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reprinted from

International Journal of
Micro-Nano
Scale Transport

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ABSTRACT

Rheological characteristics of alumina (Al_2O_3) nanofluids (NFs) were found to exhibit an unexpected behavior. Two base-fluids viz, water and ethylene glycols (EG) with particles of average diameter of 11, 45 and 150 nm were examined. An anomalous reduction in viscosity compared to that of the base fluid was seen for EG based NFs. However, viscosity reduction was absent in water based NFs. The inter-related effects of particle size, concentration and mode of dispersion (mono or poly-dispersed) were investigated. Particle migration under shear is attributed to the reduction of viscosity. The increase in bulk viscosity with particle size reduction is attributed to the surface forces acting between the particles and the medium in a suspension and the increase of effective volume with size.

INTRODUCTION

Improving the heat transfer characteristics using suspensions have been a recent excitement especially after the advent of nanofluids (NFs), which are essentially dilute suspensions of nanoparticles dispersed in a base fluid as defined by Das *et al.*(2008). The works done by Lee et al. (199), Das et al.(2003), Patel et al.(2003) and Prasher et. al.(2005) and many other researchers have demonstrated the anomalous heat transfer and thermal conductivity enhancement of these fluids in the recent past. However, the usage of such fluids demands a comprehensive picture of their flow properties and the physical basis of the effective viscosity of the suspension is one among the dominant properties as it governs the ease of flow and pressure drop during flow.

In the viscosity study of Alumina-water NFs (particle size, 13 nm) done by Pak and Cho (1998), they showed higher viscosity ratio (ratio of the viscosity of the NF to that of the base fluid) compared to titanium oxide-water NF (particle size, 27 nm). The viscosity values were significantly larger than the values predicted by the analytical theory of Einstein (1911) for dilute solutions. Putra et al.(2003) demonstrated the Newtonian nature and the effect of temperature on viscosity of alumina water NFs. To see the effect of base fluid other than water, rheological data on alumina based NFs with varying diameters (27, 40 and 50 nm) suspended in propyleneglycol were reported by Prasher et al.(2006). The viscosity ratio was largely independent of particle sizes and the aggregation of particles in NFs was indicated to be the cause of under-prediction by Einstein's equation. Similar studies were conducted with alumina-water NFs (36 and 47 nm) by Nuguen et al.(2008) and they observed a hysteresis phenomenon on viscosity measurement which sent alarms on the use of NFs in heat transfer applications. Lee et. al(2008) studied about the effective viscosity of Alumina-water NFs at low concentrations of 0.01 % − 0.3 %. They observed a non linier behaviour of viscosity with concentration.

Based on the available literature it may be perceived that studies on viscosity of NFs are still sparse as only discrete combinations of particle size, particle-fluid combination and concentrations have been reported without any systematic observation. Many investigators have not taken it to consideration that their particles may have a large distribution of sizes which influences the underlying physics. The present letter reports some surprising observations on the effective viscosity of NFs while trying to investigate the effect of various parameters such as particle size, volume fraction, mode of dispersion and nature of base-fluids.

EXPERIMENTAL METHODS

Nanoparticles used in all the experiments were alumina while the two base-fluids used were water (W) and ethylene glycol (EG). Commercially purchased nano-powders (Nanophase Technologies Corporation and Inframat Advanced Materials) produced by physical methods were used to prepare the NFs. Three particle sizes (11, 45 and 150 nm), varying over an order of magnitude, were used to analyze the effect of particle size. The particles were dispersed in the base-fluids using several hours of ultrasonication and no stabilizers were used as they may change the rheological properties. Figure 1(a)-(c) show the TEM images of typical Al_2O_3 particles in the 'as received' state. The average particle dimensions were measured by gas absorption method and were 11, 45 and 150 nm.

