

FACILE PREPARATION OF CONCENTRATED SILVER AND COPPER HEAT TRANSFER NANOCOLLOIDS

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ABSTRACT

Concentrated, yet stable silver- and copper-in-water nanocolloids are prepared using a novel method combining formation of a metal ammine complex and use of a strong NaBH₄ reductant. Maximum solid contents of the stable silver and copper nanofluids are 2000 and 5000 ppm (reported as mass fractions), respectively. The metallic nanoparticles are reduced in micellar microreactors, favoring formation of small nanoparticles. Use of stable metal ammine complexes ([Ag(NH₃)₂]⁺ and [Cu(NH₃)₄(H₂O)₂]²⁺) as metal ion sources prevent the formation of sparingly-soluble metal salts and thus, aid the nanocolloid synthesis. Several different stabilizers and combinations of them are tested for nanofluid synthesis: anionic sodium dodecyl sulfate, polymeric polyvinylpyrrolidone, sodium citrate, nonionic sorbitan trioleate and polysorbate 20. The particle sizes and size distributions are studied using dynamic laser scattering and transmission electron microscopy. Stability of the nanofluids is assessed by zeta potential measurements, repetitive particle size measurements and visual observations. The average particle sizes of the silver and copper nanofluids with optimized surfactants are < 20 nm and ~40 nm, respectively, and the fluids with optimized stabilizer compositions are stable over the storing period of a month. Specific heat and thermal conductivities of the fluids are measured using differential scanning calorimetry and modified transient plane source technique (TCi Thermal conductivity analyzer), respectively. In addition, the nanofluid viscosities are measured in order to assess the usability of the nanofluids in convective heat transfer. The chemistry of stabilizers is found to have a significant impact on the viscosity of nanofluids. Commonly used polymeric polyvinylpyrrolidone stabilizer produces viscous fluids, whereas the viscosities of the fluids stabilized with small size surfactants are close to that of water.

INTRODUCTION

Heat transfer by conventional heat transfer fluids (HTFs) can be enhanced by dispersing small amount of highly conductive metal or metal oxide particles into the fluids. However, micro- or millimeter size particles mixed in HTFs cause many practical problems due to settling of solid-liquid mixtures, such as clogging, erosion of device surfaces and severe pressure losses.

“Nanofluids” are solid-liquid mixtures, in which typically nanoparticles of 1-100 nm in size are dispersed in HTFs. Nanofluids are less prone to sedimentation making them interesting for heat transfer applications. Indeed, thermal properties and heat transfer of nanofluids have been intensively studied during the last decade. [1-12] Metallic nanofluids are particularly interesting for heat transfer due to the intrinsically high thermal conductivity of metals. [1,2,13,14]

Many studies show over 10 % increase in thermal conductivity for 0,02-0,4 w-% metal nanofluids as compared to that of the base fluid [1,2,13], whereas Eastman *et al.* [14] reported thermal conductivity of well-dispersed 0.5 vol-% Cu-ethylene glycol nanofluid being even ~60% higher than that of water.

A few experimental studies concern also the convective heat transfer of metallic nanofluids [1-10]. However, majority of these studies use commercial samples (typically metallic powders that are self-dispersed in HTFs), in which case severe agglomeration is often encountered, greatly increasing pressure losses [5-10]. Optimally, nanofluids should have low viscosity, and the particles should be small and well dispersed [11]. There exists many studies concerning preparation of copper [1,3,14,19] and silver [2-4,15-18] based fluids, but most of the nanofluids are dilute [15-17], or extremely viscous due to use of polymeric stabilizers [2-4,13]. Indeed, there are not many studies concerning preparation of stable, concentrated metallic nanocolloids with small particle size and low viscosity that could be optimal for convective heat transfer applications.

In this study, metallic nanocolloids with small particle size and high concentrations; 2000 ppm of Ag and 5000 ppm of Cu (mass fractions), are prepared using a facile and affordable chemical reduction method. Particle sizes and size distributions, stability, viscosities and thermal properties of the corresponding nanofluids are studied. Impact of stabilizers on nanofluid stability, size and viscosity are studied in detail. The metallic nanocolloids prepared here, with small particle sizes, good stability and thermal conductivity are particularly interesting for working fluids in district heating systems. As heating causes major residential expenses particularly in countries with cold climate, efficient heat transfer fluids have huge importance both in economic and ecological aspects. The fluids could also be interesting for antibacterial applications [16-18].

