



Sub-Micron Dispersions of TiO₂ in Ethylene Glycol-Water Mixture: Rheology & Thermal Conductivity

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Abstract: Experiments were conducted on the preparation and characterization of sub-micron dispersions of TiO₂ in ethylene glycol-water mixture. The influence of particle concentration (< 1 vol %), temperature (30 – 45 °C) on viscosity of dispersions have been studied, from which a linear dependence of viscosity with particle concentration was observed. The sub-micron dispersions exhibited higher thermal conductivity than that of ethylene glycol-water mixture, with the thermal conductivity enhancement varying linearly with particle concentration. An empirical correlation has been developed for the prediction of relative viscosity, whose prediction for 21 data points are within an error of ±2 %.

Key words: Sub-micron dispersion, TiO₂, ethylene glycol-water, viscosity, thermal conductivity.

1 INTRODUCTION

The use of particle dispersions is in vogue for several applications in food, pharmaceutical, paint industry etc. [1]. Particle dispersions were found to be effective in absorbing gases into liquid/liquid mixture facilitating the way for introduction of multiphase reactors in chemical industry [2, 3]. There seems to be reasonable understanding on dispersions containing micron-sized particles and polymers with respect to their rheological characteristics, as evident from literature [4, 5]. With the advancement in controlled preparation of sub-micron particles and nanoparticles, applications of dispersions made of such particles have begun to

become prominent. Nanofluids which are engineered dispersions of nanoparticles in liquid [6] are considered as promising candidates to offer solutions to thermal management, process intensification etc. During the preparation of sub-micron dispersions, sufficient care needs to be taken with respect to safety. Hence the choice of the material for preparation of dispersions is the key. For applications that utilize the physical nature of particles and not their chemical identity, a wide choice exists for material selection. Thermal management is an application of particle dispersions wherein considerable choice exists with the material selection. Several metals, metal oxides, carbon

allotropes etc. may be used for this purpose [7, 8]. The essential requirements of a material to be used for preparation of sub-micron dispersions for thermal management include (i) high thermal conductivity of particles compared to that of liquid (ii) ease of availability of material along with non-toxicity and (iii) ease of sustenance of colloidal stability.

An important consideration in the preparation of sub-micron dispersions for applications involving convective heat transfer is their viscosity. It is desirable to have the viscosity of dispersions to be as close to that of liquid to ensure that the onset of turbulence is not delayed too much, apart from requiring not-too-higher energy consumption for pumping. A higher thermal conductivity of dispersions is desired for thermal management applications. Hence it is important to have considerations of both viscosity and thermal conductivity along with colloidal stability during the development of nanofluids. In the present work, sub-micron dispersions of TiO₂ in ethylene glycol-water mixture (50 % by volume each) have been prepared by stirred bead milling of micron-sized TiO₂ particles followed by ultrasonication. The viscosity and thermal conductivity data for sub-micron dispersions of TiO₂ in ethylene glycol-water mixture prepared by stirring bead milling are unavailable in literature. Hence, appropriate experiments were conducted to obtain such data which are reported in the present manuscript.

2 EXPERIMENTAL

2.1 PREPARATION OF SUB-MICRON DISPERSIONS

The first step in the preparation of sub-micron dispersions is the preparation of a concentrated suspension of sub-micron particles in water using stirred bead milling. Titanium dioxide powder (Qualigens Fine Chemicals, India) was used as the feed material while Yttrium-stabilized Zirconia of 0.4 mm and 0.2 mm were used as the grinding media. The stirred bead mill used for the preparation was 125 mm in diameter made of stainless steel and fitted with a mild steel cooling jacket. The working volume of the mill is about 1000 mL. Sixteen pins were attached to stirrer, four each at four axial locations, to facilitate intimate contact between the grinding media and feed. A feed concentration of 120 g/L was used with a ball loading of 0.8. The total milling time was 12 hours with initial 6 hours

milling performed with 0.4 mm beads while the remaining milling was performed with 0.2 mm beads. Various concentrations of sub-micron dispersions were prepared by serial dilution of TiO₂-water sub-micron suspension with water and then with ethylene glycol (EG), to obtain a liquid composition of ethylene glycol (50 Vol %)-water (50 Vol %). These were homogenized using a high-shear homogenizer (T25, UltraTurrax, Germany), followed by ultrasonication for about 7 hours.

