightly. In the present work, the performance of nanoemulsion as cooling media is compared with the performance of pure oil through consideration of the pumping power required to achieve certain heat removal goals. Nanoemulsions are showed to perform better than their constituting oil for cooling purposes. Furthermore nanoemulsions seem to maintain the electrical insulating properties of their constituting oil and as such they are good electrical insulators. Due to these reasons, their good stability and the fact that they can be easily produced in large scale, nanoemulsions seem to be a good candidate for heat transfer applications.

2. Nanoemulsion

Nanoemulsions are dispersions of nanoscale droplets formed by shear-induced rupturing. The present convention for nanoscale materials implies structures having length scales in the range from 1 to 100 nm. Applying this convention to metastable emulsions, nanoemulsions are defined to be emulsions having droplet sizes in this “nano” range [8]. Although the definition of nanoemulsions has been extended to the 1 nm scale, it would be impossible to make a nanoemulsion smaller than the size of a surfactant micelles, typically a few nanometers. Extreme emulsification methods are required to produce nanoscale dispersions of droplets of one liquid in another immiscible liquid [9,10]. Microfluidic and ultrasonic approaches of rupturing larger microscale droplets into nanoscale droplets are providing interesting and useful non-equilibrium systems of structured liquids. Despite their metastability, nanoemulsions can persist over many months or years due to the presence of a stabilizing surfactant that inhibits the coalescence of the droplets [11]. Nanoemulsions can be characterized by specifying molecular constituents, quantities of these constituents, and the sizes of the droplet structures following the formation of the emulsion by shear. For the following discussion, we consider water-in-oil nanoemulsions. The molecular weight, $M_w$, and molecular structure of the oil (e.g. alkane, silicone, or other) are typically chosen based on the application. The surfactant type and concentration in the oil phase are chosen to provide good stability against coalescence. The droplet volume fraction, $\phi$, describes the relative degree of concentration of the droplets. Although one might initially imagine that there are no significant fundamental differences between nanoemulsions and their microscale counterparts, in fact, the physical properties of nanoemulsions can be quite different from those of microscale emulsions. Nanoemulsions have some interesting physical properties that distinguish them from ordinary microscale emulsions. For instance, microscale emulsions typically exhibit strong multiple scattering of visible light, and, as a result, have a white appearance. In the absence of optical absorption, photons that enter the emulsion are scattered many times by microscale structures before they leave the emulsion. By contrast, the structures in nanoemulsions are much smaller than visible wavelengths, so most nanoemulsions appear optically transparent, even at large loading.

To make a stable emulsion reproducibly, a large number of factors must be controlled. These include selecting an appropriate composition, controlling the order of addition of the components, and applying the shear in a manner that effectively ruptures droplets. There are several additional requirements for nanoemulsions. The dispersed phase molecules must be essentially insoluble in the continuous phase so that Ostwald ripening does not occur rapidly despite the very high Laplace pressures. Suppressing Ostwald ripening can be achieved by other means [8], but choosing a very insoluble liquid for the dispersed phase is the easiest method. In our study water-in-decane nanoemulsions are formulated following the guidelines of [7]. $n$-Decane, $C_{10}H_{22}$, with a purity above 99% is the continuous phase while de-ionized water is the discrete phase of the mixture studied here. The second requirement is a choice of components, especially surfactants, which do not result in the formation of lyotropic liquid crystalline “microemulsion” phases. The third requirement is that the continuous phase has a significant excess of surfactant to enable the new surface area of the nano scale droplets to be rapidly coated during emulsification, thereby inhibiting shear-induced coalescence. Generally this excess is in the form of surfactant micelles in the continuous phase. These micelles dissolute into monomers that rapidly adsorb onto the surfaces of newly created droplets. In our study the surfactant employed to stabilize the water droplets is a mixture of sorbitan monoluate ($C_{24}H_{42}O_{6}$ and $C_{18}H_{34}O_{6}$ (62:38)/decane/water see [7].

![Fig. 1. Existence regions of microemulsion, nanoemulsion and emulsion. C_{24}H_{42}O_{6} and C_{18}H_{34}O_{6} (62:38)/decane/water see [7].](image-url)
crossing over into the macroemulsion region when adding more and more water.