MATERIALS AND METHODS

Materials

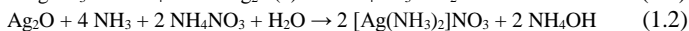
AgNO₃ and anhydrous CuSO₄ were supplied by VWR Chemicals. Ammonia (28-30%, aq) was purchased from Merck. Sodium citrate was prepared by neutralizing citric acid using ~5 wt-% NaOH (aq) made of deionized water and NaOH pellets (both chemicals supplied by Sigma-Aldrich.) Anionic sodium dodecyl sulfate (SDS) was purchased from Merck. Nonionic surfactants Span85 with hydrophilic-lipophilic balance (HLB) of 1.8 and Tween20 (HLB 16.7) were purchased from Merck and Applichem, respectively. Polymeric polyvinylpyrrolidone (PVP) capping agent (MW = 1 300 kg/mol) was supplied by Acros Organics. NaBH₄ (Merck) was used as reductant in all tests.

Methods

Silver and copper nanocolloids were prepared using metal ammine complexes as the metal ion source material and strong NaBH₄ as the reductant. The metal ions were reduced in micellar microreactors, favoring formation of small nanoparticles and preventing *in-situ* agglomeration of particles formed. The reagent amounts used are presented in Table 1. The total sample mass was 200 g.

Preparation of silver nanocolloids

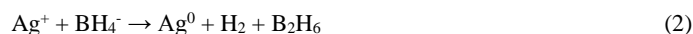
Stable silver nanocolloids were prepared by modified Tollen's method, in which Tollen's reagent, [Ag(NH₃)₂]⁺ is used as source material. [15-18] Tollen's reagent was prepared by adding ammonia to AgNO₃ (aq) (10 g H₂O) until the first formed brown Ag₂O (s) turned to a transparent ammine complex. Reaction equations of salt precipitation and complex formation upon NH₃ addition are presented below:



After complex formation, stabilizer(aq) (20 g H₂O) was added to the complex solution. If turbidity was observed due to stabilizer addition, a few drops of NH₃(aq) were added until the solution cleared. A few different stabilizers were tested for Ag nanofluid preparation: anionic SDS, mixture of SDS and co-reductant/stabilizer sodium citrate, mixture of non-ionic surfactants Span85 and Tween20 with HLB 12.5 (optimal for stabilization of O/W emulsions), Span85 and Tween20 with HLB 12.5 (optimal for stabilization of O/W emulsions), and PVP, a widely used polymeric capping agent in preparation of metal nanofluids [2-4,13,19]. Surfactant/Ag⁺ molar ratios were ½ and ¼ for ionic and non-ionic surfactants, respectively. The surfactant concentrations were kept as low as possible in order to keep the fluid viscosity low.

However, the surfactant concentration was chosen to be higher than the critical micelle concentration. The metal cations gather close to polar micelles and thus, the reduced metal nanoparticles are quickly stabilized by the surfactants. If only PVP was used for stabilization of metallic nanofluids (samples Ag_4 and Cu_4, Table 1), the molar ratio of repetitive vinylpyrrolidone unit (VP unit)/Ag⁺ was 2/1.

Contrary to the conventional Tollen's method, a strong NaBH₄ reductant was used instead of a weak aldehyde or α -hydroxy ketone reductant, such as D-glucose [15-18], D-maltose [16,17] or fructose [16]. The reduction reaction is given by:



The metal ions were reduced to metallic nanoparticles by adding the silver solution slowly (~ 1 ml/min) to NaBH₄(aq) placed in ~10 °C water bath. Excess amount of NaBH₄ was used in order to ensure complete reduction (Table 1). The solution was mixed vigorously during the reduction using a magnetic stirrer. After the addition of the silver solution, mixing was continued for ~15 min. The solution turned immediately to bright yellow or reddish orange upon Ag⁺(aq) addition, indicating formation of Ag nanoparticles. The colour of the 0.2 w-% product was dark ginger or reddish brown.

