

Influence of molecular weight of PVP on aggregation and thermal diffusivity of silver-based nanofluids

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ABSTRACT

Stable silver colloids were synthesized in water by a green method, reducing AgNO_3 with fructose in the presence of poly-vinylpyrrolidone (PVP) of various molecular weights. A silver nanopowder was obtained from the colloids and redispersed at 4 vol% in deionized water. The Ag nanopowders were characterized by Scanning Electron Microscopy and Thermal Gravimetric Analysis. The Ag colloids were characterized by UV-Visible spectroscopy, combined Dynamic Light Scattering and ζ -potential measurements, Laser Flash Thermal Diffusivity. It has been found that the molecular weight of PVP strongly affects the ζ -potential and the aggregation of nanoparticles, and thereby affecting the thermal diffusivity of the obtained colloids. It was found that the thermal diffusivity increases with aggregation and a maximum improvement by about 10 % was found at room temperature for nanofluids showing the lowest ζ -potential.

Keywords: nanofluids; thermal diffusivity; PVP; ζ -potential; aggregation

1 INTRODUCTION

Nanofluids represent a relatively new class of fluids, obtained by the dispersion of solid particles of nanometric dimensions in traditional solvents [1]. They have attracted a considerable interest in recent years by the scientific community, thanks to promising improvements of various properties of the base fluids, such as the heat exchange [2], the "pool boiling", that means the ability of nanoparticles contained in nanofluids to improve the heat transfer properties of fluids based on water in conditions close to boiling or to increase the critical heat flux [3], and the tribological properties [4]. The performance of nanofluids critically depends on the size distribution of nanoparticles and the stability of the suspension and, therefore, a fundamental step to achieve high performance is the preparation of stable nanoparticles suspensions with controlled aggregation.

Albeit with a considerable scattering of the data in the literature, it was demonstrated that the presence of particles of different nature in suspension can generally lead to a significant increase in thermal conductivity with respect to the base fluid [5-8]. The increase of the thermal

conductivity of these systems can be explained in first approximation by the so-called Maxwell model [9], developed by the scientist to explain the dielectric properties of the suspensions and then adapted to describe changes in thermal conductivity. It is a simplistic model, which assumes monodisperse, spherical, fixed in space and not-interacting particles.

During experimental investigations, considerable deviations from the predictions of this model are often encountered and, therefore, various researchers have attempted to improve it, overcoming some limitations. For example Hamilton and Crosser [10] have developed a similar model, which is able to take into account the non-sphericity of the particles by approximation with ellipsoids; Yu and Choi [11] in their model took into account the interfacial interaction between the fluid and particle; other models take into account the influence of Brownian motion [12] or aggregation of the particles [13, 14]. Anyway, none of the mentioned models can still be considered to be complete, since the increments of experimental thermal conductivity observed in the literature for some nanofluids are often much higher than those expected from each of these models.

However, as already mentioned, the literature shows significant differences between the conductivity values even for nanofluids based on the same base fluid and on the same type of nanostructured material. Considering the same type of particles and base fluid, such variations may be due to different shapes or sizes of nanoparticles [15, 16], to the different stability of the suspension that could affect the properties over time, the presence of surfactant agents that can alter the thermal conductivity, in addition to a variability of the results depending on the method of evaluation of the conductivity [17]. However, in most cases, the poor reproducibility is due to an insufficient control of the synthesis process, which must ensure reproducibility in the shape, size and stability of the suspended nanoparticles. This suggests that the development of synthesis methods of nanofluids is still one of the challenges to face in this field.

One of the problems often not considered in literature concerning the preparation of nanofluids by one-step techniques, especially those involving the chemical reduction of a metal salt, is the presence of high amounts of surfactant polymers and side-products in the produced suspension. The presence of high excesses of these chemical species can lead to detrimental effects on the heat

exchange properties as already reported for PVP [18]. For this reason, in this work a particular procedure was developed, involving a one-step synthesis of nanoparticles, followed by the precipitation of nanoparticles wrapped in a surfactant shell and by their re-dispersion in base fluid. Hence, the re-dispersion method allowed producing stable colloids even in high concentrations and purer than the one-step ones. The one-step technique was used in order to obtain redispersible silver nanopowders containing a controlled amount of PVP of various molecular weights as capping polymer. The one-step technique involved the reduction of AgNO_3 using fructose as reducing agent and PVP as surfactant polymer and allowed easily producing primary nanofluids at concentrations as high as 0.1 vol% Ag in water. The nanopowder obtained by controlled precipitation was subsequently employed to obtain physical dispersions in water at 4 vol%. The effect of the molecular weight of PVP on the ζ -potential and the aggregation of nanoparticles and consequently on the thermal diffusivity of colloids was investigated.

