Synthesis of silver nanofluid by a novel one-pot method for heat transfer applications

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Abstract
This paper focuses on the synthesis of silver nanofluid by a novel one-pot method. Silver nanofluid is prepared by reducing silver nitrate using sodium hypophosphite as a reducing agent by means of conventional heating using sodium lauryl sulphate (SLS) as surfactant. This in situ, one-pot method appears to be advantageous with high yield of product with less time consumption. Experiments were carried out to study the effect of concentration of silver nitrate, SLS on the size of the nanoparticle and the effect of pH on time of synthesis of silver nanofluid. Furthermore, the characterization of obtained silver nanofluid was done by means of particle size analyzer. The heat transfer efficiency of the nanoparticles was evaluated by transient hot wire method to find its suitability as an effective coolant for the automobile industry.

Keywords: Silver, nanofluid, nanostructures.

Introduction
Over the last several decades, scientists and engineers have attempted to develop fluids, which offer better cooling or heating performance than conventional heat transfer fluids for a variety of thermal engineering applications. Choi of Argonne National Laboratory of USA in 1995 proposed a novel concept of “nanofluid” by applying nanotechnology to thermal engineering to meet the cooling challenges (Bergles et al., 1988). This new class of heat transfer fluids (nanofluids) is engineered by dispersing nanometer-sized (one billionth of a meter) solid particles, rods or tubes in traditional heat transfer fluids. From the investigations in the past decade, nanofluids were found to exhibit significantly higher thermal properties, in particular, thermal conductivity, than those of base fluids (Ahuja et al., 1975; Ahuja et al., 1982; Eastman et al., 1997; Lee et al., 1999; Wang et al., 1999; Xuan et al., 2000; Eastman et al., 2001; Das et al., 2003; Xuan et al., 2003; Murshed et al., 2005; Hong et al., 2005; Li et al., 2006). Thus, nanofluids have attracted great interest from the research community due to their potential benefits and applications in numerous important fields such as microelectronics, transportation, manufacturing, medical and heating, ventilating and air-conditioning (HVAC).

The impact of nanofluid technology is expected to be great considering the heat transfer performance of heat exchangers or cooling devices, which is vital in numerous industries. For example, the transport industry has a need to reduce the size and weight of vehicle thermal management systems and nanofluids can increase the thermal transport efficiency of coolants and lubricants. When the nanoparticles are properly dispersed, nanofluids can offer numerous benefits. For example 0.3 vol% copper nanoparticles dispersed in ethylene glycol is reported to increase its inherently poor thermal conductivity by 40% (Eastman et al., 2001). This observation was further confirmed from our previous study where the thermal conductivity of copper nanofluid obtained by novel one step method was found to be higher than that of the base fluid ethylene glycol (Wang et al., 1999). About 10-30% increase in thermal conductivity of alumina/water nanofluids was observed with the incorporation of 1-4 vol % of alumina (Das et al., 2003).

Nanofluids are generally prepared by step-by-step method by dispersing metallic nanoparticles in the base fluid (Xuan et al., 2003). This involves agglomeration of nanoparticles that takes place during the process of drying, storage and transportation resulting in settlement and clogging of the microchannels leading to a decreased thermal conductivity. There are several other methods like the one-step physical method, in which the metal vapour is directly condensed into nanoparticles by contact with a flowing low vapor pressure liquid (Eastman et al., 2001) but this method appears to be cost ineffective. By polyol process (Das et al., 2003), monodispersed and non-agglomerated metal nanoparticles are obtained. However, the major drawback of this method is that solution of the metallic salt should be heated to its boiling point and kept under refluxing conditions for a long time (Zhu et al., 2004; Kuliwara et al., 2005). In the aqueous chemical reduction method, though the rate of the reaction is high, the agglomeration problem exists, and as a consequence, a decrease in the thermal conductivity of the nanofluid is observed in most cases. Hence the development of a new and novel method for the preparation of nanofluids is inevitable.

