

Thermal conductivities of naked and monolayer protected metal nanoparticle based nanofluids: Manifestation of anomalous enhancement and chemical effects

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Thermal conductivities of two kinds of Au nanoparticles were measured in water and toluene media. The water soluble particles, 10–20 nm in mean diameter, made with citrate stabilization showed thermal conductivity enhancement of 5%–21% in the temperature range of 30–60 °C at a loading of 0.000 26 (by volume). The effect was 7%–14% for Au particles stabilized with a monolayer of octadecanethiol even for a loading of 0.011%. Comparatively lower thermal conductivity enhancement was observed for larger diameter Ag particles for significantly higher loading. Effective enhancement of 9%, even at vanishing concentrations, points to additional factors in the thermal conductivity mechanism in nanofluids. Results also point to important chemical factors such as the need for direct contact of the metal surface with the solvent medium to improve enhancement.

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Most of the commonly encountered fluids have the inherent deficiency of low thermal conductivity. For example, while water has a thermal conductivity of 0.6 W/mK the value for copper is 386 W/mK.¹ This three orders of magnitude difference between the thermal conductivity of normal liquids and metals makes one consider enhancement of thermal conductivity of liquids by suspending metal particles in them. Although the effective thermal conductivity of such a suspension was quantified by Maxwell² recent work by Lee *et al.*³ has renewed interest in this area. Fluids with nanoparticle suspensions are called “nanofluids.” Oxide nanoparticles³ and later pure copper particles⁴ were used to achieve conductivity enhancement of 5%–40% over a volume fraction of 0.1%–0.3%. Such large enhancement defies Maxwell theory² as well as its modification by Hamilton and Crosser⁵. Eastman *et al.* looked at various explanations but a consistent picture is yet to emerge.⁶ The results reported here point to additional physical properties of metal nanoclusters, apart from optical limiting.⁷

For the studies reported here, thermal conductivity was measured by a transient hot wire method.^{3,8–10} No deposition of particles on the wire was observed during the course of the experiments. The samples were stable over a period of several months and no degradation was observed during storage or in the course of the experiment.

Our experiments were conducted with several kinds of nanoparticles prepared using well-established procedures. Gold and silver particles in the 10–20 nm range were prepared by the citrate reduction route.¹¹ These will be referred to as Au citrate. Au nanoparticles with a thiolate covering were prepared by the Brust *et al.* procedure¹² and were char-

acterized in as prepared form by a variety of techniques.¹³ Octadecanethiol was used as the monolayer forming molecule in the present experiments. Particles of 4 nm diameter were accessible by this method. These will be referred to as Au thiolate. While the former gave water soluble particles, the latter gave freely-soluble particles in variety of organic solvents. TEM images of the Au-citrate and Au-thiolate particles used in this study are shown in Fig. 1. The average particle diameter was 10–20 nm for Ag citrate and it was 3–4 nm for Au thiolate. Some studies were done with Ag citrate as well with sizes in the range of 60–80 nm.¹⁴

First, thermal conductivity values of toluene over a temperature range of 25–70 °C were measured so that the values of toluene based nanofluids could be compared with them. The increment in thermal conductivity was found to be almost linear with the temperature. For the next set of measurements, a nanofluid of toluene with Au thiolate was used. The volume percent of the particles in toluene was 0.011%. The thermal conductivity of this nanofluid was found to be 0.1116 W/mK at 30 °C and 0.1204 W/mK at 70 °C. Polynomial curves were fitted to the above experimental data (with standard deviation of less than 0.5% of the mean value). There were increments of about 7% at 30 °C and 14% at 60 °C with respect to the conductivity of toluene at 30 °C as shown in Fig. 2(a). This is astonishing because the conductivity enhancement is found to be of same order as obtained by Lee *et al.*³ and by Das *et al.*¹⁰ for oxide nanoparticles in water at a volume fraction of 1%–4%, which is more than two orders of magnitude higher than the volume fraction used here. When the conductivity of the nanofluid was compared with that of toluene at the same temperature, the enhancement was found to be 7% at 30 °C and 8.8% at 60 °C, as shown in Fig. 2(b). Any theory for thermal conductivity of

