INTECH
open science | open minds

OPEN ACCESS
ARTICLE

Nanomaterials and Nanotechnology

A Facile One Step Solution Route to Synthesize Cuprous Oxide Nanofluid

Regular Paper

Shenoy U. Sandhya[1] and Shetty A. Nityananda[1,*]

1 Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore, Karnataka, India
* Corresponding author E-mail: nityashreya@gmail.com

Received 5 October 2012; Accepted 24 April 2013

Abstract A cuprous oxide nanofluid stabilized by sodium lauryl sulfate, synthesized by using the one step method, has been reported. Nanofluids were synthesized by using a well-controlled surfactant-assisted solution phase synthesis. The method involved reduction of copper acetate by glucose in a mixture of water and ethylene glycol serving as the base fluid. The synthesized fluid was characterized by X-ray and electron diffraction techniques, in addition, transmission and field emission microscopic techniques and Fourier transform infra red spectroscopic analysis was undertaken. The rheological property, as well as the thermal conductivity of the fluid, were measured. The variation of reaction parameters considerably affected the size of the particles as well as the reaction rate. The uniform dispersion of the particles in the base fluid led to a stability period of three months under stationary state, augmenting the thermal conductivity of the nanofluid. The method is found to be simple, reliable and fast for the synthesis of Newtonian nanofluids containing cuprous oxide nanoparticles.

Keywords Cuprous Oxide, Nanofluids, Nanoparticles, Thermal Conductivity, Viscosity

1. Introduction

Nanofluids represent the cutting edge technology of liquid coolants where the heat transfer properties of conventional base fluids are enhanced by the addition of nanoparticles to form stable dispersions. The higher thermal conductivity of the heat transfer fluids transmutes into higher efficiency, better performance and reduced costs. Advancement in science and technology has led to device miniaturization. Since dispersion of microparticles results in clogging of microchannels, abrasion of the walls and increase in pressure drop, the addition of nanoparticles into the base fluids came into being [1,2]. Metals and metal oxides are found to have superior thermal conductivity than the base fluids like water, ethylene glycol, engine oil [3], etc. Copper and copper oxide nanoparticles have received much attention recently due to their promising properties. Synthesis of nanofluids using these nanoparticles ensures a logical move to satiate the ever increasing cooling need of many industrial technologies.

Synthesis of nanofluids can be done by either dispersing the commercially available nanopowders into the base fluid, or by initially synthesizing the nanoparticles by various physical or chemical techniques and then dispersing them into the fluid, both of which are two step techniques. They can also be synthesized by the in-situ preparation of nanoparticles within the base fluid with simultaneous dispersion of these particles to form stable fluids, which is the core of single step synthesis [4 – 6].

The single step synthetic method overcomes the drawbacks of two step synthesis like agglomeration of the particles during storage, transportation or re-dispersion which results in poor thermal conductivity. Single step methods could be physical methods like the direct evaporation technique and submerged arc nanosynthesis, or chemical methods like solution phase reduction, the polyol method and the microwave method [7 – 9]. The literature review shows there are only a few reports on the single step chemical method of synthesis of nanofluids.

In view of the afore mentioned facts, an attempt has been made to synthesize cuprous oxide nanofluid using single step solution phase synthesis by reduction of copper acetate by glucose in the presence of sodium lauryl sulfate (SLS) as a surfactant. The effect of various reaction parameters in both thermal as well as microwave condition has been studied. The thermal conductivity and the rheological properties of the fluid have also been measured.

2. Experimental

2.1 Preparation of cuprous oxide nanofluids

All the reagents used in the experiment were of analytical grade and were used without further purification. The cuprous oxide nanofluids were prepared by the chemical reduction of copper acetate by glucose in the presence of SLS. In this procedure, an aqueous solution of copper acetate (20 mL, 0.25 M) was made sufficiently alkaline by the addition of ammonium hydroxide. To this deep blue solution, a solution of SLS in ethylene glycol (10 mL, 0.01 M) was added and stirred for 15 min. Glucose (2.5 g) was then added and heated to 75 °C with stirring. When the colour of the solution changed from blue to golden yellow, sulphuric acid was added to neutralize the initially added base and heating was continued for some time. Finally the brown solution was cooled to obtain a cuprous oxide nanofluid. Similar reactions were carried out by varying the concentrations of reactants and also by varying the dilution of the reaction mixture.