3. Experiments

The fluid thermal conductivity of the nanoemulsions is measured by the transient hot-wire method [14]. A thin wire is immersed in the emulsion and heated by electrical current. The wire plays two roles: an electrical heating element and a resistance thermometer. The thermal conductivity of the sample is determined from the temperature change of the wire and the heat generation. The change of hot wire temperature is measured by a Wheatstone bridge. The voltage imbalance across the bridge is recorded by a data acquisition system as a function of time. The hot wire cell contains an isonel-coated platinum wire suspended horizontally in the fluid. A vertical configuration has also been employed and the results obtained with the two configurations are in agreement with each other. The wire is 15 cm long and is soldered to copper electrodes at both ends. The wire core diameter is 25 μm and the insulation layer has a thickness of 1.5 μm. The leakage of electrical current from the electrodes to the surrounding fluid is minimized in order to increase the reliability of our measurements. This is especially important for emulsion with a high water volume fraction. The thermal conductivity is measured by placing enough fluid into the hot wire cell so that the hot wire is completely immersed and the boundary effects are minimized. The potentiometer is adjusted in such a way that the voltage imbalance across the bridge is reduced to approximately 10 μV. After the bridge is balanced, the resistances of the hot wire cell and potentiometer are measured with a digital multimeter using a four-wire method. A constant current of 75 mA is applied to the bridge, and the voltage imbalance across the bridge is recorded as a function of time. The duration of data acquisition is 2 s. From the signal output of the bridge one calculates the thermal conductivity of the fluid. To ensure robustness the measurements are repeated several times. Calibration experiments were performed for pure decane, PAO, ethylene glycol and water at atmospheric pressure. The literature values were reproduced within ±0.5% discrepancy. Figure 2 shows the thermal conductivity enhancement with respect to the base fluid thermal conductivity of water-in-decane nanoemulsion as a function of the water concentration at high water loading. The thermal conductivity of the nanoemulsion predicted by the effective medium theory is also plotted in Fig. 2, solid line. When the dispersed medium is assumed to be spherical as in the case of water-in-oil emulsion the effective medium theory reduces to the Maxwell–Garnett equation that reads:

\[
\frac{k}{k_0} = \frac{k_D(1 + 2\alpha) + 2k_0 + 2\phi(k_D(1 - \alpha) - k_0)}{k_D(1 + 2\alpha) + 2k_0 - \phi(k_D(1 - \alpha) - k_0)},
\]

where \(k_D\) is the base fluid thermal conductivity, \(k_0\) is the thermal conductivity of the emulsified water, \(\phi\) is the water volume fraction, \(k\) is the effective thermal conductivity of the nanoemulsion and \(\alpha\) represents the interfacial resistance and particle size [15].

One can observe that for water loading below 50% one obtains a good agreement between the predicted results and the experimental data. Below 50% water fraction, no separation is experienced although all the different emulsion regions have been crossed. The agreement becomes worse above 50% water loading due to the fact that the mean water droplet size increases and separation is observed. At around 62% water volume fraction the inversion point between an oil continuous and a water continuous emulsion seems to be reached. This is also confirmed by measuring the electrical conductivity of the emulsion. When the emulsion becomes water continuous it conducts electricity and the measured electrical resistance is rather small. The insert in Fig. 2 shows the importance of normalizing the thermal conductivity data with the correct thermal conductivity of the base fluid that in our case is the mixture of decane and surfactant. When one considers the thermal conductivity of the base fluid \(k_0\), to be that of pure decane \(k_0 = k_0 = 0.132\, \text{W/(m K)}\) one may be inclined to conclude that the thermal conductivity enhancement is higher that what predicted by the effective medium theory see the empty triangles in the insert of Fig. 2. However, this comparison is misleading, since the base fluid should also include the effect of surfactant. When one takes into account the effect of the surfactant on the heat conductivity of the decane, the base fluid thermal conductivity becomes equal to \(k_0 = k_{D+S} = 0.138\, \text{W/(m K)}\). Using this value as that of the base fluid, the thermal conductivity enhancement is described by the empty squares in Fig. 2. This shows a good agreement between experimental data and predictions obtained from the effective medium theory (see the empty squares and the solid line in Fig. 2). The predictions assume zero thermal boundary resistance between the water droplets and decane. The effect of the presence of surfactant on the thermal conductivity of the decane is studied further. The thermal conductivity enhancement of the mixture decane–surfactant with respect to pure decane is plotted against the surfactant concentration as seen in Fig. 3. The value of the thermal conductivity enhancement of the mixture seems to be well described by a traditional rule of mixture:

