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ANOMALOUS RHEOLOGICAL BEHAVIOR OF COMPLEX FLUIDS (NANOFLUIDS)

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ABSTRACT

The rheological behavior of various complex fluids was explored in this experimental study. Nanofluids were obtained by mixing nanoparticles with various solvents. The solvents consisted of metal salt eutectics that melt at high temperatures (exceeding 200 °C) depending on the composition of the metal salts in the eutectics. The rheological behaviors of these high temperature solvents were measured as a function of temperature before and after mixing with different types of nanoparticles (chemical composition, size, shape and concentration). These nanofluids exhibited non-Newtonian behavior (shear thinning behavior) while some of the other nanofluids were surprisingly found to have Newtonian behavior. It was observed that high aspect ratio nanoparticles (e.g., stick shaped carbon nanotubes) were more likely to cause shear thinning behavior of the resulting nanofluids.

INTRODUCTION

Concentrating solar power (CSP) plants utilizes thermal energy from the sun to generate electricity by utilizing various thermodynamic cycles (e.g., Rankine cycle) [1-3]. The efficiency of the CSP plants is determined by the operating temperature of the Thermal Energy Storage (TES) system. Hence, increasing the operating temperature of the TES enables the efficiency of the system to be enhanced. Molten salts and their eutectics are typically employed in the CSP systems to increase the operating temperature. Conventional TES materials such as synthetic oils (e.g., Therminol®) suffer from large vapor pressures at higher temperatures and also suffer from chemical stability issues that limits their operating

temperatures to below 400 °C. Pacheco et al. developed a thermocline system using molten-nitrate salt as heat transfer fluid [2]. A previous study by Kearney et al. showed that a nitrate salt eutectic is more cost effective material than the typical synthetic oils used in TES [3]. Nevertheless, molten salts have poor thermal properties such as specific heat which is an impediment to their commercial application in large utilities.

In our previous studies, we demonstrated that the specific heat of molten salts eutectic can be enhanced significantly by doping with nanoparticles at minute concentrations (0.1~1% mass concentrations). Solvents doped with minute concentration of nanoparticles that are dispersed uniformly to form stable suspensions (colloids) are termed as nanofluids. The specific heat of carbonate and chloride salts (eutectics) were enhanced by ~20 % in liquid phase by doping with organic and inorganic nanoparticles at ~1% mass concentration [4-6]. These studies prove the feasibility for enhancement of the specific heat capacity of the molten salts on mixing with nanoparticles. This alludes to the possibility of improving the overall thermal efficiency of the CSP systems by using nanofluids. However, the rheological characteristics of the molten salt nanofluids should be taken into consideration, because pumping costs are affected by the rheological behavior of these nanofluids and can be a significant issue which affects the overall thermodynamic efficiency (and therefore the cost for generating solar thermal power).

While a significant number of studies have been reported in the literature on the thermal conductivity of nanofluids [7, 8], relatively less attention has been focused on the specific heat capacity and rheological properties of nanofluids. Most of

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these studies have focused on conventional solvents such as water and ethylene glycol [9-10]. Virtually no studies have been reported in the literature for the rheological properties of of high temperature nanofluids, such as involving the molten salt nanofluids.

In this study the rheological behavior of high temperature nanofluids were explored by using molten salt nanofluids as the test fluids. An alkali carbonate salt eutectic and a nitrate salt eutectic were used as the solvents. Multi-walled carbon nanotubes and silica nanoparticles were dispersed into these eutectics as solvents. It is expected that the nanofluids can demonstrate non-Newtonian behavior even though the solvents are Newtonian. Hence, in this study the viscosity measurements were performed by varying the shear rates over a large range in order to explore the rheological characteristics of these high temperature nanofluids (to ensure whether the nanofluids show non-Newtonian behavior). Finally, effect of nanoparticle shapes on viscosity was investigated by using carbon nanotubes (cylindrical) and silica (spherical) nanoparticles at the same mass concentration.