In order to investigate the effect of microwave radiation, reactions were carried out in a microwave reactor at 50 % power for seven minutes. The reactions were also carried by varying the duration of microwave irradiation and the power of microwave from 30 % to 70 %.

2.2 Characterization

The prepared cuprous oxide nanofluid was characterized by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDXA), transmission electron microscopy (TEM), selected area electron diffraction (SAED), field emission scanning electron microscopy (FESEM), and Fourier transform infrared (FTIR) spectroscopy. The thermal conductivity and viscosity of the synthesized fluid were also measured.

The nanofluid was diluted with absolute ethanol and centrifuged for one hour. The separated cuprous oxide nanoparticles were then given repeated washes with water and ethanol, and the particles were dried at 80 °C. XRD patterns of the nanoparticles were taken on a JEOL X-ray diffractometer (Model DX GE 2P) using Ni-filtered Cu K_α radiation (λ = 1.54178 Å) with an operating voltage of 30 kV. The accelerating voltage was set at 0.06 °/s in the 2θ range 25 ° – 85 °.

The TEM images of the nanofluids and SAED pattern of the nanoparticles were recorded on a Philips CM200 transmission electron microscope operating with an accelerating voltage of 20-200 kV with a resolution of 2.4 Å. The samples for TEM were prepared by sonicating the nanofluid and later placing it on carbon-coated copper grid for analysis. The FESEM images of the cuprous oxide particles were taken on a Supra 40VP FESEM, having a resolution up to 2 nm. The EDXA was carried out on a JEOL JSM 6380LA model analytical scanning electron microscope.

The FT-IR spectrum of the prepared cuprous oxide nanofluid was recorded using a Nicolet Avatar 330 FTIR spectrometer. The thermal conductivity of the nanofluid was measured using a KD2 pro thermal property analyser. The measurements were made using a KS-1 sensor in low power mode with a one minute read time. The sensor was kept absolutely still during the measurement to eliminate forced convection. The measurements were carried out at a temperature of 30 °C. Rheological measurements were made using a Brookfield LV DV III ultra rheometer.

3. Results and discussion

3.1 Results of XRD, EDX and SAED analysis

The phase structure and the purity of the products were examined by X-ray diffraction studies. The powder XRD pattern of the as obtained cuprous oxide nanoparticles is shown in Figure 1. The peaks could be indexed to the standard cubic structure of Cu_2O [JCPDS Card No. 05-0667, a = 4.2696 Å, Space group: Pn3m (224)]. The peaks at 29.5 °, 36.4 °, 42.3 °, 61.34 °, 73.5 ° and 77.3 ° corresponded to (110), (111), (200), (220), (311) and (222) planes, respectively. None of the peaks could be indexed to copper or cupric oxide, indicating that the products were highly pure. The average size of the particle is calculated using Scherrer's formula [10] shown in Equation (1).

$$D = \frac{K\lambda}{B\cos\theta} \qquad (1)$$

where D is the thickness of the crystal (in Å), K is the shape factor, λ the X-ray wavelength and θ the Bragg angle. The extra peak width is given in terms of line broadening, *B*.

The chemical composition and purity of the products were also examined using EDXA. The EDX spectrum revealed copper and oxygen as the only detectable elements, indicating that the sample is without any contamination. Their atomic ratio is close to 2:1, confirming that the nanoparticles are of Cu_2O.

The SAED pattern of cuprous oxide nanoparticles is shown in Figure 2. Six rings corresponds to (110), (111), (200), (220), (311) and (222) planes with distances 3.02 Å, 2.465 Å, 2.135 Å, 1.51 Å, 1.287 Å and 1.23 Å, respectively. These data match well with the standard data for cubic phase Cu_2O.