\[
k_{D+S} = \phi_S k_S + (1 - \phi_S) k_D,
\]

where \(k_{D+S}, k_S, k_D\) are the thermal conductivity of the oil–surfactant mixture, the surfactant and the oil, respectively and \(\phi_S\) is the surfactant volume fraction. The validity of the rule of mixture to describe the thermal conductivity of the oil surfactant mixture is also confirmed for a different oil. Note that the apparent abnormal enhancement that is observed when one does not consider the effect of the surfactants on the thermal conductivity of the base fluid (the unfilled triangles in the insert of Fig. 2) corresponds to the enhancement in thermal conductivity obtained when adding ≈ 14 vol% of surfactants. This corresponds to the amount of surfactants added to decane in order to formulate a nanoemulsion with the desired water droplet size as shown in Fig. 1. For water volume concentration below 15% the mean water droplet diameter measured

![Fig. 2. Thermal conductivity enhancement with respect to the thermal conductivity of the base fluid of water-in-decane nanoemulsion as a function of the loading of water nanodroplets (the empty symbols refer to experimental values, while solid line refers to predicted ones. In the empty triangles, one considers the thermal conductivity of the base fluid to be that of pure decane: \(k_0 = k_0 = 0.132\, \text{W/(m K)}\), while in the empty squares the thermal conductivity of the base fluid is considered to be that of the mixture decane + surfactants: \(k_0 = k_{D+S} = 0.138\, \text{W/(m K)}\).](image-url)
Thermal conductivity enhancement with respect to the base fluid thermal conductivity of surfactant-in-decane mixture as a function of surfactant concentration.

is below 40 nm, but it increases when adding more water. One can potentially obtain a constant mean water droplet diameter at higher water loading by increasing the surfactant concentration. As previously stated we have kept the surfactant concentration constant at all water loading.

Colloidal dispersions can behave in interesting and unusual ways when subjected to high shear stresses that alter their structures [16]. For instance, both non-Newtonian shear-thinning and shear-thickening can be observed [17]. In our work the viscosity in the nano- and microemulsion region was measured as a function of the shear rate as shown in Fig. 4. In the nanoemulsion region the emulsion seems to be characterized by an overall Newtonian behavior except at very high shear rate, above 5000 s⁻¹. In the microemulsion region, at water loading above 30%, the behavior is non-Newtonian above much lower shear rate. At high water loadings the non-linearity of the viscosity is more evident. Furthermore at high water loading hysteresis is also observable see for example the circles in Fig. 4, the upper most circles are obtained while increasing the shear rate while the lower most ones are obtained while decreasing the shear rate. These behaviors make a simple viscosity description inadequate to characterize the rheological complexity of these systems [17]. Although the single viscosity description is somehow inadequate we have plotted the viscosity enhancement at high water volume fraction in Fig. 5. The plot in Fig. 5 confirms the location of the inversion point somewhere above 60% water volume fraction. Fig. 5 shows the enhancement in the relative dynamic viscosity of the emulsion as a function of water volume concentration. At water loading below 15% the observed increase in viscosity is contained and it is well described by classical model such as the semi empirical model proposed by [18]. The model takes into account of the interdroplet interaction on the viscosity increment as a function of the volume fraction throughout a packing parameter $\phi_m$. At high volume fraction Pal’s model stops describing the viscosity enhancement data in a satisfactory way. One may argue that the maximum packing parameter should be varied. At low volume fraction, in the nanoemulsion region, the droplets may be thought of as non-deformable rigid spheres. In this region the packing parameter may be kept constant. At higher volume fraction the droplet size increases and although still in the micro region they may be deformable due to the presence of the surfactants on the droplet surface. The presence of surfactants has also the effect of avoiding droplet coalescence. The deformability of the water droplets may provide a more dense packing. These arguments motivate the choice of using a varying packing parameter outside the nanoemulsion region. We let $\phi_m$ vary linearly with the volume fraction outside the nanoemulsion region as shown in Fig. 5. The equation proposed by [18] with a varying packing parameter fits well our experimental data up to a higher volume fraction as illustrated in Fig. 5.