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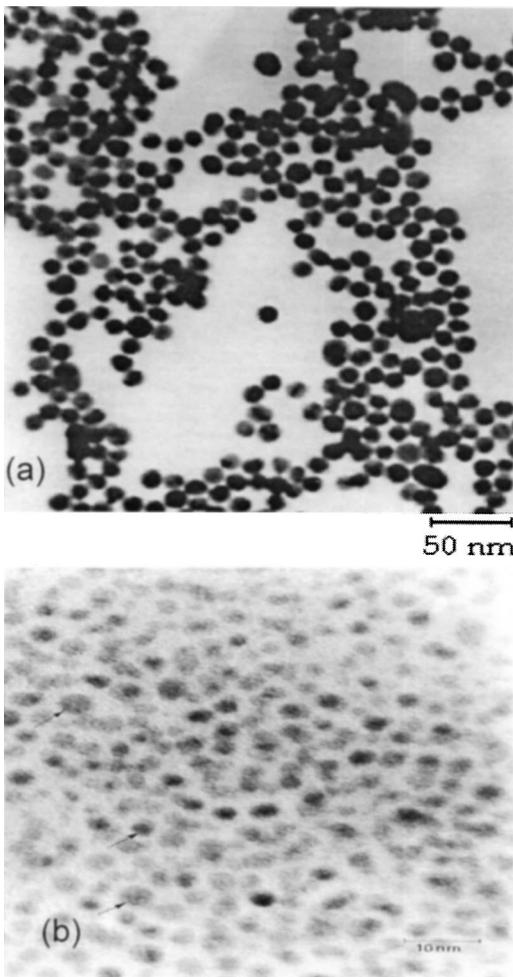


FIG. 1. TEM photographs of the (a) Au-citrate and (b) Au-thiolate nanoparticles used in this study. The arrows show the clusters where the metal lattice is resolved.

suspensions like that of Maxwell² or of Hamilton and Crosser⁵ fails to predict this enhancement of conductivity.

The above nanofluid was diluted to see the conductivity enhancement effect at lower concentrations. The volume percent of gold particles in the nanofluid was reduced to 0.0079%. The thermal conductivity of this nanofluid showed an enhancement of about 4.5% at 30 °C and 11% at 60 °C [Fig. 2(a)]. If we compare the conductivities of this nanofluid with toluene at the same temperature, it shows an enhancement of about 4.5% at 30 °C and 6.3% at 60 °C [Fig. 2(b)].

Subsequently, we diluted the nanofluid to still lower concentration of 0.005%. The thermal conductivity showed an enhancement of about 3% at 30 °C and 10% at 60 °C compared with the conductivity of toluene at appropriate temperatures [Fig. 2(a)]: it was about 3% at 30 °C and 5% at 60 °C [Fig. 2(b)]. The calculations show that the increase of thermal conductivity enhancement with particle concentration is almost linear.

In Au citrate, the nanoparticles are covered with citrate ions and there are free citrate ions in solution. In order to make sure that the conductivity enhancement of nanofluids is not due to free ions, the thermal conductivity of water with identical amount of citrate ions was prepared as the blank solution (5 mM trisodium citrate). The conductivity of the blank was higher than that of pure water by 1.6%. Nanoflu-

