

Preparation and Characterization of Various Nanofluids

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ABSTRACT

As part of an effort to evaluate water-based nanofluids for nuclear applications, preparation and characterization has been performed for nanofluids being considered for MIT's nanofluid heat transfer experiments. Three methods of generating these nanofluids are available: creating them from chemical precipitation, purchasing the nanoparticles in powder form and mixing them with the base fluid, and direct purchase of prepared nanofluids. Characterization of nanofluids includes colloidal stability, size distribution, concentration, and elemental composition. Quality control of the nanofluids to be used for heat transfer testing is crucial; an exact knowledge of the fluid constituents is a key to uncovering mechanisms responsible for heat transport enhancement.

Keywords: nanofluids, preparation, characterization

1 INTRODUCTION

Nanofluid is the common name of any sol colloid involving nanoscale (less than ~100nm) sized particles dispersed within a base fluid. It has been shown previously that the dispersion of nano-particulate metallic oxides into water can increase thermal conductivity up to 30-40% over that of the base fluid and anomalously more than the mere weighed average of the colloid [1]. An increase in thermal conductivity, and therefore heat transfer coefficients, without a noticeable increase in friction pressure losses would be a significant method for improving the heat transfer performance of any thermal system. The aim of nanofluid research at MIT is to develop the facilities and methodologies for the creation and characterization of water-based nanofluids and to investigate them as convective heat transfer media in single and two-phase flow.

2 PREPARATION OR PURCHASE OF NANOFLUIDS

Three main types of nanofluids are studied here: those made from purchased powders mixed with water, those made from chemical precipitation in the liquid, and those which are purchased. It is very important to understand fully the constituents of any nanofluid under investigation

in order to draw significant conclusions as to the heat transfer phenomenon.

2.1 Preparation

Our first attempt to make nanofluids was with nanoparticle powders available from Sigma-Aldrich mixed with a base fluid. In order to properly disperse a powder into a liquid system, the particles must be wetted by the medium, large aggregates must be broken down, particles must be homogenized in the medium, and finally reagglomeration must be prevented. Since the purity of the nanofluid is important, attempts were made to mix the particles directly with water with no additives. The metallic oxide nanopowders are not chemically reactive in atmosphere; however they do tend to form loose micro-sized agglomerates. The most effective method of breaking and evenly dispersing the powder in a fluid is through application of ultrasonic vibration (high speed stirring also works well). Using this methodology the nanofluids were created using the two oxide nanopowders (ZrO_2 and Al_2O_3) and ultrasonic vibration was applied for 12+ hours. The resulting nanofluids initially looked promising, but were not stable with time. Although some particles remained dispersed, the majority formed larger agglomerates and settled out of the liquid.

Further investigation in the literature found that the stability of nanofluids has multiple variables. As stated previously the small particle size gives the potential for the particle to escape settling due to gravity. The Brownian motion of the fluid keeps the particles aloft. However this small particle size dramatically increases the surface to volume ratio of the system. Full stability is only acquired through the separation of the two phases and the minimization of the surface area. The fully suspended system is then either unstable or metastable at best.

An energy barrier must be created between the particles in order to prevent them from passing from the unstable to stable energy states. This is known as the metastable state or "colloidally stable" [2]. The energy barrier must be strong enough to repel the majority of particles impinging on one another due to Brownian motion. The total interaction between particles is thus governed by a balance between van der Waals attraction and short range, electrostatic, and steric repulsions.

The repulsion barrier is typically created by surface charges on the particles. With like charges on the particle surfaces, the particles will repel one another thus preventing agglomeration. Surface charge is typically created by addition of acid or base to the fluid in order to create surface ionization and thus surface charges (electrostatic), or addition of like charged chemical surfactants which attach to the particle surfaces (steric). Both methods have been pursued and have proven effective in this study. Addition of HCl acid in low concentrations to the previously mentioned Al₂O₃ and ZrO₂ nanofluids created by ultrasonication created much more stable nanofluids. Various nanofluids were successfully made using oxide particles dispersed in ethylene glycol, ethanol, methanol, and isopropanol without addition of acids or bases. However the settling did slowly occur over longer periods of time.