In the previous study carried out by the authors, the synthesis of copper nanofluids was done, by optimizing various process parameters and nanofluids of desired properties were obtained. Hence as an extension of our work, in the quest to develop heat transfer fluids of superior properties the synthesis of silver nanofluids was carried out. Silver was chosen as it has high thermal conductivity and is therefore expected to have good heat
transfer properties ideally suitable for thermal engineering applications.

In this method silver nanofluids comprising of metallic silver dispersed in ethylene glycol are synthesized by a novel one pot method. The method is a unique one where preparation of nanoparticles is combined with the preparation of nanofluids and hence the process of drying, storage, transportation and redispersion of silver nanoparticles can be avoided and ultimately the production cost may be reduced as well. These aspects of this work are novel.

**Experimental procedure**

**Preparation of silver nanofluids**

All the reagents used in our experiments were of analytical purity and were used without further purification. The beakers used in this procedure were cleaned by an ultrasonic cleaner in an ultrasonic bath. In this procedure, 25 ml of ethylene glycol solution was taken in a 500 ml beaker. To this 15 ml of (0.1M) silver nitrate, 50 ml of surfactant sodium lauryl sulphate (SLS) and 100 ml water was added. Further few drops of kerosene were added to prevent oxidation. The reaction mixture was subjected to magnetic stirring for 15 minutes in a magnetic stirrer/heater. Then 30 ml of sodium hypophosphite was added and the magnetic stirring was continued for 30 minutes. The colour of the mixture turned from blue to dark red after the reaction. Silver nanofluid was obtained after cooling the reaction mixture to room temperature. To hasten the reaction, few drops of dilute sulphuric acid were added and this can be neutralized by the addition of an equal amount of dilute ammonia. The chemical reaction involved is as follows:

\[
\text{NaH}_2\text{PO}_2 + 3\text{H}_2\text{O} + \text{AgNO}_3 \rightarrow \text{NaH}_2\text{PO}_3 + \text{HNO}_3 + \text{H}_2 + \text{Ag}^+.
\]

**Characterization:** Characterization of the silver nanofluid was done by particle size analyser and transient hot wire method.

**Particle size analysis:** Before analysis of the particle size the nanofluids are subjected to ultrasonication, to keep the particles in suspension and to prevent agglomeration of the particles. The Mie theory (Stratton 1941) principle is followed for the analysis of particles by means of particle size analyser.

**Transient hot wire method:** Thermal conductivity (K) is the intrinsic property of a material, which relates its ability to conduct heat. Determination of thermal conductivity is done by transient hot wire method (Nagasaka et al., 1981; Ailoush et al., 1982; Johns et al., 1988; Xuan et al., 1994, Kestin et al., 1998). This method involves a wire (typically Platinum) suspended symmetrically in a liquid in a vertical cylindrical container.

**Fig. 1. Effect of the concentration (Molar) of silver nitrate on the size of the nanoparticles**

Briefly the method works by measuring the temperature/time response of the wire to an abrupt electrical impulse. The wire is used as both heater and thermometer and the thermal conductivity K is calculated from a derivation of Fourier’s Law.
Results and discussion

Results of Particle Size Analyzer

The size of the nanoparticles present in the nanofluid can be identified with the help of the particle size analyzer. By optimizing the various parameters such as concentration of silver nitrate, surfactant and pH the minimal particle size was obtained.

Effect of the concentration of silver nitrate on the size of silver nanoparticles

The effect of silver nitrate concentration on the formation of silver nanoparticles is shown in Fig.1. From the figure it is evident that silver nanofluid of 0.1 M concentration seems to be quite effective for obtaining silver nanoparticle of desired particle size. A minimum particle size of 0.73 μm is obtained for 0.1 M concentration of silver nitrate as seen in Fig.2. It is mainly due to the fact that growth and nucleation of the nanoparticles takes place separately and this results in a narrow distribution of the silver nanoparticles. But in higher concentrations 0.2 M and 0.4 M, the growth and nucleation takes place simultaneously. Some large particles grow continually and some newly born particles appear, so the distribution of silver nanoparticles is broadened.