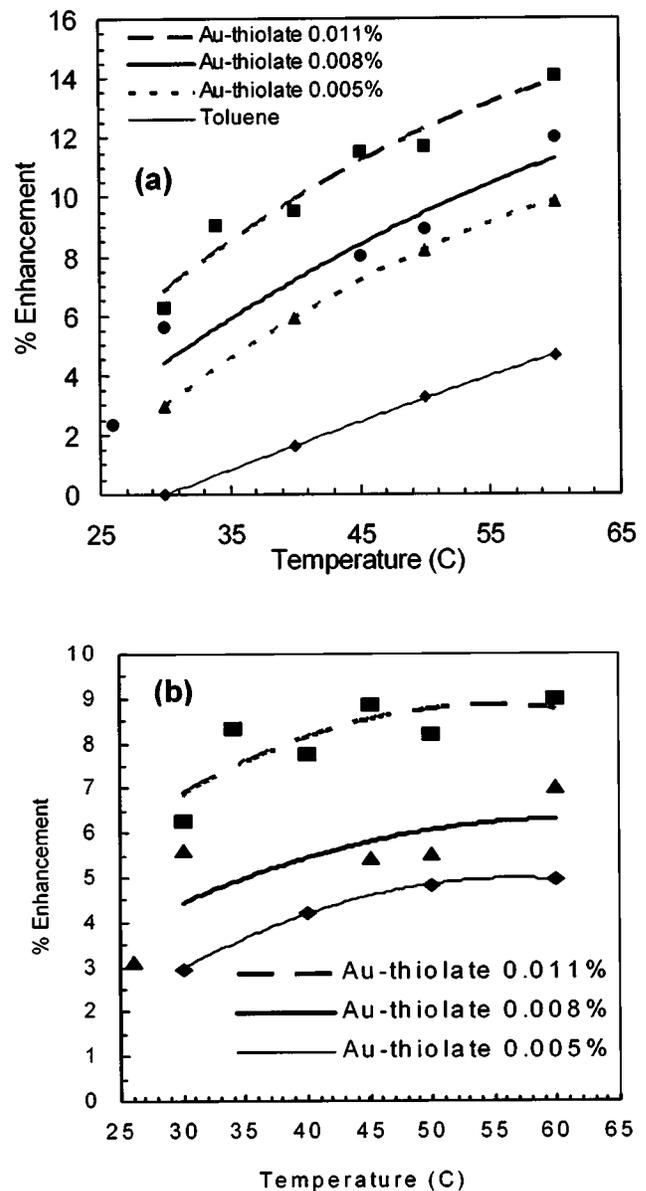


FIG. 2. Percentage of enhancement in thermal conductivity vs the temperature of Au thiolate in toluene with reference to the conductivity of toluene at (a) 30 °C and that at (b) respective temperatures.

ids were studied at the same instrument settings. The volume fraction of Au citrate was 0.000 26%. This is a two order of magnitude lower volume fraction than the toluene based nanofluids (a higher concentration was not possible because the particles aggregate at large concentrations). The conductivity of the fluid was found to be 0.656 W/mK at 30 °C and 0.757 W/mK at 66 °C. This trend shows an enhancement of about 5% at 30 °C and 21% at 60 °C compared to the conductivity of the blank solution at 30 °C [Fig. 3(a)]. The trend of enhancement of conductivity of the nanofluid over blank solution at respective temperatures shows increments from 4.6% at 30 °C to 8.3% at 60 °C [Fig. 3(b)].

At lower particle concentration (0.000 13%), the conductivity showed an enhancement of about 3.2% at 30 °C, which goes up to 17.3% at 60 °C, compared to the conductivity of the blank solution at 30 °C [Fig. 3(a)]. If the enhancement is compared with the blank solution at respective temperatures, the increment is from 3.2% at 30 °C to 5.2% at 60 °C [Fig. 3(b)].