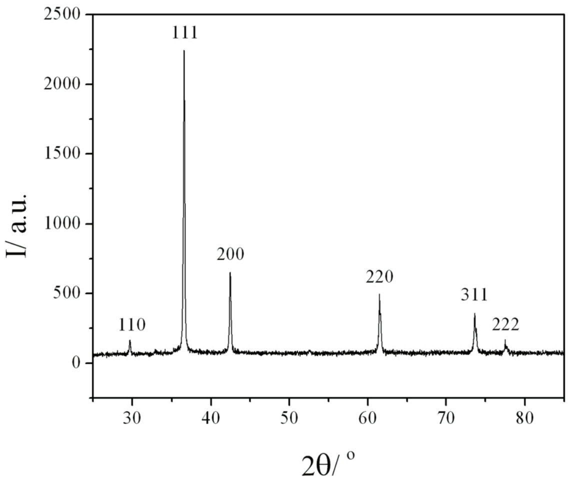

Figure 1. A typical powder XRD pattern of cuprous oxide nanoparticles.

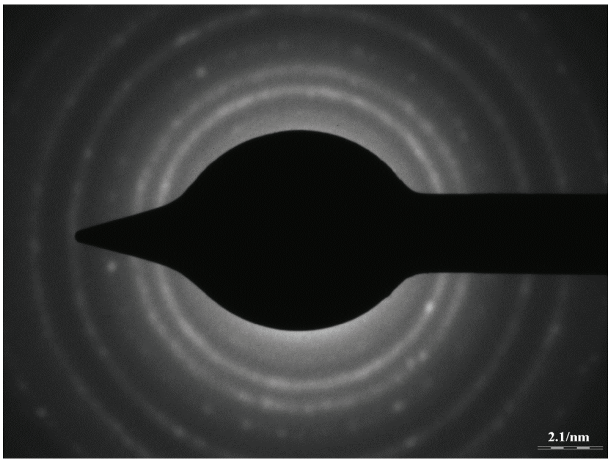

Figure 2. The SAED pattern of the cuprous oxide particles showing diffraction rings.

3.2 Effect of reaction parameters

Effect of ratio of reactants: Synthesis of nanofluids was carried out with different amounts of glucose and the effect on size was studied. It was observed that the particle size increased with the increase in the amount of glucose added. It was also observed that whenever the molar ratio of glucose to copper acetate was less than 2.8, the reaction did not go for completion. Hence, a molar ratio of more than 2.8 was always maintained. The sizes of the particles obtained were as follows: 32 nm, 36 nm, 44 nm and 49 nm for a glucose to copper acetate ratio of 2.8, 5.6, 8.9 and 11.1, respectively. The chemical reaction between cupric ion and glucose is represented by equation (2).

$$2Cu^{2+} + C_6H_{12}O_6 + 2H_2O \rightarrow Cu_2O + C_6H_{12}O_7 + 4H^+ \qquad (2)$$

It was seen that at lower concentrations of glucose the reduction rate of copper salt is slow and only a few nuclei are formed during the nucleation period, which further grow during the growth phase. However, at higher concentrations of the reducing agent, the precipitating clusters increase steeply and hence more numbers of nuclei are formed. These tiny nuclei so formed readily collided with each other, giving particles of larger size [5]. Hence, a lower molar ratio of glucose to copper acetate led to particles of a smaller size, and a higher molar ratio resulted in formation of larger sized particles.

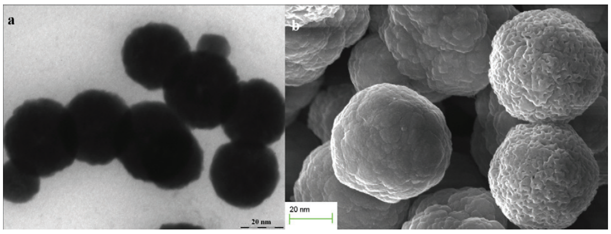

Figure 3. (a) The TEM image of cuprous oxide nanoparticles synthesized by the conventional thermal method. (b) The FESEM image of cuprous oxide nanoparticles. The scale shows 20 nm.

A typical TEM image of the nanofluid synthesized by the reduction of copper acetate (0.25 M, 20 mL) using glucose (2.5 g) is shown in Figure 3a. Figure 3b shows the FESEM image of the cuprous oxide nanoparticles formed using glucose (10 g).

Effect of addition of ammonia: Glucose reduces copper ions as shown in Equation (2) above. The standard half cell potential for the reduction of Cu^{2+} to Cu^+ (equation 3) is 0.16 V.