NOMENCLATURE

a nanoparticle radius

D fractal index

η viscosity

η_r relative viscosity

$[\eta]$ intrinsic viscosity

φ nanoparticle concentration by volume

φ_m maximum concentration

Subscripts

a aggregated nanoparticles

bf base fluid

nf nanofluid

EXPERIMENTS

Two different nanofluids were used as test fluids in the viscosity measurement experiments. Since we used molten salt eutectics as base fluids (which melts at temperatures exceeding 200 °C), the nanofluids in this study are referred to as high temperature nanofluids. One of the solvents consists of a carbonate salt eutectic which is a mixture of lithium carbonate (Li_2CO_3, procured from Sigma Aldrich Inc.) and potassium carbonate (K_2CO_3, procured from Sigma Aldrich Inc.) with 62:38 molar ratio, respectively. The other solvent consists of sodium nitrate ($NaNO_3$, procured from Spectrum Chemical Inc.) and potassium nitrate (KNO_3, procured from Spectrum Chemical Inc.) with 40:60 molar ratio, respectively. The carbonate eutectic and the nitrate eutectic have melting points of about 490 C and 220 C, respectively.

Two different types of nanoparticles were used in the experiments: multi-walled carbon nanotubes (CNT, procured from Meliorum Technologies Inc.) and silica (SiO_2) nanoparticles (procured from Alfa Aesar Inc.). The CNT was dispersed into the carbonate salt eutectic and silica was dispersed into the nitrate salt eutectic. The transmission electron microscopy (TEM, JEOL JSM-2010) images for those nanoparticles are shown in Fig. 1.
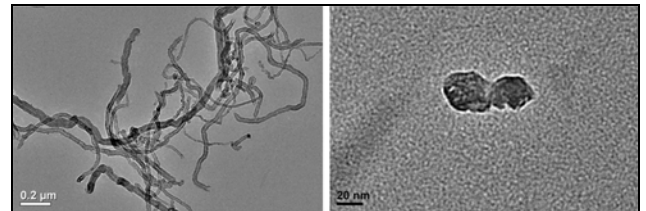

Figure 1. Transmission electron microscopy (TEM) images of carbon nanotubes (left) and a silica nanoparticles (right) used in the experiments.

The nominal size of the carbon nanotubes provided by the manufacturer was specified to be 10-30 nm in diameter and 1.5 μm in length. As shown in the Fig. 1, the size of the nanotubes is consistent with the manufacturer specification – however their typical length was observed to be less than 1.5 μm. The nominal diameter of the silica nanoparticles is 10 nm but the actual size from the TEM image is larger than 10 nm. Since CNT have a propensity to agglomerate in water, hence a surfactant Gum Arabic (GA, procured from Sigma Aldrich) was used for their dispersion. The mass concentration of the GA was 1% with respect to the base material (eutectic). Regarding silica nanofluid, additives were not used in the nitrate nanofluids, since the surfactants are typically organic material which can get oxidized by the nitrates, which can lead to uncertainty in the resultant composition of the nanofluids. In this study, all chemicals were used as received (i.e., without any surface functionalization or chemical post processing).
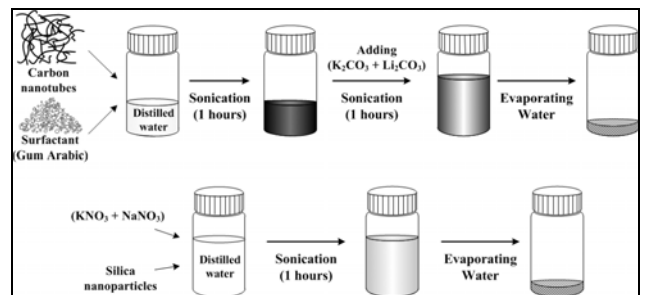

Figure 2. Schematics of synthesis procedures for carbonate eutectic-CNT nanofluids (top) and nitrate eutectic-silica nanofluids (bottom).