2.2 SCANNING ELECTRON MICROSCOPY

A small quantity of dispersion was dried on a glass slide and imaged using a Field-Emission Scanning Electron Microscope (JSM 5701 F, JEOL, Japan). A thin film of gold was sputter coated on the glass slide and introduced into the specimen chamber for imaging at a working distance of 8.1 mm.

2.3 VISCOSITY AND THERMAL CONDUCTIVITY MEASUREMENTS

The viscosity of dispersions was measured using a digital viscometer (LVDV Pro-II, Brookfield Engineering, USA) with Spindle 00. The thermal conductivity was measured by transient hot-wire technique (KD-2 Pro, Decagon Devices, USA) using KS-1 probe. The thermal conductivity measurements were done in an environment devoid of disturbance to ensure elimination of any convection effects. The instrument was able to provide reproducible values of thermal conductivity of water with ± 1 % error in the temperature range of 31-45 °C.

3 RESULTS & DISCUSSION

3.1 SCANNING ELECTRON MICROGRAPH

Figure 1 shows the scanning electron micrograph of oven-dried sample of TiO₂-EG-Water sub-micron dispersion. The presence of nanoparticles (particle size less than 100 nm) is evident from the electron micrograph. Particles of size around 30 nm are also visible. This testifies the capability of stirred bead milling to produce nanoparticle dispersions by top-down approach. The particle size information is crucial as the surface area and hence the interactions between a fluid and particle are influenced by it [9-11]. The average absolute zeta potential was found to be 27.9 mV. It may be recalled that nanoparticle dispersions with absolute zeta potential 30 mV are expected to exhibit reasonable colloidal stability due to higher electrostatic repulsion [12]. The higher value of zeta potential is responsible for the colloidal stability of TiO₂-EG-Water dispersions.