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad (3)$$

The standard half cell potential for the redox equilibrium of glucose is 0.050 V.

$$C_6H_{12}O_7 + 2H^+ + 2e^- \leftrightarrow C_6H_{12}O_6 + H_2O \qquad (4)$$

The overall standard state cell potential for the reaction given in Equation (2) is positive and hence favourable. Since the reaction is carried out in the presence of ammonia, most of the copper ions are therefore present as

$[Cu(NH_3)_4]^{2+}$ complex ion. The half cell potential for the reduction of this complex is considerably smaller than that for the reduction of Cu^{2+} ion to Cu^{+}. This leads to a significant decrease in the overall cell potential for the reaction because the complex ion is a much weaker oxidizing agent than the Cu^{2+} ion.

Due to the involvement of a pair of H^{+} ions in the reaction, the presence of ammonia alters the electrode potential of the glucose system. The half cell potential for the reaction given in Equation (4) therefore depends on the pH of the solution. Because two H^{+} ions are given off when glucose is oxidized, the reaction quotient for this reaction depends on the square of the H^{+} ion concentration. A change in the solution pH from the standard state conditions to a pH of 11 therefore results in a decrease of half cell potential for this reaction and an increase in the reducing strength of the glucose. The increase in the reducing strength of glucose under this condition more than compensates for the decrease in the oxidizing strength of Cu^{2+} in the presence of ammonia and therefore the reaction is more favourable.

Effect of dilution: A varying amount of water was used to dilute the reaction mixtures. It was seen that with dilution, the size of the particle decreased. The particle size ranged between 32 nm to 13 nm for zero dilution to 200 mL dilution. The particle size was 29 nm and 24 nm for 50 mL and 100 mL dilution, respectively. The observed trend can be explained as follows. With the increase in the dilution, the overall concentration of the species decreases, the proximity between the precipitating atoms decreases and hence the collision between them is reduced, preventing the growth of particle and hence resulting in smaller size of the nanoparticles formed [11].

Effect of surfactant: The effect of surfactant concentration on particle size and stability was studied. In the absence of the surfactant, the particles of 52 nm size were obtained. When the effective concentration of the SLS was changed from 3.3 mM to 16.7 mM to 33.3 mM the particle size decreased from 32 nm to 26 nm to 17 nm, respectively. This decrease in size could be attributed to the capping effect of SLS, resulting in restriction on the growth of particles and controlling the size of copper oxide particles. With the increase in concentration of SLS, the capping action increases and hence the size of the particles decreases.

The SLS not only had an effect on the size of particles, but also endowed the nanofluid with the required stability. In the absence of surfactant, the fluid was highly unstable and the particles started settling quickly. Sedimentation measurements showed that in the presence of surfactant, the fluid was stable for a minimum period of three months at room temperature under stationary conditions. Such high stability can be accredited to the small size and uniform distribution of the formed particles.

Effect of microwave irradiation: The reaction carried out using conventional heating was also carried out with microwave irradiation at varying power and reaction time. The reaction was incomplete for seven minutes irradiation at 30 % power. At 50 % irradiation the reaction proceeded to completion, resulting in the formation of particles with size of 60 nm and 10 nm. For 70 % power, particles of size 70 nm were formed.

The duration of irradiation also had a significant effect on the size as well as progress of the reaction. The power was set to 50 % and the duration of irradiation was varied. For a duration of five minutes, the particles formed had a size of 45 nm but the reaction was incomplete. When the duration was increased to seven minutes, particles of two different sizes were formed. A second nucleation event resulted in the formation of new particles with size around 10 nm and the particles formed during the first nucleation showed growth up to 60 nm. When the irradiation was extended up to 10 minutes, the particles grew bigger due to Ostwald ripening and attained a size of 75 nm. As the duration of the irradiation increases, the temperature of the reaction mixture increases, resulting in an increase in the solubility of the particles which promotes Ostwald ripening [12]. The relatively larger particles grow at the expense of the smaller particles. This results in the elimination of smaller particles, and thus, the size distribution of nanoparticles becomes narrower. When the temperature is increased, the concentration of solid in the base fluid falls below the equilibrium solubility of small nanoparticles and the small particles dissolve into the solvent. As the dissolution of nanoparticle proceeds, the nanoparticle becomes smaller and has higher solubility. Once a nanoparticle starts dissolving into the base fluid, the dissolution process stops only when the nanoparticle is dissolved completely. On the other hand, the concentration of solid in the base fluid is still higher than the equilibrium solubility of larger particles, and thus, these particles would continue to grow. Such a growth process would stop when the concentration of solid in the base fluid equals the equilibrium solubility of these relatively large nanoparticles. Therefore, the smaller particles observed when the irradiation duration was seven minutes, disappeared when the irradiation duration was increased to 10 minutes.

