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# A Simple Approach Towards Synthesis of Nanofluids Containing Octahedral Copper Nanoparticles

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Nanofluids are a new kind of heat transfer fluids engineered by suspending nanoparticles with higher thermal conductivity in conventional heat transfer fluids with a motive of achieving enhanced heat transfer properties. Copper nanofluids have been synthesized by a simple and cost effective way by reducing copper nitrate using ascorbic acid. The employed solution phase synthesis utilizes a mixture of ethylene glycol and water as base fluid. Octahedral copper nanoparticles were formed when polyvinylpyrrolidone was added as a stabilizing agent. The synthesized nanofluids have been characterized by XRD, microscopic and spectroscopic techniques. The sedimentation measurements showed that the as synthesized nanofluid had a stability of more than 6 weeks. Rheological measurements revealed that the nanofluid is Newtonian in nature in the temperature range of 20 °C to 50 °C. The thermal conductivity of the copper nanofluid has been found to be 1.774 W $m^{-1}$ $K^{-1}$ for the particle weight fraction of 0.167%. The proposed single step method is facile, mild, low cost and extendible technique for the synthesis of nanofluids with enhanced thermal conductivity.

**KEYWORDS:** Copper, Nanofluid, Nanoparticle, Thermal Conductivity, Viscosity.



## 1. INTRODUCTION

Nanofluids are an innovative class of heat transfer fluids which finds most of its applications in cooling, tribology and biomedical field.[1–3] The thermal conductivity of heat transfer fluids plays an important role in the field of electronics, transportation, and defense and in space stations.[4–7] The poor thermal conductivity of the conventional base fluids like water, ethylene glycol, engine oil acts as a stumbling block in meeting the ever increasing need for cooling.[8] Hence there is a need for formulating cooling fluids possessing better heat transfer properties. Suspension of metallic or nonmetallic particles or their oxides having thermal conductivity higher than the base fluid would be a simple way to enhance the thermal conductivity of heat transfer fluids.[8,9] Since nanoparticles have large surface area its interaction with the surrounding medium can overcome the difference in density and hence the particles can remain stably suspended. The nano size of the particles also overcomes the drawbacks of micro particles such as clogging of the channels, abrasion and pressure drop.[10] Hence incorporation of nanoparticles into the base fluids would be a convenient way to bring about an increase in the thermal conductivity of these fluids along with desired stability.

Nanofluids could be synthesized either by two step method or one step method. Two step method involves the preparation of nanoparticles in first step and their dispersion into base fluids in the second step. One step method involves simultaneous synthesis and dispersion of the nanoparticles into the base fluid. One step approach for synthesis of nanofluids could be physical or chemical. It overcomes the drawbacks of two step techniques like agglomeration during storage and partial dispersion. Single step physical techniques like direct evaporation and condensation technique, submerged arc nano synthesis, pulsed laser ablation, dual plasma process involve complex procedures, need high boiling liquids, sophisticated equipment and rigorous experimental conditions while single step chemical method overcomes even these drawbacks.[8–13] Literature reveals that there are only a few reports on one step chemical method of synthesis of copper nanofluids.[10] Herein we follow a one step solution phase approach for synthesis of copper nanofluids. Copper nitrate precursor is reduced by ascorbic acid, in the presence of polyvinylpyrrolidone (PVP) in a mixture of water and ethylene glycol acting as base fluid. The as synthesized nanofluids are characterized and studied for its stability, thermal conductivity and rheological properties.

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## 2. EXPERIMENTAL DETAILS

### 2.1. Synthesis of Nanofluids

All the chemicals used in the investigation were of analytical grade and were used without any further purification. Standard solutions of copper nitrate (0.1 M), PVP (0.1 M) and ascorbic acid (2 M) were prepared by dissolving required amount in water or ethylene glycol as required. The solutions were diluted as per the requirement. Deionized water was used for preparing aqueous solutions. Onida Power convection 20, microwave oven equipped with 800 watt microwave power was used for carrying out microwave assisted reactions.