2 EXPERIMENTAL

2.1 Materials and equipment

Deionized water (Millipore, Billerica MA, USA, 18.2M Ω) was used as solvent and base fluid; AgNO_3 (>99 % pure provided by Sigma-Aldrich) as a metal precursor; PVP-10 (average molecular weight 10000) and PVP-40 (average molecular weight 40000) provided by Sigma-Aldrich as surfactant polymers; D-Fructose (99 % provided by Alfa-Aesar) as a reducing agent and NaOH (anhydrous pellets provided by Carlo Erba) as a catalyst of the metal salt reducing reaction were used in the synthesis of water soluble silver nanoparticles.

A Sigma Zeiss Field Emission SEM operated at 5 kV was used for the microstructural characterization of the nanopowders; a Malvern Zetasizer Nano ZS exploiting the Dynamic Light Scattering (DLS) technique was used for the evaluation of the aggregate size distribution within the colloids and the ζ -potential; a Perkin-Elmer Lambda 15 UV-Visible spectrometer equipped with a quartz sample holder for liquids was used for the optical absorption characterization; thermal gravimetric analysis (TGA) were performed on the nanopowders in air using a TA-Instruments SDT-Q600. A Netzsch LFA 457 Microflash (laser flash thermal diffusivity) was used for the thermal diffusivity characterization of the two-step colloids, employing an especially designed sample holder for liquids where the liquid sample is measured between two 100 μm thick stainless steel plates spaced by a 1.5 mm polymer ring.

2.2 Production of the one-step colloids

Ag colloids were obtained by the chemical reduction of AgNO_3 in water using fructose as a reductant in an alkaline

environment. PVP of different average molecular weight was used as a capping agent.

The synthesis was optimized to achieve very stable colloids. Four samples containing different weight ratios of PVP-10 and PVP-40 were prepared: PVP-10 alone (colloid 1); 2/3 PVP-10 and 1/3 PVP-40 (colloid 2); 1/3 PVP-10 and 2/3 PVP-40 (colloid 3); PVP-40 alone (colloid 4). In a typical synthesis, 3 g of PVP blends + 1.66 g of fructose were dissolved in 40 mL of deionized water; 5 mL of a 2 M solution of NaOH in water was added to this solution. The whole solution was heated under reflux up to 75 °C. At this temperature, 5 mL of a 0.93 M solution of AgNO_3 in water (corresponding to 0.5 g Ag) was rapidly injected. The solution immediately assumed a dark-brown color, yellow when diluted. The obtained colloid was removed from the heating bath after 1 min.

2.3 Production of the redispersed colloids

A major concern in the production of a two-step nanofluid consists in obtaining a good particles re-dispersion, minimizing the aggregation phenomena. The approach followed in this work was to obtain a controlled precipitation of the nanoparticles and the surfactant polymer (in this case PVP of various molecular weights) from the one-step colloid, so that the particles are covered by the minimum amount of polymer, which provides a sufficiently stable dispersion. This purpose was achieved by diluting the suspensions with acetone. Being PVP poorly soluble in acetone, it is possible to tailor the amount of polymer that precipitates along with the particles by changing the volume ratio between acetone and the suspensions. For each of the 4 samples a volume ratio of 2:1 among acetone and colloid was used. The mixtures were subsequently centrifuged at 4000 rpm for 25 minutes. The supernatant liquid was eliminated and the precipitate was dried at 70 °C for 35 minutes to eliminate the acetone and partially water. The four nanopowders (nanopowder 1, 2, 3, 4 in the following text) were subsequently ground in an agate mortar and characterized by TGA in order to quantify the residual solvent and the adsorbed polymer on nanoparticles. Suitable amounts of each nanopowder were used for the production of re-dispersions in deionized water (colloid 1r, 2r, 3r, 4r within the following text). Colloidal suspensions in water at 4 vol% of the nanopowders were obtained by heating and periodically shaking the samples at a constant temperature of 60 °C for 4 hours.

3 RESULTS AND DISCUSSION

Figure 1 shows the UV-Vis of the four one step colloids diluted to a concentration of 0.001 vol%. The spectra show a plasmonic absorption peak centered at 410, 409, 405 and 412 nm for samples a, b, c and d respectively, which is typical of Ag nanoparticles. The plasmonic peak becomes weaker by increasing the molecular weight of PVP used during the synthesis. At the same time the background

considerably increases over 450 nm, where all the curves meet to an isosbestic point. This behavior is very well known and it is due to a partial and increasing aggregation of nanoparticles into the fluid that in this case is obtained by increasing the molecular weight of PVP. This is due to the fact that the molecular weight of PVP considerably affects the ζ -potential of nanoparticles as reported in the inset of figure 1, which is gradually reduced from -20.4 mV for sample (1) to -8.9 mV for sample (2). Despite this reduction of ζ -potential, all the samples were stable for several days not showing any particle settling. The aggregation is also confirmed by DLS measurements whose results are reported in the inset of figure 1 where the hydrodynamic size is reported as a function of the measured ζ -potential. All the hydrodynamic sizes follow the trends found for the ζ -potential values.