Rheological properties of EG based NFs were measured using a rheometer (Anton Paar, Physica MCR 301) with a cone and plate geometry (50 mm diameter 2° angle with 47 μm gap) with the plate temperature controlled by a Peltier unit. The measurement was done at the rate of 50 readings in 10 second interval and the shear rate was varied from 50 s^{-1} to 250 s^{-1}. The relative viscosities of water based NFs were measured using an Ubbelohde viscometer as the viscosity values were smaller for applying the rheometer with sufficient accuracy. The above comparative viscometer had a capillary bore of 0.5 mm. The ratio of efflux time of NF, t_{nano} to that of base-fluid t_{bf} was taken as the experimental relative viscosity ratio.

i.e,
$$\eta_r = \frac{t_{nano}}{t_{bf}} \tag{1}$$

The time was measured with an accuracy of 0.5 s and the total experimental time involved was 50 to 100 s; thus the inaccuracy involved in the determination of viscosity ratio was in the range of 0.5 to 1%.

In each sample, the particle sizes varied over a wide range (e.g., in a 11 nm particle size sample, the size of particle may vary from 3 nm to 50 nm) and hence the suspension with these particles was polydispersed. For obtaining a more uniform size distribution of particles, the parent suspension was centrifuged successively. For example first, a NF solution of 1 vol% concentration was prepared by
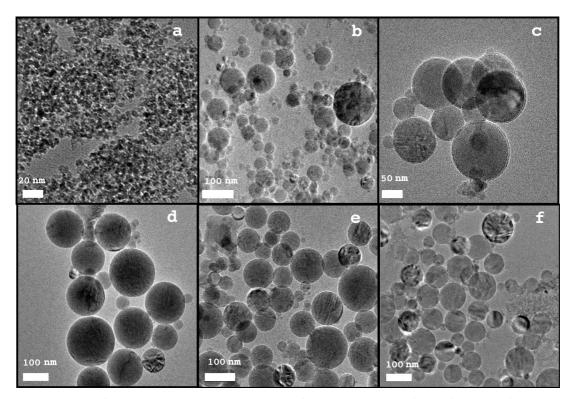

Figure 1. TEM of particles used in the preparation of NFs. 'As received' a) 11, b) 45 and c) 150 nm samples and centrifuged 45 nm (average size) particles at speeds of d) 1200, e) 2200 and f) 3200 rpm.

sonicating the required amount of 45 nm Al_2O_3 nanoparticles with EG as the base fluid. This solution was centrifuged at 1200 rpm and the residue was extracted. The mother liquor (remaining solution after extracting the residue) was again centrifuged at 2200 rpm and the residue was extracted. At last, the centrifugate was further centrifuged at 3200 rpm to extract a residue. These residues were corresponded to three narrower size distributions, collected from an average particle size. The TEM images of 45 nm Al_2O_3 nanoparticles after centrifugation at the three speeds are shown in Figure 1(d)-(f), which clearly suggest that the particles prepared are more uniform in size. These particles are labeled as 45-1200, 45-2200 and 45-3200, respectively in the subsequent description. In 150 nm average size, different centrifugation speeds were employed.

After drying these particles, the NFs of 0.5, 0.25 and 0.125 vol% were prepared by mixing the required amount of nanoparticles in EG and sonicating the mixture for 5-6 hrs. Similarly other samples were also prepared starting from 11 nm and 150 nm nanoparticles. Fifty readings in the shear rate range, $50 \ s^{-1}$ to $250 \ s^{-1}$ were taken for these nearly monodispersed NFs.

For measurement of thermal conductivity of NFs, the transient hot wire instrument developed by Patel et al.(2003) was used.

RESULTS AND DISCUSSIONS

Figure 2 shows the rheological behavior of EG based polydispersed 1vol% alumina NFs. The linear
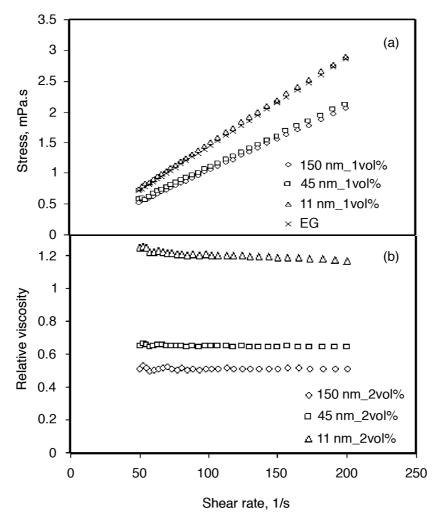