Preparation of copper nanocolloids

Similarly to silver nanofluid preparation, copper ammine complex was first formed by addition of ammonia to CuSO₄(aq) (10 g H₂O). A slightly excess amount of NH₃ was used for preparing the ultramarine coloured [Cu(NH₃)₄(H₂O)₂]²⁺ complex. Therefore, part of the Cu²⁺ ions form a dark blue [Cu(NH₃)₆]²⁺ complex. Anionic SDS was found to form a gel with the Cu²⁺ complex due to formation of an insoluble ion-pair [20]. Therefore, SDS could not be used for preparation of the Cu nanofluid. Sample compositions are presented in Table 1. A few different combinations of non-ionic surfactants were tested for stabilization of Cu colloids: a mixture of Span85 and Tween20 with HLB 12.5 (Cu_1), Span85+Tween20 mixture with sodium citrate (Cu_2) or PVP (Cu_3), or polymeric PVP alone (Cu_4).

Surfactant/Cu²⁺ molar ratios were similar to those in the preparation of Ag nanocolloids. The reduction of [Cu(NH₃)₄(H₂O)₂]²⁺ was completed under N₂ at ~10 °C using an excess amount of NaBH₄. The Cu nanofluids were stored in tightly sealed bottles.

Analysis methods

Particle sizes, particle size distributions and zeta-potentials of the nanofluids were measured with Malvern Zetasizer Nano-ZS

Table 1. Sample compositions of Ag and Cu nanocolloids

Sample name	Metal concentration (ppm)	Surfactant(s)	Surfactant/metal molar ratio	NaBH ₄ concentration (ppm)
Ag_1	2000	SDS	½	700
Ag_2	2000	SDS+citrate	½ SDS +1/5 citrate	700
Ag_3	2000	Span85+Tween20 (HLB 12.5)	¼	700
Ag_4	2000	PVP	2/1 (VP units)	700
Cu_1	5000	Span85+Tween20 (HLB 12.5)	¼	6000
Cu_2	5000	Span85+Tween20(HLB 12.5) / citrate	¼ Span85+Tween20 (HLB 12.5) + 1/5 citrate	6000
Cu_3	5000	Span85+Tween20 (HLB 12.5) / PVP	¼ Span85+Tween20 (HLB 12.5)/ + 1/5 VP units	6000
Cu_4	5000	PVP	2/1 (VP units)	6000

based on dynamic laser scattering (DLS), and Tecnai F-20 transmission electron microscope (TEM) with energy dispersive x-ray (EDS) detector. Copper grids (Quantifoil carbon film, 300 M) were used for TEM imaging.

Stability of the fluids was assessed by zeta-potential measurements, visual observations, and repetitive size distribution measurements.

Viscosities of the fresh metal nanocolloids and stabilizer-water solutions were determined at 20-50 °C with cone and plate-type Brookfield DV3T viscometer connected to a temperature controlled bath. In preliminary tests, the rheology of the fluids was studied using a 50-200 rpm shear rate. The samples behaved as Newtonian fluids, apart from fluids containing polymeric PVP (Ag_4, Cu_3 and Cu_4). The viscosity of these samples was studied in detail by varying the shear rate from 50 to 200 rpm. Viscosities of other samples are reported using a 150 rpm shear rate.

Specific heats of selected nanofluids were determined at 30-50 °C with Netzsch DSC204FI Phoenix differential scanning calorimetry (DSC) using sapphire standard, 5 K/min scanning rate and 30-40 mg samples. Thermal conductivities of the nanofluids were studied at 30 °C using C-Therm Thermal Conductivity Analyzer based on modified transient source plane technique.

RESULTS AND DISCUSSION

Particle size and stability of silver nanocolloids

Particle sizes and size distributions of the Ag nanofluids are shown in Fig. 1 and Table 2. Particle sizes and shapes of selected samples (Ag_1 and Ag_3) were verified with TEM (Fig. 2.)

Table 2. Particle sizes and size distributions of Ag nanocolloids at 25 °C determined with DLS. Abbreviations: Z-avg – Z-average value, PdI – polydispersity index, Mean num. – particle size based on the number distribution, Mean vol. – particle size based on the volume distribution, zeta-potential – zeta-potential value, Z-avg, old – Z-average value of a one month old sample

Sample	Z-avg (nm)	PdI	Mean num. (nm)	Mean vol. (nm)	zeta-potential (mV)	Z-avg, old (nm)
Ag_1	26.6	0.27	13.4	19.4	-69,4	32.4
Ag_2	26.6	0.43	2.2	2.8	-80,6	36.2
Ag_3	35	0.45	1.3	1.6	-28,2	31
Ag_4	89	0.57	9.8	19.4	-4,0	163

Particle sizes of Ag samples were less than 20 nm (sizes based on number and volume distributions.) Reduction of Ag_1-Ag_3 takes place in micellar 'microreactors' rapidly due to strong NaBH₄ surfactant, favoring formation of small particles. Volume and particle number based distributions of silver nanofluids are alike (Fig 1.) The particle size was smallest, only ~1.5 nm, for the Ag_3 nanofluid.