In a typical synthesis, aqueous solution of copper nitrate tri hydrate (30 mL, 0.1 M) was added to a solution of PVP in ethylene glycol (5 mL, 0.01 M). The reaction mixture was diluted with water (45 mL) and stirred for 15 minutes. Then solution of ascorbic acid in ethylene glycol (30 mL, 0.5 M) was added and stirred at 70 °C. When the color changed from blue to reddish brown the solution was cooled to obtain copper nanofluid. Similar reactions were carried out by varying concentration of ascorbic acid, PVP and dilution.

Microwave assisted reactions were also carried out at 50% power for 4 minutes. The reactions were also carried out at different concentration of reducing agent, irradiation duration and microwave power.



### 2.2. Characterization

The prepared copper nanofluid was characterized by several techniques. The nanofluid was diluted with absolute ethanol and centrifuged for one hour. The powder sample obtained was given repeated wash with water and ethanol and finally dried at 80 °C.

XRD studies were carried out using JEOL X-ray Diffractometer (Model DX GE 2P) using Ni filtered Cu $K_\alpha$ radiation ($\lambda = 1.54178$ Å) with an operating voltage of 30 kV. The scan rate was set at 0.06°/s in the $2\theta$ range 35°–80°. The chemical composition and purity of the products were also examined using EDX analysis (JEOL JSM 6380LA model Analytical Scanning Electron Microscope).

The spectroscopic analysis of the nanofluid was carried out using Ocean optics, inc SD2000 fibre optic spectrometer and Nicolet Avatar 330 FTIR spectrometer at room temperature.

The TEM images of the nanofluids were recorded on a Philips CM200 transmission electron microscope operating with an accelerating voltage of 20–200 kV having 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 copper nanoparticles were taken on a Supra 40VP FESEM having a resolution up to 2 nm.

The thermal conductivity of the nanofluids were measured with KD2 pro thermal property analyzer using KS-1 sensor which was oriented vertically in the sample and the measurements were recorded at low power mode with read time of 1 min. Rheological measurements were made using Brookfield LV DV III ultra rheometer.

## 3. RESULTS AND DISCUSSION

### 3.1. Results of XRD and EDX Analysis

The phase structure and the purity of the products were examined by X-ray diffraction studies. The powder XRD pattern of the obtained copper nanoparticles is shown in Figure 1. The diffraction peaks could be indexed to the face centred cubic Cu [JCPDS Card No. 04-0838, $a =$ 3.6150 Å, Space group: Fm3m (225)] corresponding to (111), (200) and (220) planes, respectively.

The average size of the particle is calculated using Scherrer's formula[14] given in Eq. (1).

$$\tau = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where $\tau$ is the thickness of the crystal (in Å), $K$ is the shape factor, $\lambda$ the X-ray wavelength and $\theta$ the Bragg angle. The line broadening, $B$ is measured from the extra peak width. The high purity of the products was suggested by the absence of peaks of impurities such as those of cuprous or cupric oxide.

The chemical composition and purity of the products were also examined using EDXA. A typical EDX spectrum of the copper nanoparticles is shown in the Figure 2. Only copper is detected in the spectrum indicating that there is no contamination.

### 3.2. Results of FTIR and UV Analysis

Though ascorbic acid was used to reduce copper nitrate to form copper nanoparticles, there is a probability of ethylene glycol itself acting as a reducing agent. In order to ascertain the fact, whether ethylene glycol acts as a reducing agent in the process of nanofluid preparation, the FTIR spectra of the pure ethylene glycol and copper nanofluid