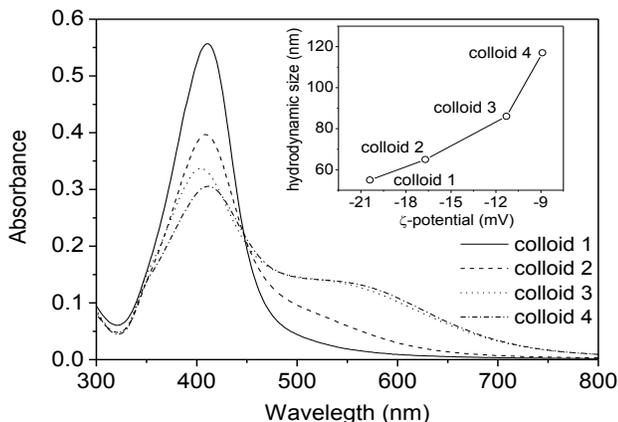


Figure 1: UV-Vis spectra of one-step colloids. The inset shows the DLS hydrodynamic size as function of ζ -potential for each sample.

As an example, figure 2 shows a SEM micrograph of the Ag nanopowder (3) obtained from the corresponding one-step colloid (3) by controlled precipitation and centrifugation, as reported in the experimental section. The histogram obtained from image analysis shows that the nanoparticles have a mean diameter around 20 nm and a quite narrow distribution. Similar micrographs (not shown here) were also collected for the other three samples, showing comparable sizes and distributions. This confirms that aggregation is the only phenomenon affecting the UV-Vis spectra, the ζ -potential and the DLS measurements. The TGA analyses of the four nanopowder samples (not shown here) performed in the temperature range RT-700 °C showed a metal residual weight of 88.2, 88.4, 90 and 90.4 wt% for nanopowder (1), (2), (3) and (4) respectively. Therefore, a ~ 10-12 wt% of PVP was precipitated along with the nanoparticles, with a slightly higher content in the case of samples having only or mostly PVP10. After re-dispersion of nanopowders in deionized water the UV-Vis spectra reported in figure 3 show a similar behavior observed for the one-step colloid. The spectra still show the typical plasmonic peak centered at 403, 403, 401 and 406 nm for redispersed colloid (1r), (2r), (3r) and (4r)

respectively, with the same trends observed for the one-step colloids though the peaks are broader and the backgrounds are higher over wavelength 450 nm. Hence, the redispersed sample, as could be expected, shows a higher aggregation with respect to original samples. Also the ζ -potential values reported in the inset of figure 3 show the same trend observed for the one-step colloids, even if the redispersed samples are characterized by significant higher values, as expected considering the reduced ionic strength of the suspensions. Anyway, the DLS measurements show that the redispersion process leads to bigger aggregates. Also in this case all the samples showed to be stable for several days since preparation, as predictable by the high absolute values of ζ -potential.

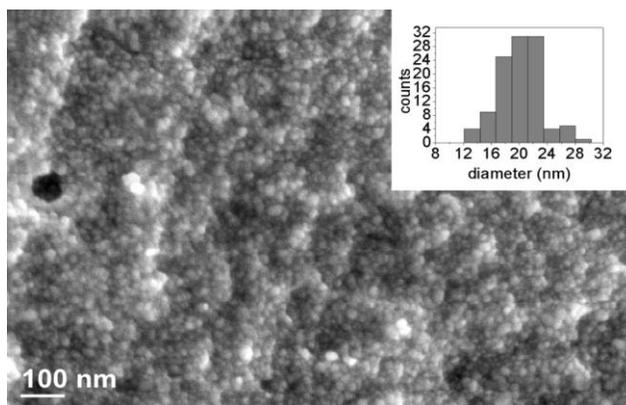


Figure 2: SEM micrograph of nanopowder (3).

Therefore, four silver colloids, purified from undesirable chemical species, were obtained with a controlled aggregation degree just acting on the chain length of the capping agent and thus avoiding the presence of ionic species, that could influence the physical properties of the colloids.