4. Discussion on the efficacy of nanofluids as coolants from an engineering point of view

The viscosity increase becomes significant at high water loading. This suggests that just nanoemulsions with relatively small water loading are a good candidate for heat transfer application due to their little penalty in pressure drop increase. Although we are aware of the fact that droplet migration may have a significant effect on the flow thermal behavior during heat transfer we assume...
as a first approximation that micro- and nanoemulsions behave as single-phase liquids in turbulent flow and convective heat transfer in a heated tube. Under such an assumption one can directly compare nanoemulsion performance with the performance of other coolants through consideration of the fluid properties. Comparison of coolant performance usually involves investigation of the pumping power required to achieve certain heat removal goals under certain constraints, for example, a limited maximum temperature in the system. The methodology used in this work follows the outline of Bonilla from the Nuclear Engineering Handbook [19]. The cooling performance or efficacy of a certain coolant reads:

$$\bar{\epsilon} = \frac{\bar{P}_{pump}}{\bar{P}_{Npump}},$$  (3)

where $\bar{P}_{pump}$ is the pumping power for the base fluid and $\bar{P}_{Npump}$ is the pumping power for the nanoemulsion. A relevant constraint for practical applications is a fixed coolant-film temperature difference ($\Delta T_f$). Further we consider a system that has a large film temperature difference as compared to the bulk temperature difference from inlet to outlet ($\Delta T_f \gg \Delta T_b$). This is the case for short channels with high heat flux. If the film temperature difference is held constant (i.e. heat transfer coefficient is held constant), the Dittus–Boelter correlation [19] can be employed to express the pumping power as:

$$\bar{P}_{pump} = \frac{49850S\mu^3.5}{\rho_{0.5}^{1.85}} = \frac{\mu^{1.85}}{\rho_0^{2.4}c_p^{1.67}k^{1.4}}.$$  (4)

Eq. (4) is valid for fully developed turbulent flow in a tube of non-metallic coolants [19]. $D$ is the effective diameter of the flow geometry, $S$ is the cross-sectional area of the flow, $L$ is the effective length of the flow channel, $\mu$ is the coolant viscosity, $k$ is the thermal conductivity and $c_p$ is the coolant heat capacity. The efficacy of the nanoemulsions studied in the present work is calculated and plotted in Fig. 6. The efficacy is greater than unity when the nanoemulsion has better performance than that of the reference fluid, in our case decane. It can be seen that nanoemulsions with a water volume fraction below 15% are potentially beneficial coolant under turbulent flow regime and constant film temperature case.

5. Conclusion

The concept of emulsifying water in oil by means of non-ionic surfactant has been employed. De-ionized (DI) water is emulsi-

fied into pure n-decane with a constant amount of a mixture of sorbitan monolurate (C_{24}H_{44}O_6 and C_{18}H_{34}O_6) by using an ultrasonic disruptor. Loadings of water nanodroplets up to 70 vol% are produced and tested. The existence of nanoemulsion regions is confirmed with dynamic light scattering technique. At constant surfactant-to-oil ratio, the mean water droplet size is dependent on the water concentration. An experimental investigation of the thermal conductivity and viscosity of nanoemulsions with different water concentration is carried out. The thermal conductivity enhancement due to the present of water droplets seems to be well predicted by the effective medium theory for water loading below 50%. No separation is observed for water loading below 50% although we have been crossing the three different emulsion region. The agreement becomes worse above 50% water loading due to the fact that the mean water droplet size increases and separation takes place. At around 62% water volume fraction the inversion point between an oil continuous and an water continuous emulsion seems to be reached. The inversion point is dependent on the amount of de-emulsifier used to formulate the emulsion. The inversion point is confirmed by measuring the electrical conductivity of the emulsion. Viscosity increases very slightly in the low water loading nanoemulsion region while it peaks for water loading above 15%. The performance of nanoemulsion as cooling media is compared with the performance of pure oil through consideration of the pumping power required to achieve certain heat removal goals. It is very important to maintain the viscosity as low as possible, while obtaining the thermal conductivity enhancement. Nanoemulsions with water loadings below 15% are showed to perform slightly better than their constituting oil for cooling purposes. Furthermore nanoemulsions maintain the electrical insulating properties of their constituting oil and as such they are good electrical insulators. For these reasons, their good stability and the fact that they can be easily produced in large scale, na for heat transfer applications that requires good electrical insulations properties.

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References