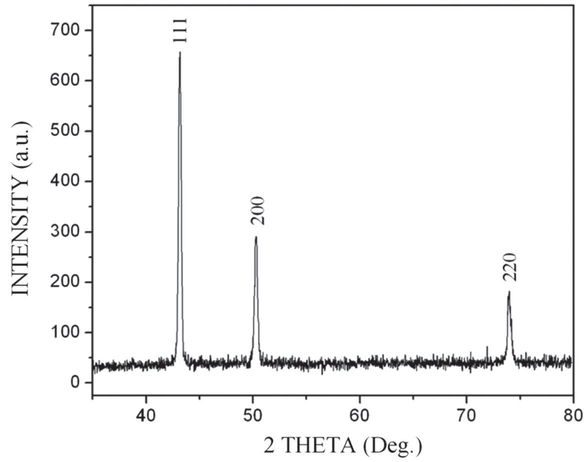


**Fig. 1.** A typical powder XRD pattern of copper nanoparticles.

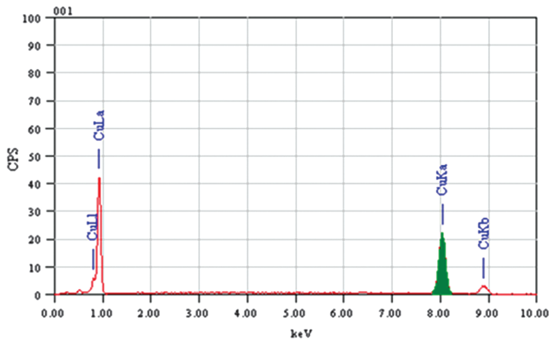


**Fig. 2.** A typical EDX spectrum of copper nanoparticles.

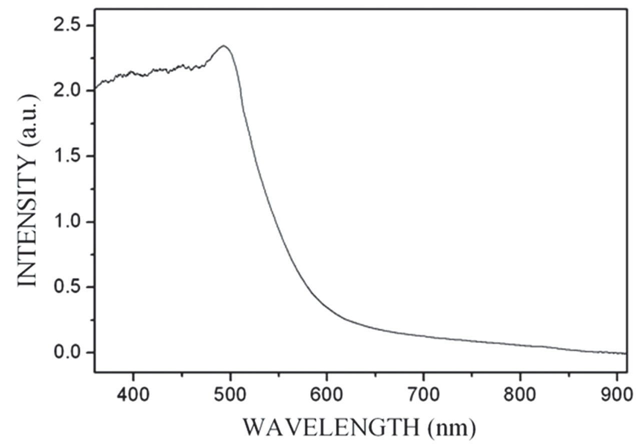


**Fig. 4.** UV-Visible spectrum of copper nanofluid.

were compared. The FTIR spectra of copper nanofluid (B) stacked with pure ethylene glycol (A) is shown in Figure 3. It is seen that the two spectra resemble each other indicating that the ethylene glycol is not oxidized. It suggests that ascorbic acid was the one acting as reducing agent and not ethylene glycol. This method preserves the advantages of the polyol process and aqueous chemical reduction method as well.

Figure 4 shows UV Vis spectrum of copper nanofluid. The absorption edge at 496 nm indicates the peak due to copper nanoparticles.[15]

### 3.3. Results of Variation in Reaction Parameters

#### *3.3.1. Effect of pH*

The effect of the pH of the reaction mixture was studied. The variation in the pH of the reaction mixture showed a significant effect on the size of copper nanoparticles. When the pH of the reaction mixture was brought down to 3 by the addition of sulfuric acid, the size of the particles increased from 32 nm to 56 nm. With the decrease in the pH value, the size of the copper particle was found to be increasing. This trend is attributed to the decrease in the reducing power of ascorbic acid.[16] The chemical reaction between $Cu^{2+}$ ions and ascorbic acid is represented by the Eq. (2).

$$Cu^{2+} + C_6H_8O_6 \rightarrow Cu + C_6H_6O_6 + 2H^+ \quad (2)$$

The electrode potential for the redox equilibrium of ascorbic acid as given in Eq. (3), is given by Eq. (4)

$$C_6H_6O_6 + 2H^+ + 2e^- \leftrightarrow C_6H_8O_6 \quad (3)$$

$$E = E^0 - 0.059 \text{ pH}, \quad \text{at } 298 \text{ K} \quad (4)$$



It is evident from the above equations that the reducing power of ascorbic acid decreases as the pH decreases. The larger particle size of copper particles at lower pH values are due to the formation of smaller number of nuclei when the reducing power of ascorbic acid is weaker. The metal atoms precipitating at a later stage are involved in the growth of the existing nuclei rather than the formation of new nuclei. This results in the growth of the fewer particles into a larger size. As the pH is increased, the reducing power of ascorbic acid increases, which in turn increases the reaction rate between $Cu^{2+}$ and ascorbic