This was further confirmed by the elimination of smaller particles from the nanofluid and the growth of the relatively larger particles when the reactant mixture was heated by conventional means after microwave irradiation for a duration of seven minutes.

Figure 4 and Figure 5 show the FESEM images of the cuprous oxide particles formed at 50 % irradiation for seven minutes and 10 minutes, respectively.

3.3 Results of FTIR spectroscopic analysis

Figure 6 shows the FTIR spectra of pure ethylene glycol (a) and cuprous oxide nanofluid (b). The oxidized products of ethylene glycol are not detectable in (b) indicating that the copper ions are reduced by glucose and not ethylene glycol. The two spectra resemble one another except for the appearance of a prominent band at 1648.6 cm^{-1} in the case of the nanofluid spectrum. The band is due to the bending of O-Hof water which is added during the preparation of the nanofluid.

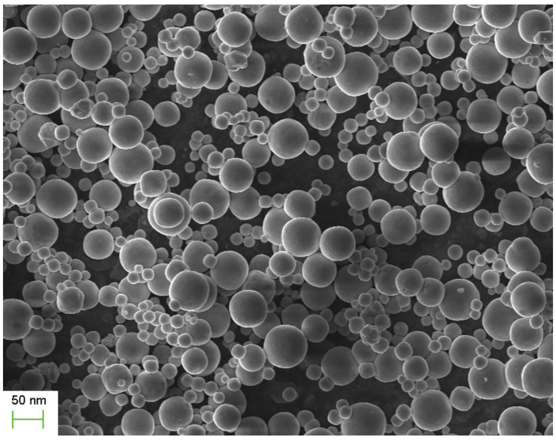

Figure 4. The FESEM image of particles synthesized at 50 % irradiation power for seven minutes.

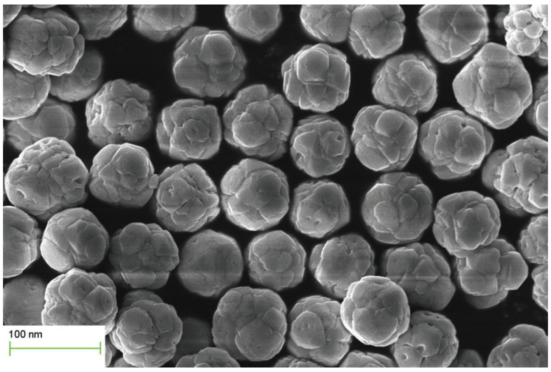

Figure 5. The FESEM image of particles synthesized at 50 % irradiation power for 10 minutes.

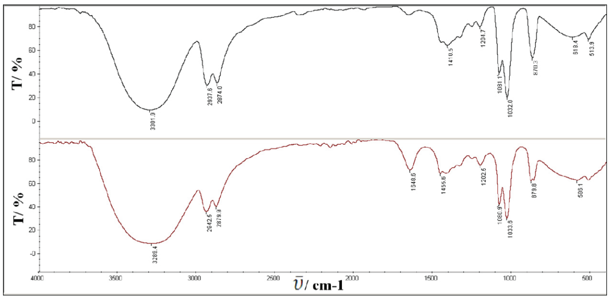

Figure 6. The FTIR spectra of pure ethylene glycol (a) and cuprous oxide nanofluid (b).

Figure 7. (a) Image of reaction mixture in the absence of glucose. (b) Image of nanofluid formed in the presence of glucose.

When the reaction was carried out in the absence of glucose there was no reduction of copper ions at the reaction temperature mentioned in this work, as indicated by the blue colour of the reaction mixture (Figure 7a). But in the presence of glucose the reaction mixture changed its colour to brown (Figure 7b), indicating the reduction of copper ions to cuprous oxide. Thus, this unambiguously proves that glucose is the reductant. The reported method is found to preserve the advantages of both the chemical reduction method and the polyol method.