Effect of pH

Besides concentration of silver nanofluid pH also plays a significant role in the synthesis of silver nanofluid. A low pH results in a faster reaction time. So inorder to fasten the reaction, a low pH is maintained. This is done by the addition of dilute sulphuric acid. As the pH decreases, the time taken to obtain the silver nanoparticle also decreases. For example as seen in Fig.3, when the pH is maintained at 8, the time taken for obtaining silver nanoparticle is found to be 90 minutes, whereas if the pH is brought down to 2,
the silver nanoparticles could be obtained within 20 minutes of time. This behaviour may be explained due to the fact that, the sodium hypophosphite causes the reduction of silver ions to silver only if the pH is more acidic. However, the silver nanofluid obtained would be in a highly acidic state and it may even corrode the engines when it is used as a coolant. Thus, the silver nanofluid is neutralized with dilute ammonia, which reverts it back to the basic state and can be used in engines without causing corrosion.

**Effect of the concentration of the surfactant**

It was analyzed from the particle size analyzer studies that silver nanofluids of smallest size (0.73 μm) were obtained by using 0.1 M silver nitrate solution. Hence an attempt was made to further reduce the size by modifying the concentration of the surfactant. Silver nanoparticles were synthesized using varying concentrations of surfactant. It was found that sodium lauryl sulphate surfactant played a key role in determining the size of the nanoparticles. When the concentration of the surfactant was increased, the sizes of the silver nanoparticles formed keep decreasing as seen in Fig.4. At 0.1 M concentration a particle size of 0.99 μm is obtained as seen in the Fig. 5 and at 0.2 M concentration a reduction in particle size to 0.83 μm as seen in Fig.6. At 0.5 M concentration a particle size of 0.36 μm is obtained as seen in the Fig.7. Thus the increase in the concentration of the surfactant favored the formation of micelles around the metal nanoparticles, prevented their growth and agglomeration and in turn favored the formation small-sized silver nanoparticles.

**Stabilization of the nanoparticle**

The stabilization of the nanofluid is very important for industrial applications. It has been shown at room temperature the obtained nanofluid is stable for more than 4 weeks in the stationary state and more than 8 h under centrifugation at 5000 rpm without sedimentation. It could also be suspended for more than two weeks in stationary state at 120°C. The stabilization of the obtained silver nanofluid was found to be better than that of the one prepared by the step-by-step method in which the nanofluid lasted for only one week in the stationary state at room temperature. Two factors contribute to this improvement: one is the small size and hence better dispersity of copper nanoparticles and the other is due to the addition of the surfactant (SLS) which prevents the agglomeration and the growth of the metal nanoparticles.

**Thermal conductivity**

The thermal conductivity of the silver nanofluid developed in the present study is found to be significantly higher (0.8 Wm⁻¹K⁻¹) than the reported value for Cu nanofluid (0.6 Wm⁻¹K⁻¹) (Kulihara et al., 1995) and that of pure ethylene glycol (0.256 Wm⁻¹K⁻¹), which is used as a conventional coolant.

**Conclusions**

A novel one-pot method was developed for preparing silver nanofluids by reducing silver nitrate using sodium hypophosphite as reducing agent and ethylene glycol as base fluid by means of conventional heating. This is advantageous over other conventional methods, as it is an in situ, economical and one-step. The non-agglomerated and stably suspended silver nanofluids are obtained in a short time and the synthesized silver nanofluid has superior thermal conductivity. Hence, the silver nanofluid resulted from this study may be used as an effective coolant in automobile industry in place of the conventional fluids that are currently in use.

**Acknowledgements**

The authors are thankful to National Metallurgical Laboratory (NML) Madras Centre and Anna University, Chennai for having provided the facility to carry out this work.

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