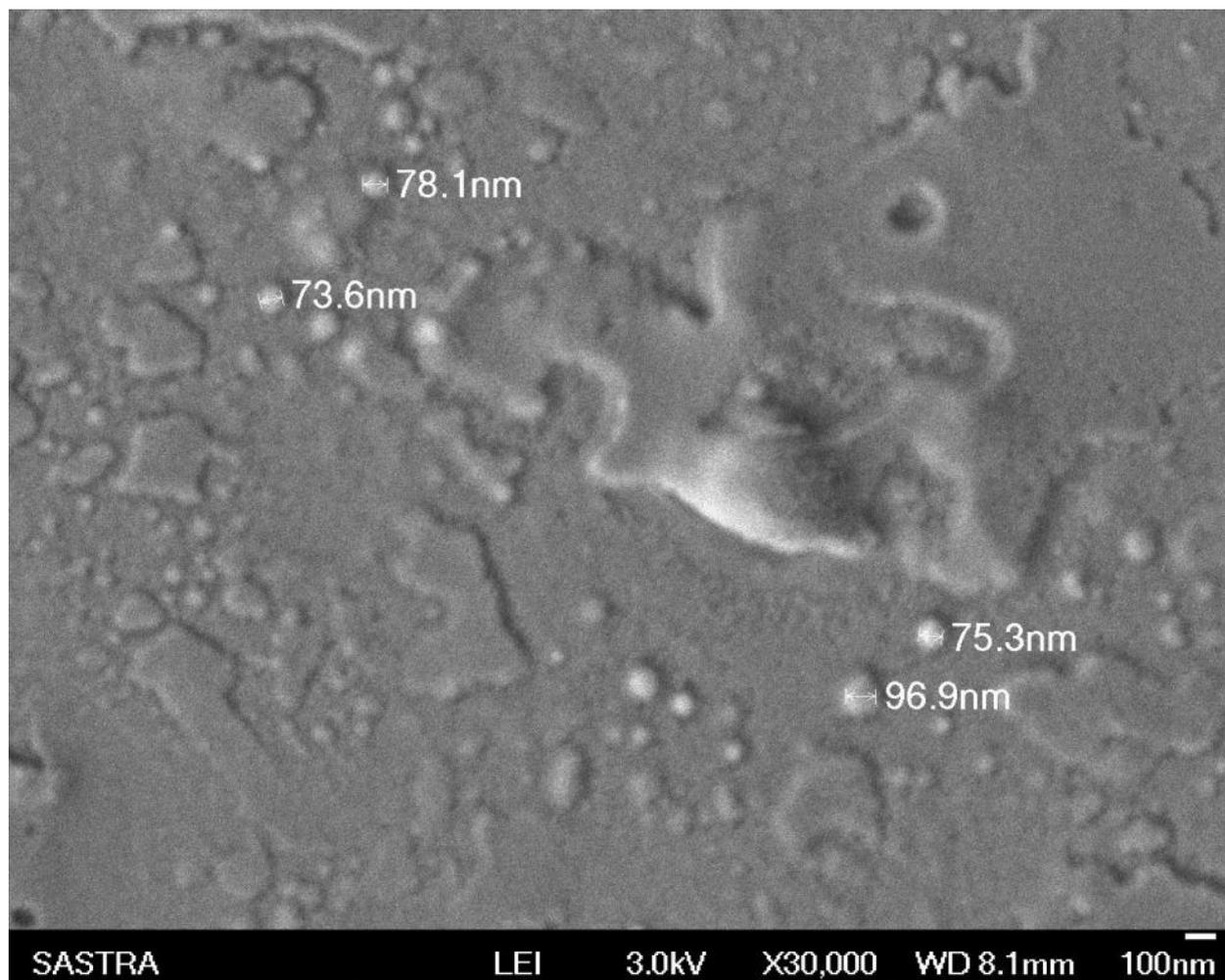


Figure 1. Scanning electron micrograph of dried sample of TiO₂-EG-water nanofluid

3.2 EFFECT OF PARTICLE CONCENTRATION ON VISCOSITY

The influence of particle concentration on viscosity of TiO₂-EG-water dispersions has been studied over a concentration range of 0-1 vol %. The choice of this concentration range is driven by two factors:

- (i) Stability of dispersions is influenced by inter-particle forces. At higher particle concentrations, distance between two colloidal objects would be less. Attractive Van der Waals forces are stronger at short inter-particle distances [13] and hence chances for agglomeration are greater.
- (ii) The rheological characteristics of concentrated dispersions may differ drastically from that of pure liquid. For example, dispersions of high concentration Fe₂O₃ nanoparticles in water

exhibit Non-Newtonian characteristics [14], while the liquid (water) is Newtonian. For applications aimed at process intensification, the change in rheological characteristics is undesirable.

Figure 2 shows the influence of particle volume concentration on the viscosity of TiO₂-EG-water sub-micron dispersions. An increase in viscosity with particle volume concentration is evident from Fig. 2. The influence of particle concentration in increasing the viscosity of dispersions is well-documented [4, 5]. The increase in viscosity of dispersion over that of pure liquid is attributed to the influence of particles in altering the flow field [15], which increases with increase in particle concentration. Hence viscosity of dispersions increases with increasing particle concentrations.