3.4 Results of thermal conductivity and rheological measurements

The thermal conductivity studies were carried out at different particle weight fractions keeping the ratio of ethylene glycol to water 1:1. The thermal conductivity of the nanofluid increased linearly with the increase in particle weight fraction. A maximum thermal conductivity of 2.948 $Wm^{-1}K^{-1}$ was observed at 0.282 % particle weight fraction. Thereafter it showed a gradual decrease in conductivity. The enhancement of the conductivity of the base fluid with the increase in particle weight fraction could be attributed to the higher conductivity, nanosize and uniform dispersal of the cuprous oxide nanoparticles. The free Brownian motions of the particles could have also facilitated higher thermal conductivity [13]. Figure 8 shows the variation of thermal conductivity ratio (K_f/ K_b) with particle weight fraction. K_f and K_b represent the thermal conductivities of the nanofluid and the base fluid, respectively. F_w indicates the nanoparticle weight fraction. The thermal conductivity ratio (K_f/ K_b) of 7.48 of the synthesized nanofluid is found to be significantly higher than the reported value of 1.24 by Wei et al. [6]. This could be attributed to the fact that the size of the particles reported by Wei et al. [6] was about 200 nm and the particles reported in the present study are less than 75 nm. Hence the smaller size and higher stability of the fluid lead to the enhanced thermal conductivity.

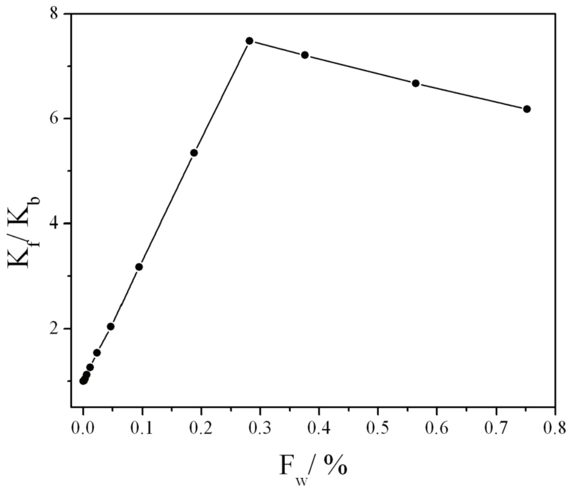

Figure 8. The variation of the thermal conductivity ratio with nanoparticle weight fraction.

The viscosity (η) of the synthesized fluid was measured at various temperatures (T) and particle weight fraction (F_w). The variation of shear stress (τ) with shear rate (γ) at 30 °C is as shown in Figure 9a.

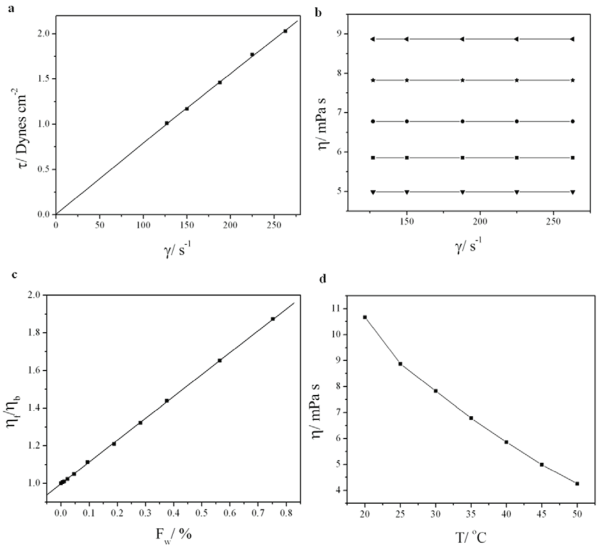

Figure 9. Rheological measurements. (a) Shear stress (τ) versus shear rate (γ) at 30 °C for particle loading of 1.5 %. (b) Viscosity (η) as a function of shear rate (γ) for particle loading of 1.5 % at different temperatures. ◀25 °C, ★30 °C, ●35 °C, ■ 40 °C, ▼45 °C. (c) Variation of relative viscosity (η_f /η_b) of nanofluid with particle weight fraction (F_w). (d) Viscosity (η) as a function of temperature (T) for particle loading of 1.5 %.