Ultrasonic dispersion with surfactants was also somewhat successful. Attempts were made to disperse alumina nanoparticles in ethanol, methanol, isopropanol, and FC-72. Results good dispersion of the particles in ethanol, methanol, isopropanol, but stability was not long lasting. However the FC-72 was found to not wet the particles and therefore no dispersion could be achieved. After further investigation it was found from other works [3] that van der Waals attraction is highly dependent on the dielectric constant of the base fluid. Therefore the overall stability of the colloid or nanofluid depends greatly on the dielectric constant as shown in Figure 1. Dielectric constants are given in Table 1.

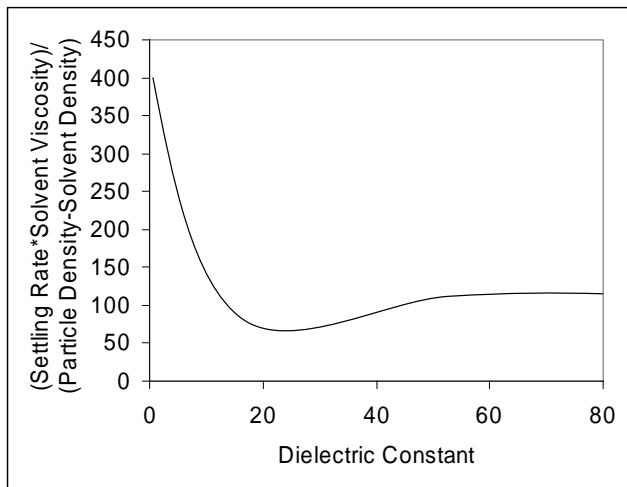


Figure 1: Stability of bare alumina particles in various fluids [3]

The effect of the dielectric constant on van der Waals forces and hence stability was seen first hand in the dispersion of alumina particles. Water, ethylene glycol, methanol, ethanol, and isopropanol all made colloids which were not very stable. If settling is normalized as in Figure 1, then ethanol nanofluid was the most stable and water

nanofluid the least stable. Finally FC-72 would not form a colloidal state at all; the low dielectric constant even prevented wetting.

<i>Water</i>	80
<i>Ethylene Glycol</i>	37
<i>Methanol</i>	32.7
<i>Ethanol</i>	24.5
<i>Isopropanol</i>	17.9
<i>FC-72</i>	1.7

Table 1: Dielectric constants of various fluids

The other method for creating nanofluids tried in this study is through chemical precipitation with the addition of surfactants (steric). Making of a Fe₃O₄ nanofluid is described as follows: To begin, excess oxygen is removed from deionized water by bubbling through nitrogen. Then, a 1:2 molar ratio of FeCl₂·4H₂O and FeCl₃·6H₂O are added to the water. The mixture is stirred and heated to 80°C and becomes yellowish in color and the polymer/surfactant is added to the mixture until it is foaming.

In order to precipitate the particles a solution of Ammonium Hydroxide ~28% is added and the solution immediately turns black with the iron oxide nanoparticles. This solution is allowed to stir and fully react at 80°C for 30 minutes. The resulting nanoparticles are cleaned with acetone and separated from the liquid by using an electromagnet (particles are magnetite). Centrifuging is also possible. The cleaning process is repeated with deionized water, acetone, and the magnet several more times. The final particles are then heated to boil off the excess acetone and can then be dispersed in water. The final dispersion has been found to be stable indefinitely.

Attempts were made to disperse the separated iron oxide particles in to various other fluids. However the results were poor. The surfactant can have an adverse effect depending on the dielectric constant as well. It can almost invert the curve as shown in Figure 1, thus making very high and very low dielectric constant fluids more stable and moderate values less stable [3].

2.2 Purchase

Several companies were approached for samples in this project: Nyalcol, Sigma-Aldrich, Nanophase Technologies, Applied Nanoworks and Meliorum Technologies to name a few. These companies produce various nanofluid products with varying quality. The major candidates for this project which are purchased are water-based with zirconia and alumina particles, however some other fluids have also been investigated, like silica, gold, and platinum in water. Gold in ethylene glycol was also available for purchase. Many powders are also available which come with surfactant coatings which allow for easy dispersion.

3 CHARACTERIZATION

It is important to be able to fully characterize the nanofluids under inspection for heat transfer enhancement. The first steps are to quantify the composition, size and loading of the nanoparticles and search for impurities in the nanofluids. Tools utilized to characterize and qualify nanofluids for this study include neutron activation analysis (NAA), inductively-coupled plasma spectroscopy (ICP), transmission electron microscopy (TEM) imaging, thermogravimetric analysis (TGA) and dynamic light scattering (DLS).