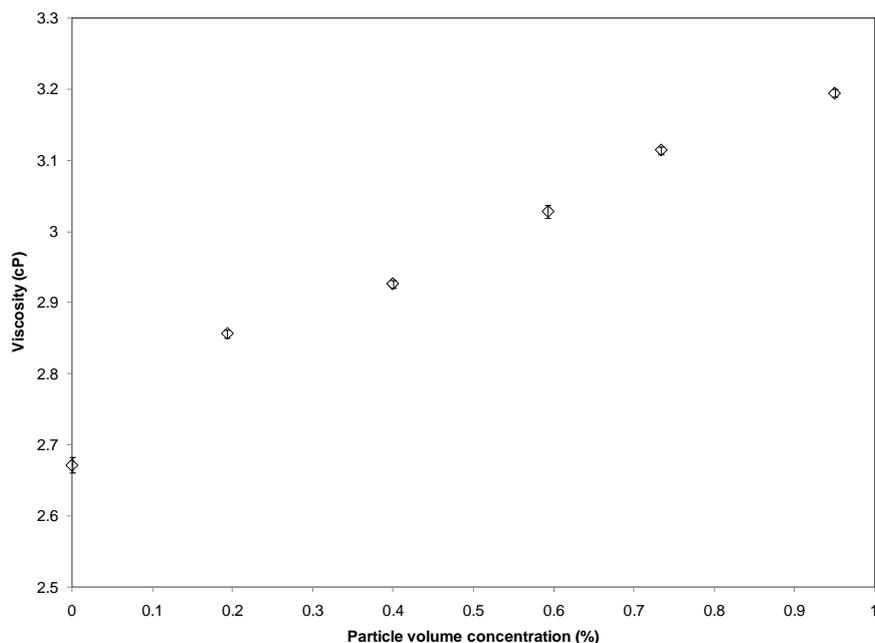


Figure 2. Influence of particle volume concentration on viscosity of sub-micron TiO₂-EG-water dispersion

3.3 EFFECT OF TEMPERATURE ON VISCOSITY

When particle dispersions are to be used in place of pure liquid for the purpose of obtaining improved heat transfer rates, it becomes essential to study their flow property as a function of temperature. The intermolecular and inter-particle forces are functions of temperature [13] and hence a study of variation of viscosity of dispersions with temperature can provide insight into such forces influencing microstructure of dispersions.

Figure 3 shows the influence of temperature on viscosity of TiO₂-EG-water sub-micron dispersions. It is evident from Fig. 3 that the viscosity of dispersion decreases with temperature. The trend is qualitatively similar to that of liquid mixture (EG-water mixture). It is well-known that the viscosity of liquids or liquid mixture decreases with temperature. Since the viscosity of dispersion also decreases with temperature, it may be understood that the flow behavior of dispersions will be similar to that of liquid mixture, when subjected to a temperature change. The maximum temperature was restricted to 45 °C above which some sedimentation of particles was observed.

3.4 RELATIVE VISCOSITY

The increase in viscosity of dispersions over that of liquid in which they are dispersed can be denoted

using relative viscosity which is the ratio of viscosity of dispersions to the viscosity of liquid in which particles are dispersed [16]. Figure 4 shows the influence of particle concentration on the relative viscosity of TiO₂-EG-water dispersion at two different temperatures. It is evident from Fig. 4 that the relative viscosity increases with increase in particle concentration. The trendlines show linear variation of relative viscosity with particle concentration at both the temperatures. For dispersions containing particles that are hydrodynamically non-interacting, the relative viscosity-particle concentration relationship is linear [17]. Einstein (as cited in [16]) proposed the following equation for relative viscosity (μ_r) of dilute dispersions containing non-interacting spherical particles:

$$\mu_r = 1 + 2.5W \quad \dots\dots\dots (1)$$

In the above equation ‘ ϕ ’ represents particle volume fraction in the dispersion.

Expressing the relative viscosity-particle concentration data of the present study in the form of Eq. (1), we get-

$$\mu_r = 1 + 21.9W \quad (T = 31 \text{ }^\circ\text{C}) \quad \dots\dots(2)$$

$$\mu_r = 1 + 28.3W \quad (T = 40 \text{ }^\circ\text{C}) \quad \dots\dots (3)$$

Comparing Eq. (1), (2) and (3), the following observations can be made:

(i) The slope of relative viscosity-particle concentration data (21.9 and 28.3) is higher than the value (2.5) proposed by Einstein, which suggests that the conditions in dispersions are farther away from those applicable for Eq. (1). This could be attributed to the presence of particle aggregates such that the local particle concentration due to

aggregation is greater than the particle concentration in the bulk .