Figure 2. Rheological behavior of EG based polydispersed alumina NFs: (a) shear stress versus strain rate and (b) viscosity versus shear rate.

dependence of shear stress to strain rate shows the Newtonian nature of the NF in the shear rate range 50 s^{-1} to 250 s^{-1},. Figure 2(b) shows that the relative viscosity ratio for Al$_2$O$_3$-EG polydispersed NF (2 vol%) is independent of strain rate. It may be also noted that for NFs with average particle diameters of 150 and 45 nm, the relative viscosity has reduced below unity. This is a unique and anomalous phenomenon since with the addition of particles; the suspension viscosity is expected to increase generally. Also as the particle size reduces, the bulk viscosity increases. To confirm this unique behavior and its size sensitivity, similar curves were drawn for nearly monodispersed NFs derived from 45 nm nanoparticles (Figure 3). The relative viscosity for 0.5 vol% is below unity for all samples 45-1200, 45-2200 and 45-3200, but not for lower concentrations of 0.25 vol% and 0.125 vol%. It shows that this unique behavior occurs only at certain combinations of particle size and concentration. It can be concluded here that there are threshold concentrations at both end (higher and lower concentration side) for getting reduced viscosity. For 11 nm and 150 nm (not shown) particles, similar behavior is observed. For 150 nm particles, reduced viscosity is not visible. For 11 nm Al$_2$O$_3$-EG centrifuged NF, reduced viscosity behavior is obtained only for 800 rpm and 0.5 vol% NF. Probably at 800 rpm centrifugation, we get approximately 45 nm alumina nanoparticles.

However, this phenomenon was observed for only EG based NFs and was absent for water based NFs. In this case, the viscosity increased in all the cases, as expected. The viscosity ratio variation for polydispersed NFs is plotted in Figure 4(a) at a constant strain rate of 150 s^{-1} for different particle sizes. For EG based NFs, with 150 nm and 45 nm particles, the viscosity ratio reduces with particle concentration while for NFs with 11 nm particles, the ratio increases. Theoretical prediction
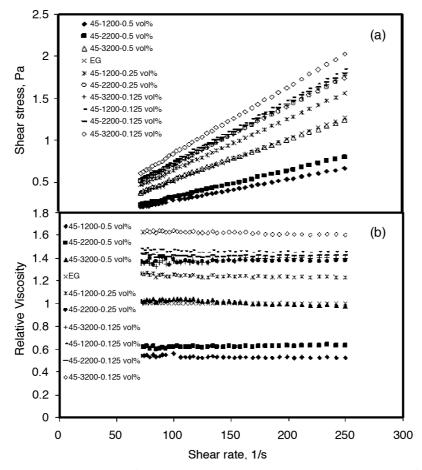

Figure 3. Rheological behavior of EG based nearly monodispersed NFs derived from 45 nm particles: (a)shear stress versus strain rate and (b) viscosity versus shear rate.

using Einstein's equation is also plotted for comparison. This figure also shows the variation for Al_2O_3-water NF. In almost all cases with water as the based fluid, the viscosity ratio is above unity and the effect of concentration on viscosity of NFs made with 11 nm particle is more significant. Einstein's theory predicts the viscosity of 150 and 45 nm water based NFs more or less reasonably while the prediction for 11 nm deviates considerably. This brings out the fact that water based NFs, although do not exhibit the phenomenon of viscosity reduction, does show a size effect in the lower size range, making it different from conventional dilute suspensions. The above result shows that the particle diameter, concentration and nature of the base fluid have profound influence on NF
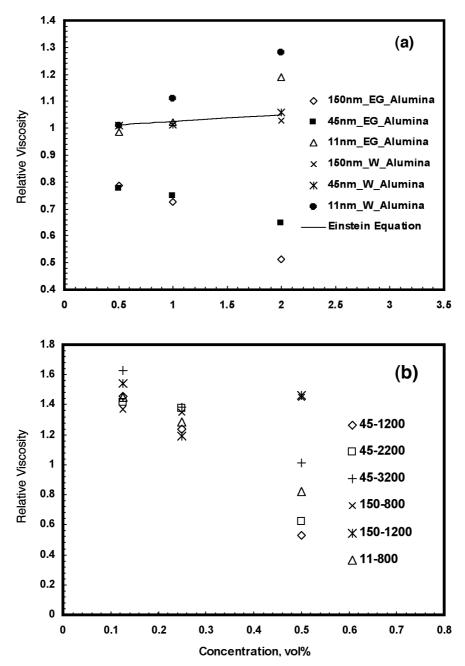