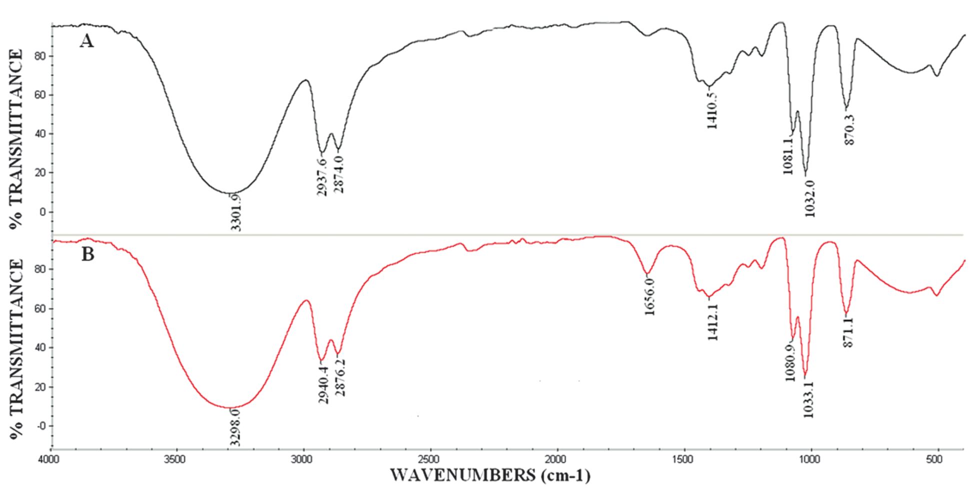


**Fig. 3.** FTIR spectra of ethylene glycol (A) and copper nanofluid (B).

acid, and results in more number of particles with smaller sizes.

### 3.3.2. Effect of Ascorbic Acid Concentration

The ratio of reactants is one among many factors influencing the size of the particles formed.[17] The effect of ratio of reactants on the particle size was studied by varying the molar ratio of ascorbic acid to copper nitrate from 5 to 20. It was found that the particle size increased from 32 nm to 49 nm under thermal conditions and decreased from 33 nm to 19 nm under microwave irradiation, when the ratio was changed from 5 to 20, respectively. The observation under thermal conditions could be explained as, with the increase in the ascorbic content in the mixture the pH of the reaction mixture decreases. This in turn decreases the reducing power of ascorbic acid leading to formation of fewer numbers of bigger particles.

Microwave radiation is a highly effective heating source compared to conventional ones providing uniform and selective heating of the reaction mixture. Also with higher heating rate it accelerates the nucleation of copper particles. This results in the formation of more number of nuclei, and therefore, more particles with smaller sizes. Also, the intense friction and collisions of the particles created by the microwave irradiation suppresses the ready growth of the copper particles and results in smaller particles.[17] With increase in concentration of ascorbic acid the number of collision increases and this factor dominates over the pH effect. Hence the opposite trend is seen.



### 3.3.3. Effect of Dilution

Dilution of the reaction mixture with water decreases the overall concentration of the reactants in the reaction mixture, which has the bearing on the reaction rate and the particle size as well. Reactions were carried out by diluting the reaction mixture with different volumes of water. It was found that the particle size decreased with dilution. In addition to the initially added 45 mL of water during synthesis, 55 mL, 105 mL and 155 mL of water was further added. The particles yielded had 32 nm, 26 nm, 22 nm and 19 nm size for 45 mL, 100 mL, 150 mL and 200 mL total dilution, respectively. With the increase in dilution, the reaction proceeded very slowly due to the decrease in effective concentration of the reacting species. The observations can be explained as follows, with the increase in the overall dilution the proximity between the precipitating metal atoms decreases and hence the collision between them is reduced preventing the particle growth and hence resulting in smaller size of the nanoparticles formed.