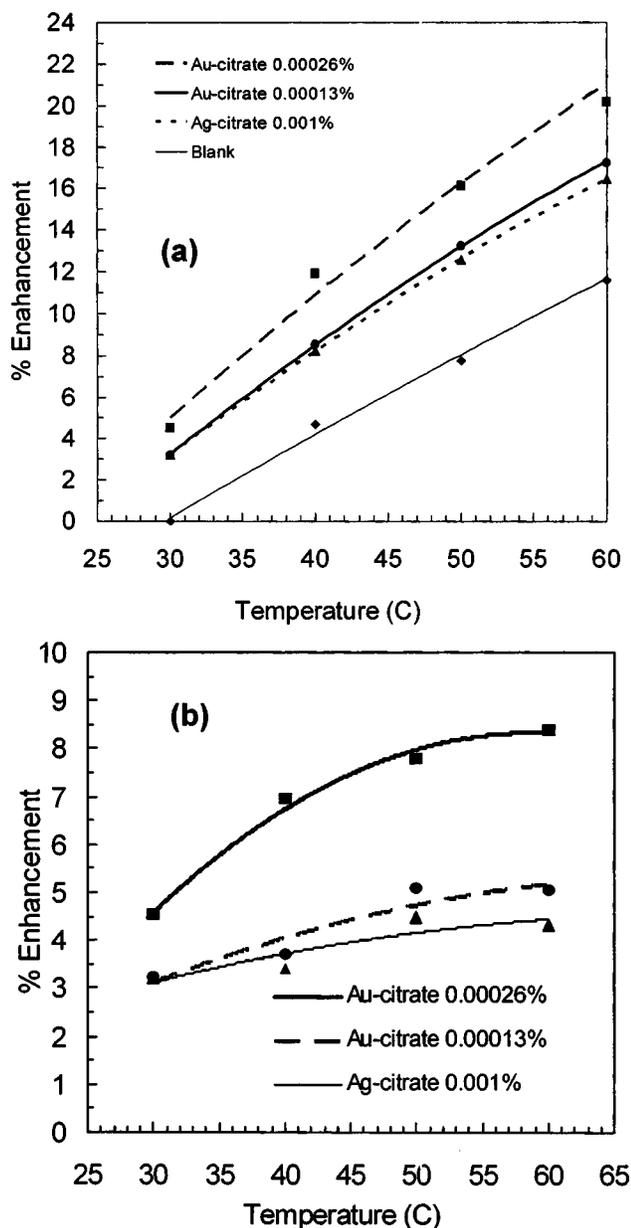


FIG. 3. Percentage of enhancement in thermal conductivity vs the temperature of Au citrate and Ag citrate with reference to the conductivity of blank water (with 5 mM trisodium citrate) at (a) 30 °C and that at (b) respective temperatures. The data for Ag citrate are also given.

Finally, the conductivity of Ag-citrate particles of around 60–80 nm diameter was measured. The concentration of the particles in the nanofluid was 0.001 vol %. The conductivity of this fluid was 0.6376 W/mK at 29 °C and 0.735 W/mK at 66 °C (Fig. 3). It was seen that the conductivity enhances from about 3.2% at 30 °C to 16.5% at 60 °C with respect to the conductivity of the blank solution at 30 °C. The enhancement of the conductivity of the nanofluid with respect to the blank solution at respective temperatures shows increments from 3.2% at 30 °C to 4.5% at 60 °C. This clearly shows the particle size effect. Silver, although having higher conductivity and an order of magnitude higher concentration than gold, showed less enhancement of the conductivity only because its particle size is larger. The total surface area of particles in Au-citrate nanofluid with 0.000 26% volume of par-

ticles and in Ag-citrate nanofluid with 0.001% volume of particles with the above mentioned sizes is to of the same order even though the concentration of silver particles is higher. But the enhancement in Au-citrate nanofluid is almost double that of Ag-citrate nanofluid. This indicates that the surface area increase can explain the phenomenon of conductivity enhancement only partially; there are more parameters in the enhancement process which also contribute to the temperature effect. Probably surface activity increases with an increase in temperature, which may be in the form of micro-convection.

At room temperature, the enhancement in Au-citrate nanofluid is more than half that of Au-thiolate nanofluid, but at 60 °C, the enhancement is almost the same. This suggests that the surface actions taking place in both fluids are different. It is possible that these actions may enhance more effectively at higher temperatures in a polar liquid like water than in an organic liquid. Structural differences in these two nanosystems may also contribute to the differences observed.

There is a profoundly interesting aspect from this study. The nanoparticles with a coating (Au thiolate) of a covalent molecular chain are less effective than uncoated metal clusters (Au citrate) as far as thermal conductivity enhancement is concerned. To produce the same effect, the former had to be used at a larger volume fraction than the latter. This suggests that effective heat transfer at the surface of the nanoparticles is decided by the type of coating. Thus chemical effects come into play in determining the extent of energy transfer and future studies have to address this in more detail.

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