Figure 4. Variation of relative viscosity with concentration for (a) water and EG based poly dispersed NFs and (b) EG based nearly monodispersed NFs for different speeds of centrifugation.

viscosity and deviates considerably from conventional theory, and this phenomenon has not been reported in literature. Similarly, for nearly monodispersed EG NFs, viscosity ratio variation for various concentrations of EG based NFs is shown in Figure 4(b) at constant strain rate of 152 s^{-1} for all sizes (or all speeds) of particles. For 45 nm NFs, viscosity decreases with concentration at all speeds. For 150-800 and 150-1200 rpm, the trends are mixed, but the15-1600 rpm viscosity increases with concentration. For 11- 800 the trends are the same as that of 45 nm. It may be said that at 800 rpm, we get a particle size comparable to 45 nm.

Two major observations are made from the experimental results. Firstly, viscosity of EG based alumina NF shows anomalously reduced viscosity compared to the base fluid, while it was not observed for water based NFs. A similar behavior of Alumina-EG NFs (reduced viscosity behaviour) was also observed by Jermey B. Gorden (2007) at MIT in his MS study. He has attributed this strange behaviour to the presence of water in as-received high concentration sample, which is questionable, since the reduced viscosity behaviour occurs at some particular sizes and concentration only. Secondly, as the particle size was reduced, the viscosity increases and in the nanometer range, it starts deviating from the conventional theory. In usual cases, dilute suspensions display higher viscosity than the base fluid and follows Einstein's equation for suspensions (1911),

$$\mu_s = \mu_{bf}(1+2.5\phi) \tag{2}$$

where μ_s stands for viscosity of the suspension, μ_{bf} for viscosity of base fluid and ϕ for volume fraction. Any deviation from the above requires an explanation.

Particle migration in NFs has been reported in detail by Buongiorno (2006) and Ding and Wen (2005). In the present study, the reason for reduction of viscosity ratio for ethylene glycol based NFs is likely to be due to shear induced particle migration. Particle migration of Brownian suspensions under shear was shown experimentally by Frank et al.(2003) using confocal microscopy. According to Ding (2005), due to this shear induced particle migration, viscosity may be non uniform across the transverse plane, but if we see the overall measured viscosity of some particular nanofluids, it is reduced. Also one may argue that this reduced viscosity behavior is due to slip taking place near the walls through the sticking nanoparticles to the walls. If this is true, viscosity should reduce for all sizes, fluids and concentrations. But this behavior is seen only at some particular combinations of fluid, particle size and concentration with perfect repeatability. Hence, definitely any sweeping reason such as instrument error or particle slip is not the reason behind this strange behavior. Therefore the only probable reason left is in the physics of particle–fluid-surface interaction such as shear induced particle migration, which needs to be confirmed by theoretical estimation of the order of various forces at different ranges of particle sizes, fluids and concentrations, which is presented below.

A non-dimensional Peclet number, which is conceptually a ratio of time required for Brownian diffusion to move a particle to the time required for shear flow to move the same distance, may be used as yard stick for determining the influence of shear. Thus Peclet number (Pe) may be defined as

$$Pe = \frac{6\pi\eta_0\gamma a^3}{kT} \tag{3}$$

Where a is the particle radius, η_0 is the base-fluid viscosity, γ is the strain rate, k the Boltzmann constant and T is the absolute temperature.