3.1 Transmission Electron Microscopy (TEM)

TEM is the primary technique to verify single particle dimensions and to identify agglomerations of particles. The electron beam can be used to see features on the nanometer level. A major drawback to the use of TEM is that samples must be dried out of solution in order to be attached to the carbon matrix. Therefore the particles are not exactly in nanofluid state and agglomeration might occur during drying. However TEM can be used in connection with dynamic light scattering to acquire exact sizing in nanofluid form. An example of one of the nanofluids (Sigma-Aldrich Al_2O_3 in water) can be seen in Figure 2. It is not known by this image alone as to the time of agglomeration, before or after drying of the base fluid. The mean particle size appears to be in agreement with the specifications of Sigma-Aldrich.

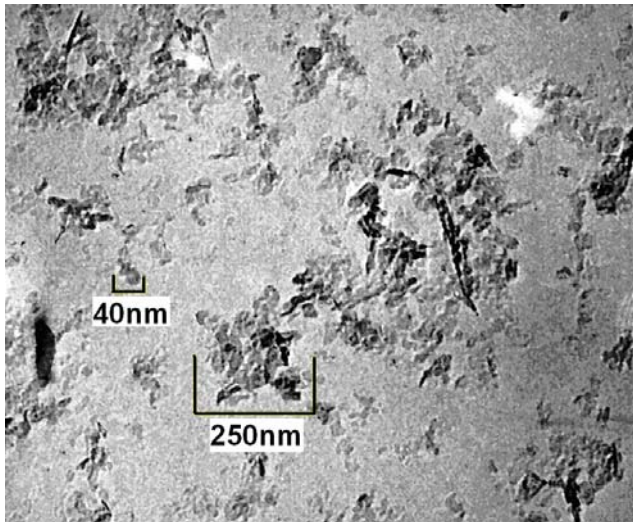


Figure 2: TEM image of Sigma-Aldrich Al_2O_3 nanofluid

3.2 Dynamic Light Scattering (DLS)

DLS can also be used to size particles in a dilute solution. When light from a laser is passed through a colloid the light will scatter uniformly from particles which are less than $\sim 250\text{nm}$. The time measurement of this

scattered light intensity can be used to determine the size of the particles in the colloid. The time variation of the intensity can be correlated to the diffusion of the particles and, through the Stokes-Einstein equation and the fluid viscosity, the hydrodynamic radius of the particles which are moving.

However one of the main drawbacks of DLS is the measurement of very polydisperse systems. The intensity of the light scattered is proportional to the diameter of the particle. Therefore the sizes measured are correct, but the distribution of the particles in these size bins needs to be weighted according to their diameters. The scattering should follow Rayleigh's law for scattering and thus intensity is proportional to the diameter to the sixth order. If the DLS results, from the same Sigma-Aldrich Al_2O_3 nanofluid as viewed with the TEM, are corrected in this way then the majority of the particles are in the 40nm range with a few larger agglomerations around $200\text{-}300\text{nm}$, which reinforces previous findings and the technical specifications of the fluid. The pH of the Sigma-Aldrich is around 4 in order to maintain the particles in dispersion. If the pH is allowed to rise to 7, the agglomerations were seen to increase significantly. This is expected from DLVO theory. Therefore care must be taken to maintain the nanofluid pH stable during dilution for the DLS measurement.

3.3 Neutron Activation Analysis (NAA)

Particle concentration and contamination in the nanofluid solution is another problem of characterization. MIT's research reactor was used to perform neutron activation analysis for the determination of nanoparticle and other impurity concentrations in the nanofluids. NAA is a method that uses the gamma decay emissions of the samples after having undergone neutron irradiation. Irradiation times depend on the materials under investigation and the half life of the gamma decay modes. Around sixty elements detectable using NAA.

Two zirconia nanofluid samples were irradiated, because of the long zirconium half life the samples were irradiated for 6 hours. Both samples were supplied as 10 percent zirconia by weight in water from the vendors. Samples will be designated as A and B. The results found that both nanofluids contained zirconium, sample A has 0.1027 gm/gm or 10.27 wt\% zirconia and sample B has 0.0274 gm/gm or 2.74 wt\% zirconia. It appears that sample B is dramatically different than the specifications. It was found that there was more zinc than zirconium in sample B. The zinc was found at 0.026 wt\% in sample B, which is significantly contaminated. Sample A only has $6.5\text{e-}5\text{ gm/gm}$ which is insignificant. It is believed that the sample B specifications are either unreliable or that the batch is overly contaminated. Trace amounts (ppm levels) of other elements (K, Cl, Na) were found which are assumed as additives for pH control.