Figure 2 shows the synthesis procedure for the high temperature nanofluids. We employed three-step method for the carbonate eutectic-CNT nanofluids and two-step method for the nitrate eutectic-silica nanofluids. In the former case, CNT were

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dispersed into water using surfactant (GA) and the suspension ultrasonicated for 1 hour. Next carbonate salt eutectic was added to the aqueous nanofluid along with additional amounts of water. Then, the suspension is sonicated again for 1 hour. Finally, the suspension was evaporated on a hot-plate to obtain the dehydrated samples. In the two-step method, silica nanoparticles and the nitrate salt eutectic were mized together and dissolved in water. The suspension was ultrasonicated for 1 hour and then the suspension was evaporated on a hot-plate (by the same procedure as the previously mentioned three-step method).

A Rheometer (AR-2000ex, TA Instruments) and a steel cone-and-plate test section (40mm in diameter and 53 μm in truncation gap, TA Instruments) were employed to investigate rheological behavior of the high temperature nanofluids. The viscosity of the nanofluids was measured over a wide range of shear rate from 1 to 1000 [1/s]. During the measurements, temperature was set to 550 C and 300 C for the carbonate eutectic-CNT nanofluids and the nitrate eutectic-silica nanofluids, respectively. These temperature ranges were adequate for the nanofluids to be in liquid state. The temperature was controlled by an external convection/radiation oven in the instrument. The temperature uniformity in the test sample and the oven was monitored in the instrument. The mass concentrations for both CNT and silica nanoparticle were set to an identical value of 1%. The viscosity of the nanofluids was compared to a base line value for the shear rate of 1000 [1/s]. For the nitrate nanofluids, additionally, an effect of the temperature on the viscosity change was investigated by performing the experiments at both 300 °C and 400 °C. Finally, the experimental results were compared with the predictions from several theoretical models.

RESULTS

The rheological behaviors of the pure solvent (for the carbonate eutectic) and the CNT doped nanofluid are compared in Fig. 3. As expected, the pure solvent demonstrated Newtonian behavior (viscosity values were independent of shear rate). There is a large measurement uncertainty at low shear rates due to limited resolution of torque measurements and the behavior at shear rates less than 10 s^{-1} can be discarded. Fig. 3 shows that the CNT nanofluids demonstrated non-Newtonian characteristics (shear thinning behavior). For low shear rates the nanofluids have much higher viscosity than the eutectic but it decreased with an increase of the shear rate. At the shear rate of 1000 s^{-1}, the viscosity of the pure eutectic asymptottes to a value of 0.0124 [Pa·s]. This is consistent with literature value of 0.0131. Hence the experimentally measured value is within 5% of the literature data [12]. The viscosity of the nanofluid at CNT mass concentration of 1% was measured to be 0.0137 [Pa·s]. Hence the viscosity of the nanofluid is enhanced by 10.5 % (when compared to that of the pure solvent).

Figure 4 shows the rheological behaviors of the pure nitrate eutectic and the silica nanofluid at 300 °C. Similarly to the rheological behavior of the carbonate eutectics, the pure nitrate eutectic demonstrated the characteristics of a Newtonian fluid (i.e., the viscosity was found to be independent of the shear rate). However, the nanofluid demonstrated non-Newtonian behavior (shear thinning liquid). For the pure nitrate eutectic, the experimentally measured value of viscosity was 0.00327 [Pa·s]. The measured value was within 4% of the literature data of 0.00315 [Pa·s] [13]. As shown in Fig. 4, the viscosity of the silica nanofluid was enhanced significantly by 63% to a value of 0.00534 [Pa·s].
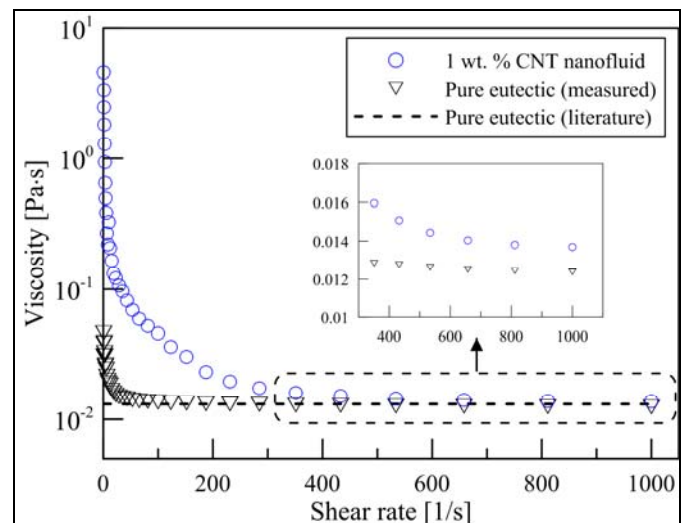