The linear relation between shear stress and shear rate demonstrates the Newtonian behaviour of the nanofluid [14]. Figure 9b demonstrates that the viscosity (η) of the fluid is independent of shear rate (γ) at temperatures ranging from 25 °C to 45 °C [15]. Figure 9c shows the variation of relative viscosity (η_f/ η_b) with particle weight fraction and Figure 9d shows variation of viscosity with temperature (T). η_f and η_b represents the viscosity of the nanofluid and the base fluid, respectively. It is observed that the viscosity increases with the increase in particle concentration and decreases with temperature. This trend is similar to the one reported by Li et al. [16].

4. Conclusions

A simple single step method for the synthesis of copper oxide nanofluid has been reported using copper acetate and glucose. The reduction is carried out in the presence of SLS using water and ethylene glycol as base fluids. The synthesized fluid is well-characterized by diffraction, microscopy and spectral techniques. The in-situ formation of copper oxide nanoparticles lead to the enhancement of thermal conductivity. Thermal conductivity of 2.948 Wm^{-1}K^{-1} was observed at particle weight fraction 0.282 %. The fluid exhibits Newtonian behaviour in the temperature range studied. This method proves to be simple, rapid, cost effective and highly useful for enhancing the thermal conductivity of the synthesized fluids.

5. References

[1] Li Y, Zhou J, Tung S, Schneider E, Xi S (2009) A review on development of nanofluid preparation and characterization. Powder Technol. 196: 89 – 101.

[2] Kumar A S, Meenakshi K S, Narashimhan B R V, Srikanth S, Arthanareeswaran G (2009) Synthesis and characterization of copper nanofluid by a novel one step method. Mater. Chem. Phys. 113: 57 – 62.

[3] Wang X Q, Mujumdar A S (2008) A review on nanofluids - part I: theoretical and numerical investigations. Braz. J. Chem. Eng. 25: 613 – 630.

[4] Manna I (2009) Synthesis, characterization and application of nanofluid - an overview. J. Indian Inst. Sci. 89: 21 – 33.

[5] Chang M H, Liu H S, Tai C Y (2011) Preparation of copper oxide nanoparticles and its applications in nanofluid. Powder Technol. 207: 378 – 386.

[6] Wei X, Zhu H, Kong T, Wang W (2009) Synthesis and thermal conductivity of Cu_2O nanofluids. Int. J. Heat Mass Transfer 52: 4371 – 4374.

[7] Eastman J A, Choi S U S, Li S, Yu W, Thompson L J (2001) Anomalously increased effective thermal conductivities of ethylene glycol based nanofluids containing copper nanoparticles. Appl. Phys. Lett. 78: 718 – 720.

[8] Lo C H, Tsung T T, Chen L C, Su C H, Lin H M (2005) Fabrication of copper oxide nanofluid using the

Submerged Arc Nanoparticle Synthesis System (SANSS). J. Nanopart. Res. 7: 313 – 320.

[9] Zhu H, Lin Y, Yin Y (2004) A novel one step chemical method for preparation of copper nanofluids. J. Colloid Interface Sci. 277: 100 – 103.

[10] Patterson A L (1939) The Scherrer formula for X ray particle size determination. Phys. Rev. 56: 978 – 982.

[11] Shenoy S U, Shetty N A (2012) Simple glucose reduction route for one step synthesis of copper nanofluids. Appl. Nanosci. DOI 10.1007/s13204-012-0169-6.

[12] Cao G (2003) Nanostructures and Nanomaterials - Synthesis, Properties and Applications Imperial College Press 24 – 25.

[13] Wang B, Wang X, Lou W, Hao J (2011) Ionic liquid based stable nanofluids containing gold nanoparticles. J. Colloid Interface Sci. 362: 5 – 14.

[14] Namburu P K, Kulkarni D P, Misra D, Das D K (2007) Viscosity of copper oxide nanoparticles dispersed in ethylene glycol and water mixture. Exp. Therm. Fluid Sci. 32: 397 – 402.

[15] Yu W, Xie H, Chen L, Li Y (2009) Investigation of the thermal conductivity and viscosity of ethylene glycol based ZnO nanofluid. Thermochim. Acta 491: 92 – 96.

[16] Li D, Xie W, Fang W (2011) Preparation and properties of copper oil based nanofluids. Nanoscale Res. Lett. 373: 1 – 7.