(ii) The different values for the slope at different temperatures (21.9 at 31 °C and 28.3 at 40 °C) suggests that the temperature plays a role in particle aggregation. This aspect needs to be investigated further.

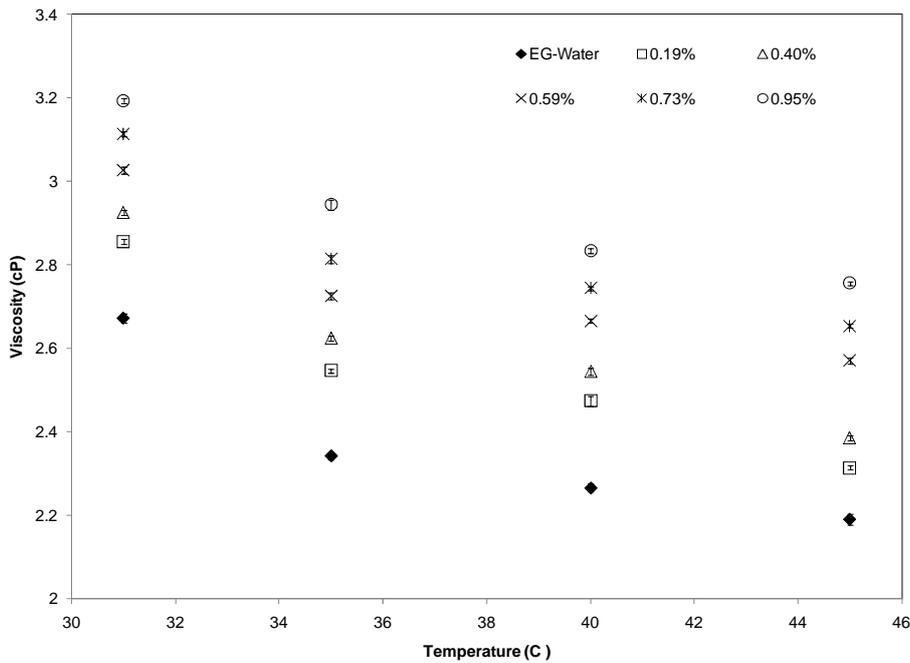


Figure 3. Influence of temperature on viscosity of sub-micron TiO₂-EG-water dispersion

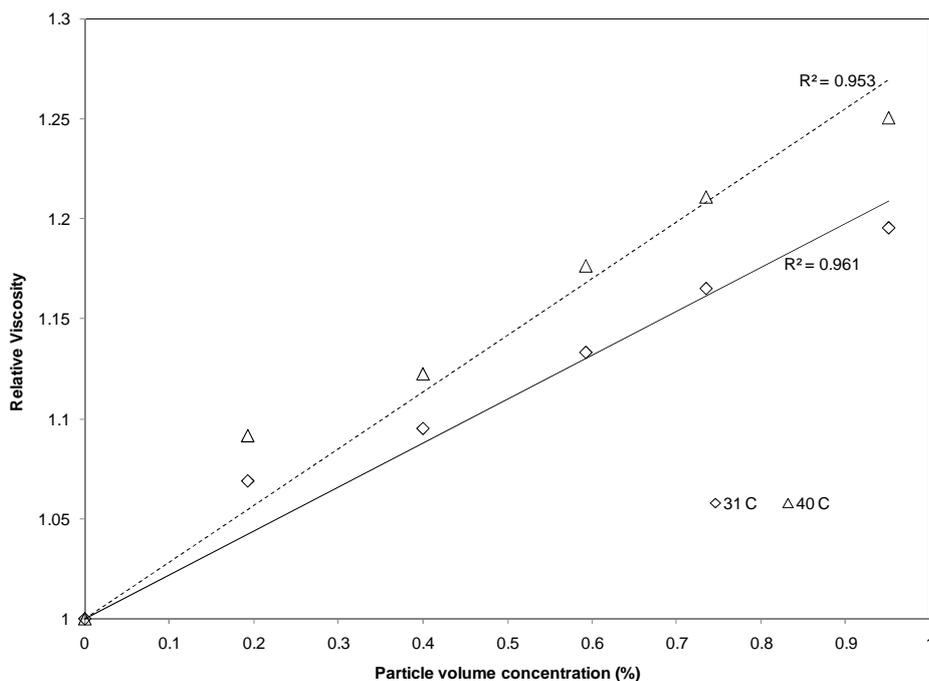


Figure 4. Influence of particle volume concentration on relative viscosity of sub-micron TiO₂-EG-water dispersion at two different temperatures