Figure 3. Rheological behavior of carbonate eutectic and the CNT nanofluid as function of shear rate at 560 °C.
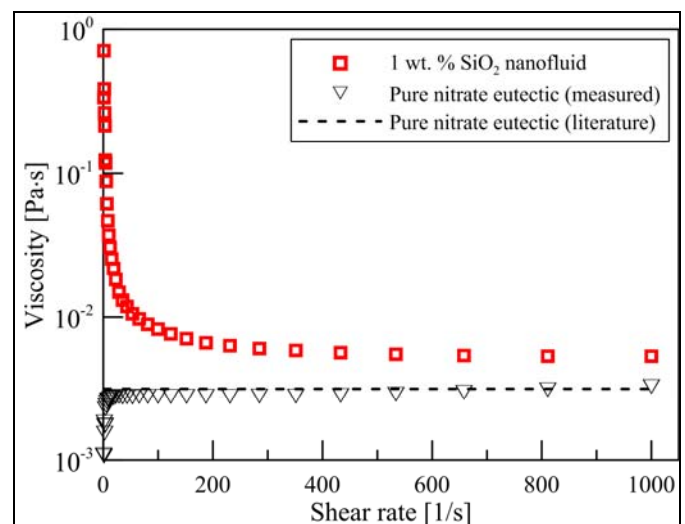

Figure 4. Rheological behavior of nitrate eutectic and silica nanofluids as function of shear rate at 300 °C.

The rheological behavior of the nitrate eutectic and the silica nanofluid was also measured at 400 °C and is plotted in

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Fig. 5. It was observed that the viscosity of the eutectic decreased as the temperature increased and the same trend was observed for the silica nanofluid. The viscosity enhancements at the two temperatures were marginally different. The viscosity on the nanofluids was enhanced by 63% and 79% at 300 °C and 400 °C, respectively. Therefore, the viscosity enhancement increased with temperature for the silica nanofluid.
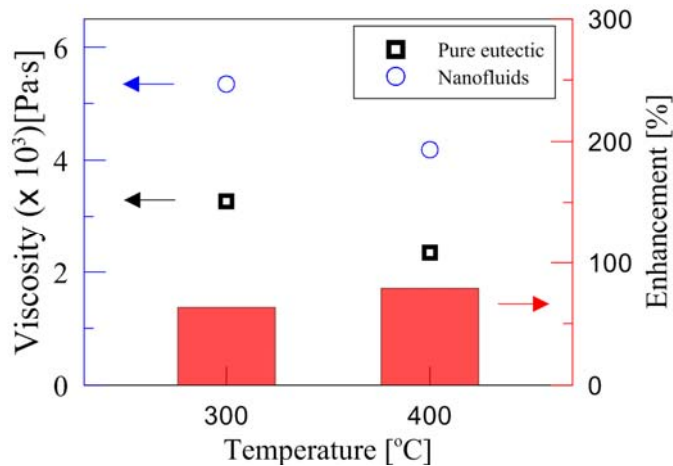

Figure 5. Viscosity of the silica nanofluid and pure nitrate eutectic at 300 °C and 400 °C.