### 3.3.4. Effect of Addition of PVP

The long term stability of nanofluids is one of the key issues during its application in real world devices. The effect of PVP on the size of the copper nanoparticles as well as stability was studied by varying the concentration of PVP. The results are tabulated in the Table I.

It was observed that the addition of PVP decreases the size of the copper particles. The results suggest that PVP efficiently restricts their growth. This could be attributed to the capping effect of PVP in controlling the size of particles. It forms a layer around the nanoparticles covering the growth sites and preventing further diffusion of growth species from surrounding solution hence reducing the growth of particles and also prevents agglomeration of formed particles.

When prepared in the absence of PVP the nano fluid was unstable and the particles began to settle down. The samples of nanofluid prepared in the presence of PVP under different conditions were stable for several weeks at room temperature under stationary conditions as revealed by sedimentation measurements; and even the least stable fluid was stable up to 6 weeks.

The stability of the as synthesized fluid is better than the one achieved by the two step method where in they could achieve it for one week in case of copper–transformer oil system and 30 h for copper–water system and in case of one step chemical method where the copper nanofluid stayed stable for a duration of 3 weeks.[10,18] The stability of the nanofluid in the presence of PVP is attributed to two factors. One of the factors is the smaller sizes of the particles, which facilitate their better dispersity in the medium and the second factor is that the addition of PVP prevents the agglomeration of the metal nanoparticles.

### 3.3.5. Effect of Power of Microwave Radiation and Irradiation Duration

At 30% microwave irradiation for 4 minutes the reaction was incomplete with size of the resulting particle being 25 nm. When the power was increased to 50%, the reaction proceeded to completion. When the power of microwave was increased from 50% to 70% to 90% the particle size decreased from 33 nm to 28 nm to 21 nm. The decrease in the particle size with the increase in power of microwave radiation is attributed to the formation of large number of small particles due to rapid nucleation.

The effect of microwave irradiation duration on the formation of nanoparticles in the reaction medium was also investigated. Table II summarizes the variation of particle

**Table I.** Effect of concentration of PVP on the size of particles.

| Concentration of PVP added (M) | Effective concentration of PVP in the reaction mixture (mM) | Particle size (nm) |
|---|---|---|
| 0 | 0 | 60 |
| 0.01 | 0.45 | 32 |
| 0.05 | 2.27 | 21 |
| 0.1 | 4.55 | 16 |



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**Table II.** Effect of irradiation duration on the size of particles.

| Irradiation duration (min) | Particle size (nm) |
|---|---|
| 4 | 33 |
| 7 | 37 |
| 10 | 48 |

size with the microwave irradiation duration. The results are consistent with the results reported in the literature.[17] The continued interaction of the particles might be the cause for the growth of the particles, resulting in the increase in particle size.

TEM and FESEM were used to investigate the morphology as well as size of the sample. The sizes obtained from the TEM and FESEM matches well with those obtained from XRD. Figure 5 shows a typical TEM image of the copper nanoparticles. Figure 6 shows the FESEM image of the same. The particles are somewhat octahedral in shape.

### 3.4. Results of Thermal Conductivity Measurements

The thermal conductivity of the copper nanofluid synthesized by reduction of copper nitrate using ascorbic acid was found to be 1.774 W $m^{-1}$ $K^{-1}$ when the weight fraction of copper nanoparticles was 0.167%, significantly higher than the reported value of 0.279 W $m^{-1}$ $K^{-1}$ for copper nanofluid (0.1%) prepared using sodium hypophosphite and 0.259 W $m^{-1}$ $K^{-1}$ for copper nanofluid (0.5%) prepared by single step physical method of direct evaporation technique.[8,9] The variation of thermal conductivity ratio with nanoparticle weight fraction of the above synthesized fluid is as shown in Figure 7. The ratio of water and ethylene glycol was maintained 1:1 during the measurements. Similar trend was observed for different ratios of the base fluids indicating that trend is independent of base fluid composition. It was observed that with the increase in the particle concentration the thermal conductivity as well as the thermal conductivity ratio of the nanofluid increased. The increase in thermal conductivity could be attributed to the higher conductivity of copper, its nano size and uniform distribution of the particles in the fluid.[19,20]