Figure 5(a) shows the variation of Pe with particle size for two base fluids at a constant strain rate of 200 s^{-1}. It can be observed that the values of Pe increases with particle size and are one to two orders higher for EG based NFs when compared with that of water based NFs. It may be comprehended from this figure that the effect of particle migration due to shear is likely to be predominant for EG based NFs compared to that of water based ones. Figure 5(b) shows variation of Pe with shear rate for different particle sizes, both for water and EG based NFs. Even though the above analysis was carried out for mono-dispersed suspensions, the effect of particle migration due to shear would be much more profound for a poly-dispersed suspension due to random filling of particles of different sizes in the interstitial space between larger particles.
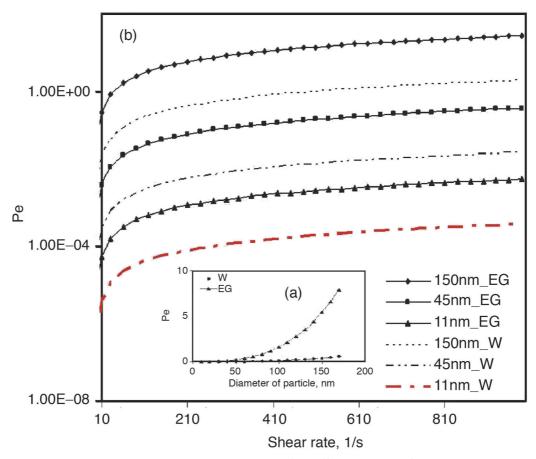
Figure 5. Peclet number variation with shear rates for different particle/fluid combinations. The variation with particle sizes at a constant shear rate for water and EG based NFs is in the inset.

In order to figure out the effect of particle size and concentration on the bulk viscosity of suspensions, it is important to analyze the forces acting between the particles. The study of Derjaguin–Landau–Verwey–Overbeek (DLVO) theory done by Verwey et al. (1948) states that the total inter-particle potential energy is mainly the sum of van der Waals attraction and electrical double layer repulsion. Thus, according to this theory, the total interaction force, F_T between two spherical particles of radius 'a' may be given as,

$$F_T = \frac{Aa}{12D^2} - 2\pi\varepsilon\varepsilon_0 a\varphi_0^2 \kappa e^{-\kappa D} \tag{4}$$

where φ_0 the surface potential, ε the relative permittivity of the base-fluid, ε_0 the permittivity of free space, A the Hamaker constant, D the surface to surface particle separation distance and κ the inverse Debye length. For force analysis, the surface to surface distance may be calculated assuming a cell model with BCC (body centered cubic) structure with a particle at center and four quarters occupying the corners of the cube. An order of magnitude analysis of the total interaction force with data from Zhou et al.(2000) for alumina suspensions at some particular ph (A~ 10^{-20}J, $\varphi_0 = 50$mV(order of Zeta potential), $\varepsilon_0 = 8.88 \times 10^{-12}$ C^2/Jm, $\varepsilon = 80$ for water and $\kappa = 0.32$ nm^{-1}), shows that F_T for 11 nm suspension with 2 %volume concentration is 10^{-15}N while that for 150 nm suspension for the same concentration is 10^{-14} N. This shows the fact that as the particle size is reduced, the interparticle

repulsion force increases as the total surface area increases, resulting in net increase of bulk viscosity of the suspension.

It may be perceived here that within the interplay of cohesive forces and shear forces for suspensions with 11 nm particles, the cohesive forces dominate over the shear thus showing a relative viscosity above unity. In the case of EG based NFs, the particle migration under shear force helps as a lubricating effect, reducing the relative viscosity. The story is, however, different with water based NFs due to the polar nature of water. Due to this, van der Waals forces and the electric double layer dominate which reduce the particle migration under shear and induce the fluid to behave in the expected way.