Figure 5 shows the influence of temperature on relative viscosity of dispersions. It is evident from Fig. 5 that the relative viscosity increases with temperature up to a temperature of 40 °C, after which reduction in relative viscosity with temperature is observed for dispersions with <0.5 vol % particles. For dispersions with particle concentrations > 0.5 vol %, the relative viscosity seems to be independent of temperature. This indicates that the temperature influence on relative viscosity is affected by particle concentration also.

Taking into account of the concentration-dependent temperature influence on relative viscosity and linear variation of relative viscosity with particle concentration, an equation of the following form

may be proposed for relative viscosity-particle concentration-temperature (T) relationship:

$$\sim_r = 1 + f(T)w \quad \dots\dots\dots (4)$$

Upon statistical analysis of the relative viscosity-particle concentration-temperature data, the following correlation has been obtained:

$$\sim_r = 1 + (9.2E - 3T^3 - 1.1278T^2 + 45.8224T - 588.8)w \quad \dots\dots\dots (5)$$

Equation (5) predicts the present experimental data on relative viscosity for 21 data points with a standard deviation of 0.0089 and within an error of ±2 %, as shown in Fig. 6.

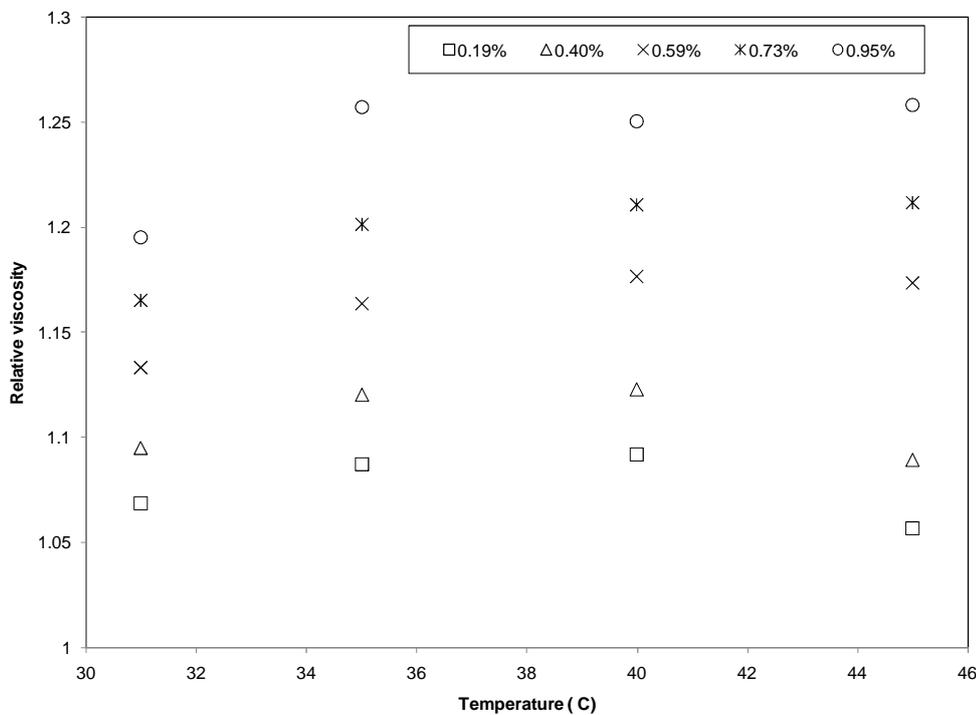


Figure 5. Influence of temperature on relative viscosity of sub-micron TiO₂-EG-water dispersion