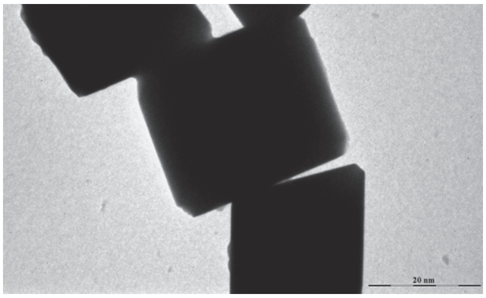


**Fig. 5.** TEM image showing octahedral copper nanoparticles.

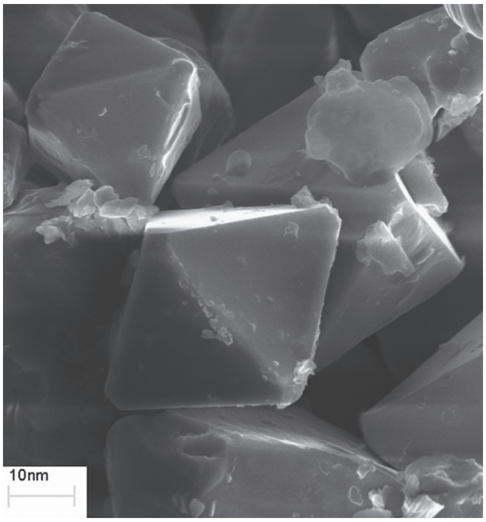


**Fig. 6.** FESEM image showing octahedral copper nanoparticles.

### 3.5. Results of Rheological Measurements

Viscosity is one of the key properties of nanofluids. It is believed that viscosity is as critical as thermal conductivity in engineering systems because the nanofluid is expected to show an increase in thermal conductivity without an increase in pressure drop, which in turn is related to fluid viscosity. The variation of shear stress with shear rate of copper nanofluid at 30 °C for a particle loading of 0.167% is as shown in Figure 8(a). The linear relation between the shear stress and shear rate demonstrates the Newtonian behavior of the nanofluid. Viscosity as a function of shear rate for 0.167% particle loading at different temperatures, shown in Figure 8(b) demonstrates that viscosity is independent of shear rate.[21] The results for other particle concentrations are similar.

The viscosity of the above nanofluid was measured at different particle weight fractions at 30 °C and the changes