The effect of size can be explained by adopting the theory given by Larson (1999) also. He proposes that in a solution to keep particles apart, the surface charged increases the effective particle diameter. This effective particle diameter is defined as

$$d_{eff} \approx \frac{1}{\kappa} \ln\left\{\left\{ \alpha / ln\left[\alpha / ln\left(\alpha / .... \right) \right] \right\}\right\}$$

(5)

Where the infinite series of logarithms can in practice be truncated after the third one.
And the α is defined as

$$\alpha \equiv \frac{4\pi\varepsilon\varepsilon_0 \varphi_s^2 a^2 \kappa \exp(2a\kappa)}{k_B T}, \text{ Here } k_B \text{ is Boltzman constant}$$

And the effective volume fraction of particles in the solution will be

$$\phi_{eff} \equiv \phi\left(\frac{d_{eff}}{2a}\right)^3$$

(6)

The ratio $(d_{eff}/2a)$ against particle size is drawn in fig. 6 and it shows that the ratio $(d_{eff}/2a)$ decrese with the increase in particle diameter. It is obvious from equation (6) that for the same volume fraction of NFs for different size of nanoparticles, the effective volume fraction is higher for smaller size of particles and so also the viscosity.
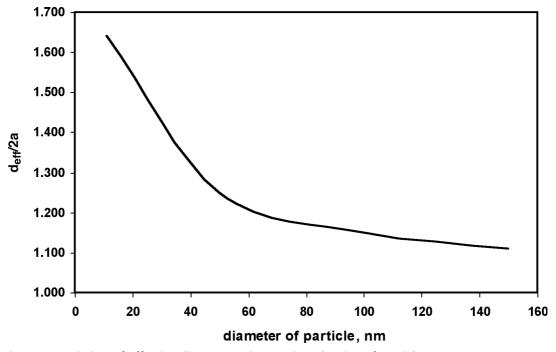

Figure 6. Variation of effective diameter ration against the size of particles.

For using these NFs for heat transfer applications, it is sensible to compare the effect of thermal conductivity along with viscosity. It was shown by Prasher et al. (2006) that for NFs to be advantageous, the ratio of viscosity enhancement coefficient, C_μ to thermal conductivity enhancement coefficient, C_k should be less than four. A comparison of viscosity ratio with conductivity ratio for water based alumina NFs for varying concentrations (Fig. 7) reveals that this is indeed the case. It may thus be mentioned here that even though the viscosity has increased with reduction in particle sizes, the thermal conductivity values also increase proportionally, thus making it a prominent candidate as a cooling fluid. On the other hand, EG based alumina nanofluids are favorable for heat transfer applications, due to observed behavior of reduced viscosity and increased thermal conductivity.
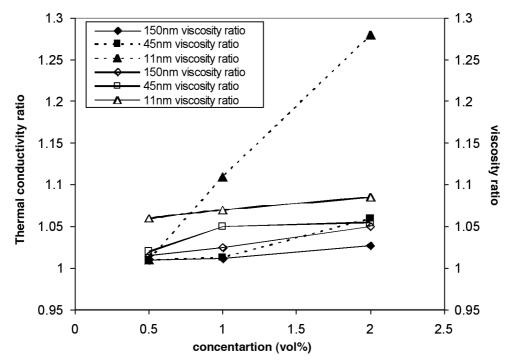

Figure 7. Variation of thermal conductivity ratio and viscosity ratio for water based Alumina NFs.

CONCLUSIONS

In conclusion, the experimental data has shown typical Newtonian behavior for both W based and EG based alumina NFs. For the latter, for higher particle sizes a unique phenomenon of reduction in viscosity is observed in polydispersed NFs at certain range of concentration. These results and trends have been further confirmed by NFs obtained by centrifugation and resuspension of particles so that nearly monodispersed NFs are obtained, thus eliminating the effect of size variation. This phenomenon was found to be absent in the water based NFs. Analysis of these results attributes this phenomenon to particle migration under shear. It is also observed that as the particle size reduces the bulk viscosity values get increased, which is mainly due to the increase in surface attractive forces. Comparison with increase of thermal conductivity reveals that even with the increase in viscosity, NFs remain attractive candidates for next generation cooling.

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