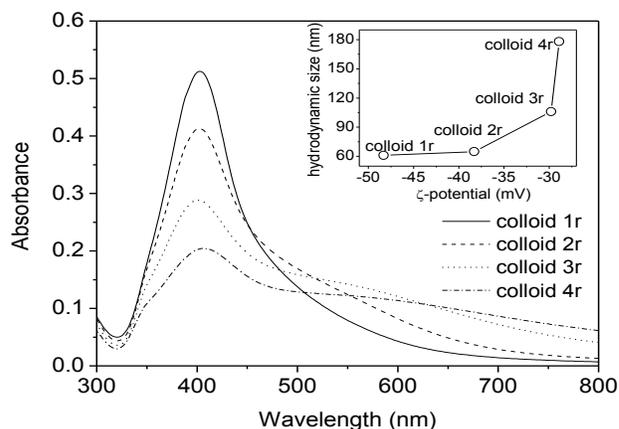


Figure 3: UV-Vis spectra of re-dispersed colloids. The inset shows the DLS hydrodynamic size as function of ζ -potential for each sample.

The suspensions were investigated to evaluate the effect of nanoparticle aggregation on the thermal diffusivity of water based Ag colloids. A concentration of 4 vol% was

chosen for this study since in our experimental setup concentrations lower than 1 vol% did not lead to any appreciable thermal diffusivity improvement with respect to pure water. Figure 4 shows the enhancement ratio of thermal diffusivity of the samples with respect to deionized water in the temperature range 25-50 °C. The reported results are the average of three measurements for each sample. As can be noted, around room temperature the nanoparticle aggregation leads to an increase of thermal diffusivity from 7.4 % for redispersed colloid (1r) to 10 % for colloid (4r). The thermal diffusivity enhancement seems affected by ζ -potential, showing close values for samples (1r) and (2r) and similar and higher values for fluids (3r) and (4r). The inset of figure 4 also shows the average thermal diffusivity enhancement over the investigated temperature range as a function of ζ -potential, showing a monotonous dependence. In agreement with the benchmark study by Buongiorno et al. [17], in the present work no anomalous enhancements of thermal diffusivity were detected beyond the Maxwell model, which provides an evaluation of 12 % enhancement for a 4 vol% Ag colloid in water. The lower values compared to the Maxwell model that have been reported in figure 4 can be attributed to the presence of the surfactant polymer wrapped around the nanoparticles leading to thermal contact resistance, which is not taken into account by the Maxwell model.

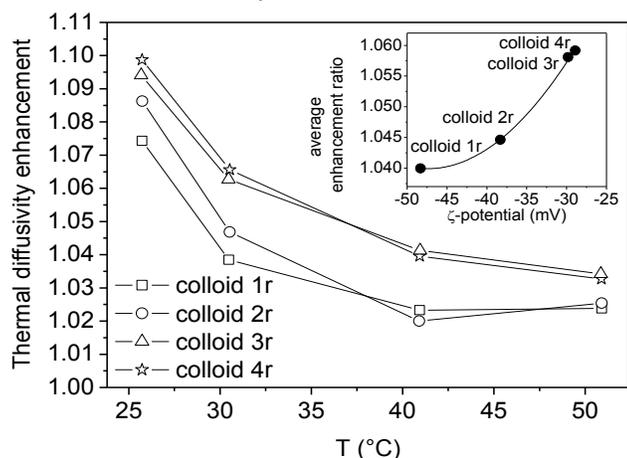


Figure 4: Thermal diffusivity enhancement ratios of redispersed colloids with respect to de-ionized water. The inset shows the average enhancement ratio vs. ζ -potential.

Other authors [13, 14] have also predicted this effect by considering the possible fractal morphology of aggregates arranging in connected matrix through the fluid. In this model heat transferred more efficiently through the fluid by this three dimensional aggregates structure.

The thermal diffusivity enhancement observed at room temperature progressively decreases for all samples to 2.5 % for samples (a) and (b), and 3.4 % for sample (c) and (d) at 50 °C. The thermal diffusivity reduction with temperature could be due to the fact that aggregates are partially dissolved by increasing temperature.

4 CONCLUSIONS

Ag colloids in water at 4 vol% were obtained from an easily redispersible nanopowder obtained on high concentration and yield by fructose reduction of AgNO_3 in water. The precipitation and redispersion processes helped to easily obtain stable, pure and highly concentrated colloids. The ζ -potential and, as a consequence, the aggregation of nanoparticles was boosted and controlled by gradually increasing the average chain length of PVP, which was used as a capping agent. It has been shown that aggregation plays a key role on the thermal diffusivity of Ag colloids and leads to significant enhancements in the temperature range 25-50 °C. This behavior was previously predicted by other authors as the effect of a three dimensional and connected arrangement of aggregates within the fluid.

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