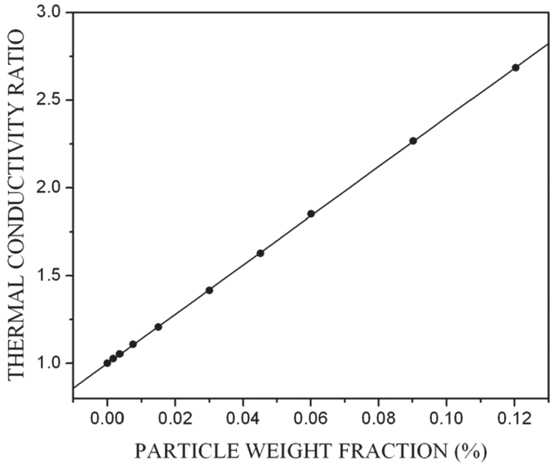


**Fig. 7.** The variation of thermal conductivity ratio with nanoparticle weight fraction.

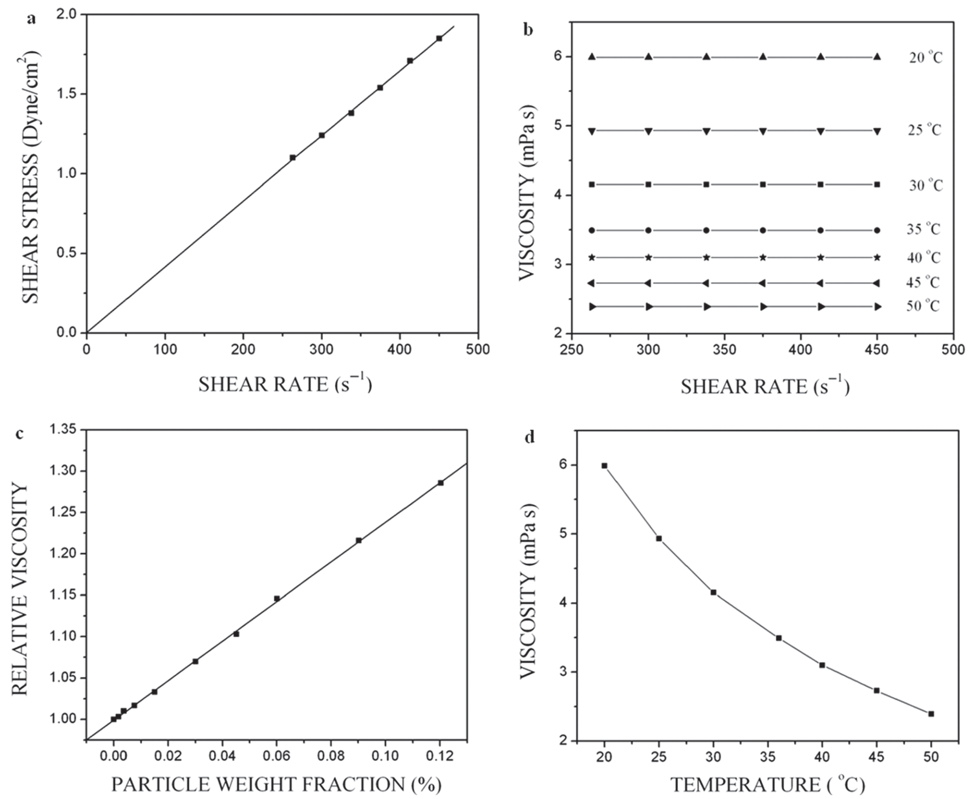


**Fig. 8.** Rheological measurements: (a) the variation of shear stress with shear rate at 30 °C for a particle loading of 0.167%. (b) Viscosity as a function of shear rate for 0.167% particle loading at different temperatures. (c) Variation of relative viscosity of the nanofluid with particle weight fraction. (d) Variation of viscosity of the nanofluid with temperature.



in relative viscosity of the nanofluid with particle weight fraction are shown in Figure 8(c). It is seen from the figure that the relative viscosity increases with the increase in particle concentration. The effect of temperature in the range of 20 °C–50 °C, on the viscosity of the nanofluid was studied and is shown in Figure 8(d). It was seen that the viscosity decreases with the increase in temperature of the fluid. The trend is similar to the one reported by Li et al.[22]

## 4. CONCLUSIONS

A simple single step solution phase approach has been made for the synthesis of copper nanofluids in the presence of PVP. Ascorbic acid has been used to reduce copper nitrate in mixture of water and ethylene glycol, which acted as base fluid. The synthesized fluids were characterized by diffraction, microscopic, spectroscopic techniques and the obtained results were in agreement with each other. It was shown that by tuning the reaction parameters particles of desired size could be obtained. The resulting Newtonian nanofluid showed appreciable stability of minimum 6 weeks under stationary conditions at room temperature. Stably dispersed octahedral copper nanoparticle has been reported in nanofluids for the very first time. The thermal conductivity of the synthesized nanofluid was 1.774 W $m^{-1}$ $K^{-1}$ at low weight fraction of copper nanoparticles (0.167%). The reported method has been found to be simple, quick, efficient and cost effective way to produce nanofluids.

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