DISCUSSION

A simple theoretical model (Eq. 1) for estimation of the viscosity of fluids containing spherical particles in low concentration was suggested by Einstein (1906) [14]. Brinkman (1952) [15] generalized the Einstein model for incorporating high concentration of spherical particles (Eq. 2).

$$\eta_r = \frac{\eta_{nf}}{\eta_{bf}} = 1 + 2.5\,\varphi \tag{1}$$

$$\eta_r = \frac{1}{\left(1 - \varphi\right)^{2.5}} \tag{2}$$

The theoretical models above did not incorporate the effects of agglomeration on the viscosity of the nanofluids. Therefore, the predictions from these models were not consistent with the observed experimental measurements. The Krieger-Dougherty model (Eq. 3) accounts for the effect of aggregation of the nanoparticles [16].

$$\eta_r = \left(1 - \frac{\varphi_a}{\varphi_m}\right)^{-[\eta]\varphi_m} \tag{3}$$

Typically, the maximum concentration (φ_m) is chosen to be 0.605, and the intrinsic viscosity ($[\eta]$) is 2.5 for monodisperse systems [17]. The effective volume fraction of aggregates (φ_a) is substituted by the ratio of radii of the aggregates to primary nanoparticles (a_a/a) as follows [18, 19].

$$\varphi_a = \varphi \cdot \left(a_a/a\right)^{3-D} \tag{4}$$

In Eq. (4), the fractal index (D) is chosen to be 1.8 for both CNT and silica nanoparticles [11, 17, 20]. Finally the volume concentration of the nanoparticles was calculated from the mass concentration of the nanoparticles, density of the nanoparticle, and density of the pure eutectic – which is the base fluid (solvent). Subsequently, Krieger-Dougherty model is rewritten as follows in Eq. (5):

$$\eta_r = \left(1 - \frac{\varphi}{0.605}\left(\frac{a_a}{a}\right)^{1.2}\right)^{-1.5125} \tag{5}$$

Given the mass concentrations of the CNT and the silica nanoparticles, the volume concentration can be determined. Thus, the aggregation factor (a_a/a) can be estimated from the experimental measurements. For the carbonate eutectic-CNT nanofluids, the relative viscosity was 1.107 and the volume concentration of the CNT was 1.6 %. The aggregation factor of the CNTs was obtained to be 2.1. In previous studies, a value of 3.3 (or 4) was used for for a_a/a for ethylene glycol-based titania nanofluid [21] and a value of 9.46 was used to explain the viscosity increase of the ethylene glycol-titanate nanofluid [11]. Therefore, the estimated value of 2.1 for the carbonate eutectic-CNT nanofluids is reasonable, even though it is lower than expected value from the literature data. However, the aggregation factors for the nitrate-silica nanofluids have much higher values. As reported in the previous section, the relative viscosities of the nanofluids are increased to 1.63 and 1.79 at 300 and 400 °C, respectively. From Eq. (5), the aggregation factors were 13.8 and 16.0. Comparing with the aggregation factors from the CNT nanofluids they are observed to be larger than the typical values reported in the literature.

Realistically, it is not reasonable for the silica nanoparticles to have the aggregation factor more than 10, because of lower volume concentration and the results reported for CNT in the literature. The density of the CNT is much less than that of the silica so the volume concentration of the silica is smaller than that of CNT. Moreover, the structure of the CNT causes it to have a higher propensity for agglomeration. Our previous study into ethylene glycol (EG)-based nanofluids proves that CNT nanoparticles can induce larger increase in viscosity than the silica nanoparticles.

CONCLUSION

The viscosity of two high temperature nanofluids has been measured for a wide range of shear ratse using the rotational rheometer using the cone-and-plate test section. The enhanced viscosity in the nanofluids was observed over the whole shear rate range. For the two different nanoparticles, the enhancements in the viscosity of the high temperature

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nanofluids were examined. The results from this study are summarized as follows:

(a) It was observed that the high temperature nanofluid exhibited non-Newtonian behavior (shear thinning liquid). In other words, as the shear rate increases the viscosity was decreased.

(b) The viscosity of the nanofluids was significantly enhanced by up to 11% in the carbonate eutectic-CNT nanofluid and up to 79 % in the nitrate eutectic-silica nanofluids.

(c) The predictions from various theoretical models were compared with the experimental results. Krieger-Dougherty model is expected to be the most appropriate model for matching the experimental measurements. The aggregation factors in Krieger-Dougherty model were estimated from the experimental results.

ACKNOWLEDGMENTS

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