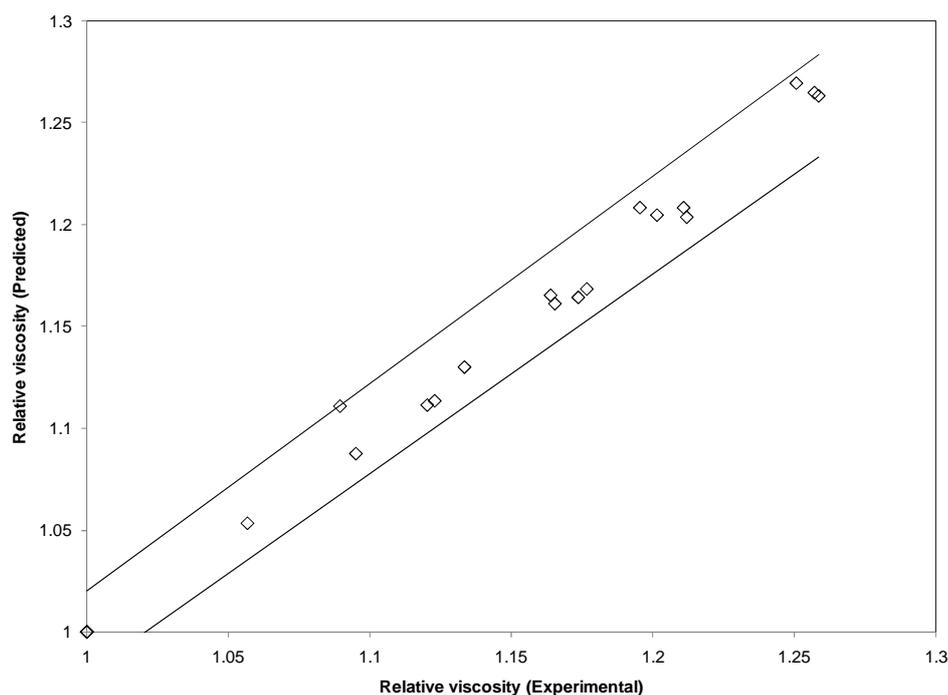


Figure 6. Comparison between the experimental relative viscosity data and that predicted using Eq. (5)

3.5 EFFECTIVE THERMAL CONDUCTIVITY

When particles with thermal conductivity higher than that of the liquid are dispersed in the liquid, the resultant mixture exhibits a thermal conductivity greater than that of liquid. Maxwell (as given in [18]) proposed effective-medium theory to predict the thermal conductivity of particle dispersions in liquid. The thermal conductivity of such particle dispersions is called effective thermal conductivity.

Figure 7 shows the influence of particle volume concentration on the effective thermal conductivity of TiO₂-EG-water dispersions. It is evident from Fig. 7 that the effective thermal conductivity increases with particle concentration. With increase in particle concentration, the volume fraction of higher thermal conductivity phase (solid) is more and hence an

increase in effective thermal conductivity is observed.

Thermal conductivity ratio, defined as the ratio of effective thermal conductivity of dispersions to the thermal conductivity of the liquid, is used to ascertain the gain in thermal conductivity achieved with the dispersions. The influence of particle concentration on thermal conductivity ratio is shown in Fig. 8 from which the thermal conductivity ratio is found to increase linearly with particle concentration. The prediction by Maxwell equation is also shown in Fig. 8. Higher values of measured thermal conductivity ratio compared to Maxwell equation highlight the role of more than one mechanism in influencing the thermal conductivity ratio.