Some alumina nanofluids were also considered. Nyacol at 20 wt% (NY), Meliorum (ML) and Sigma-Aldrich (SA2) at 10 wt% were the three measured fluids. For the alumina both short and long irradiations were required. The long (6 hours) was for the majority of elements and the short (5 mins) was for the aluminum due to the short half life. The results of the long showed that the samples all contained nearly insignificant levels (ppm) of Na, K, and a few other common elements like Zn.

The results of the shorts gave the loading of the aluminum and thus alumina for the nanofluids. It was found that the NY had 19.37 wt%, specs gave 20wt%. The ML had 9.74 and the SA2 had 8.68 wt% for 10wt% in the specs. These seem to be in good agreement with the specifications of the vendors. The discrepancy of the SA2 is assumed to be due to settling of the nanofluid, because it was an older sample. It is concluded that NAA can be used for quality control of nanofluids. The major limiting factors of NAA is the time and cost of the procedure. It also involves handling of radioactive materials.

3.4 Inductively-Coupled Plasma Spectroscopy (ICP)

A more cost and time effective approach was also used for determining the nanoparticle loading and composition, i.e., the ICP spectrometer. Tests could be done using the ICP to determine concentration and contamination characterization of nanofluids much more effectively. ICP spectrometry uses the light spectrum released from injecting materials into an extremely high temperature plasma. Roughly sixty elements are detectible by ICP. Two samples were tested using the ICP: Al₂O₃ (Sigma-Aldrich) and Fe₃O₄ in water. One key to the analysis is that the nanofluid samples need to be diluted to stay below the concentration of calibration standards. Therefore the Al₂O₃ which was initially at 10wt% was diluted to 0.05wt% (200:1) and the Fe₃O₄ which was initially at 3.5wt% was diluted to 0.035wt% (100:1), both using deionized water.

It was found that the Al₂O₃ was at a concentration of 0.047wt% which is within ~5% of the specified value. Sodium and potassium were also found, which is consistent with the NAA results. These are used to stabilize the nanofluid using the pH method. The Fe₃O₄ was found to have a concentration of 0.034wt% which is within ~2% of the specified value. The sodium of the stabilizing polymer could also be seen by the ICP. These results are determined to be valid. The advantage of ICP is its speed. It was also found to be more accurate than the NAA with respect to the alumina sample. However, the nanoparticles may not be effectively introduced in the nebulizer if large agglomerations occur. Therefore care must be taken to prevent agglomeration when diluting pH stabilized nanofluids.

3.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of nanofluids provides another means of analyzing different components of a nanofluid by weight. This may be desirable when one needs to know an accurate weight percentage of nanoparticles in solvent, or when the amount of polymer (added to improve the nanoparticle stability) in a nanofluid must be known. Thermogravimetric analysis works by heating a small sample on an extremely sensitive balance in a high temperature furnace. The weight vs time curve combined with knowledge of the boiling point of the species in the samples provide the sample composition. The specific equipment used was the Perkin Elmer TGA7. Samples, typically less than 40mg, are placed on a platinum balance and can be heated to over 1000 degrees Celsius.

Results showed for the Fe₃O₄ nanofluid that the surfactant polymer did not completely “cook off” until fairly high temperatures, around 700 or 800 degrees Celsius. It was found the polymer makes up about ¼ of the weight of coated Fe₃O₄ nanoparticles which were found at 3.5wt%. The weight loading of a nanofluid can easily be determined in this fashion. A sample of the 20wt% Nyacol Al₂O₃ nanofluid was also tested. The results showed that the particles consisted of 21.8wt%, which is slightly higher than the specified value. It is believed that this extra weight could possibly be due to the left over hydroxide groups on the surface of the particles. A possible remedy for this would be to push the temperature up to the highest point and allow it to remain there for a longer period of time.

4 CONCLUSIONS

A description of the methodology of preparation and characterization of nanofluids being done at MIT has been given. Insights were found as to the important mechanisms involved in nanofluid creation and stability. A description of the techniques to quantify and characterize nanofluids was also given. These results and methodologies are being incorporated into MIT's project on the determination of nanofluid heat transfer phenomenon.

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