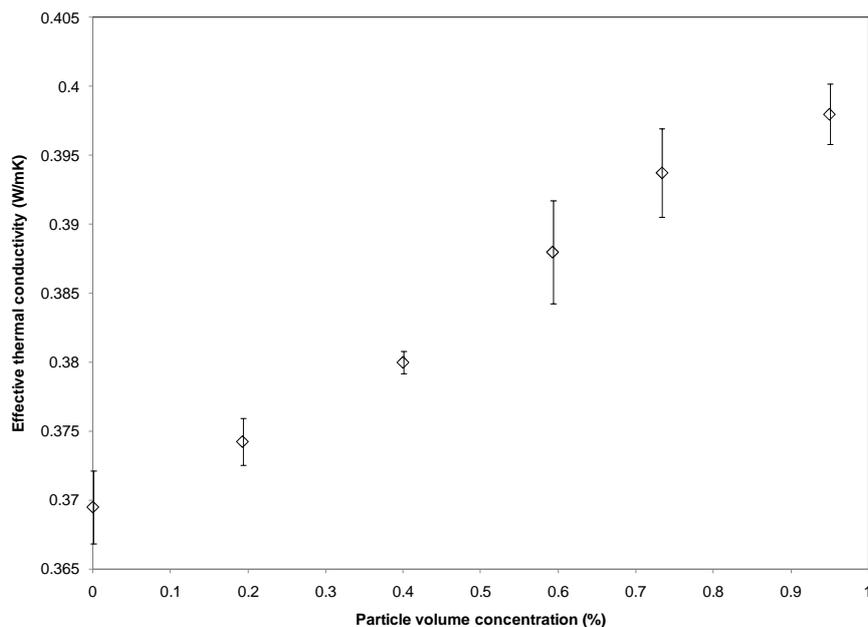


Figure 7. Influence of particle volume concentration on effective thermal conductivity of sub-micron dispersions of TiO₂ in ethylene glycol-water mixture

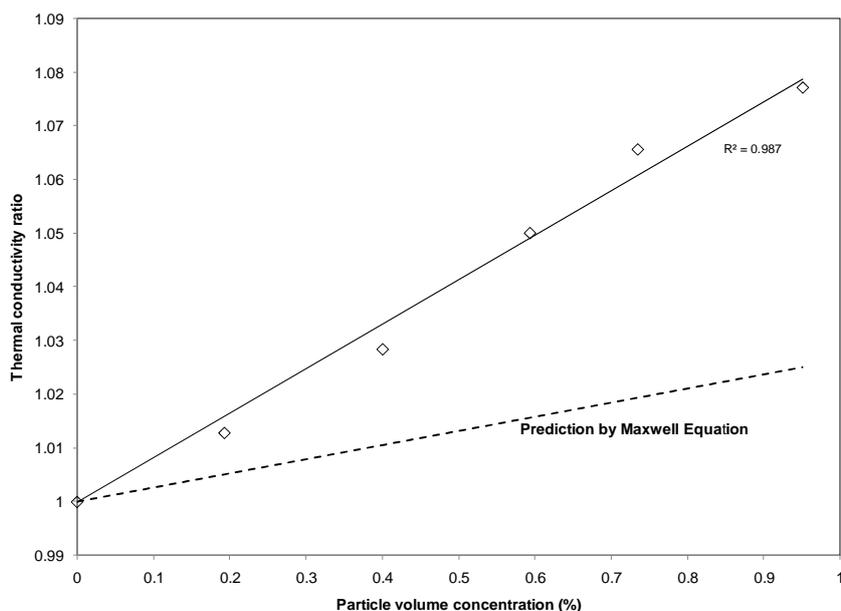


Figure 8. Influence of particle volume concentration on thermal conductivity ratio of sub-micron dispersions of TiO₂ in ethylene glycol-water mixture and comparison with the prediction by Maxwell Equation

4 CONCLUSION

Stirred bead milling followed by probe ultrasonication is a suitable method for preparation of stable dispersions of sub-micron TiO₂ particles in ethylene glycol-water mixture. The presence of nanoparticles and nanoparticle aggregates in the dispersion, as evident from the scanning electron micrograph and particle size distribution respectively, has profound influence on viscosity

manifested as relatively large increase in viscosity for a small increment in particle concentration. The thermal conductivities of dispersions are larger than those predicted by classical theories based on effective medium approximation, suggesting that some phenomena dependent on particle size and concentration too influence the thermal conductivity apart from the inherent higher thermal conductivity of particles.

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