Particle sizes of Ag_1 and Ag_3 were verified with TEM. The average TEM particle sizes of Ag_1 and Ag_3 were 5.5 and 1.6 nm, respectively (calculated manually from 150 particles). The TEM particle sizes of Ag_1 and Ag_3 were between 1-20.6 nm and 0.5-8.4 nm, respectively. The TEM particle size of Ag_3 is really close to that determined with DLS, whereas the DLS particle size of Ag_1 is larger. DLS calculates the hydrodynamic

diameter, whereas the bare nanoparticle diameter is determined with TEM. Therefore, slightly smaller particle size can be expected from TEM imaging. The particles were verified as Ag using EDX.

The Z-average (intensity based harmonic mean) and polydispersity index of Ag_4 were substantially larger than those of Ag_1-Ag-3, indicating a wider particle size distribution and existence of larger particles. Only polymeric PVP was used in the stabilization of Ag_4. In contrast to the surfactants used for Ag_1-Ag_3, polymeric PVP does not form separate micelles, but its stabilization is based on steric hindrance and coordinative interactions with Ag⁺ and the metal nanoparticles formed. Particle growth may be less restricted in the Ag_4 fluid, in which separate micelles are not formed.

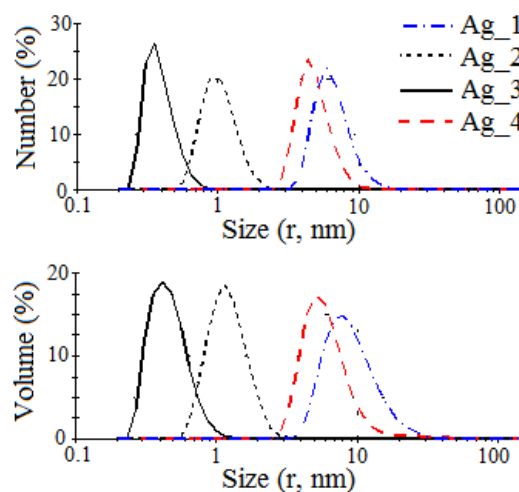


Fig. 1. Top: Number particle size distributions, reported as particle radii. Bottom: Volume particle size distributions of fresh Ag nanofluids. Sample compositions are presented in Table 1.

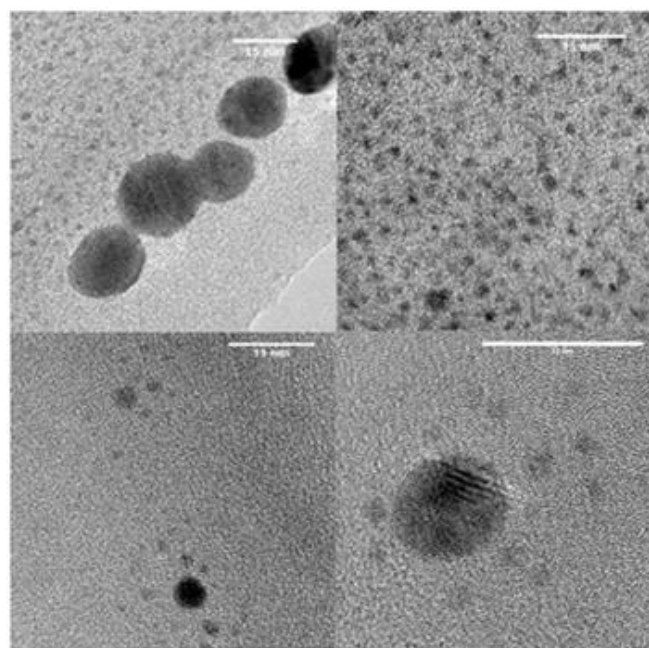


Fig 2. Top: TEM images of Ag_1. Bottom: Ag_3 nanofluids. All scale bars are 15 nm.

Stability of the nanocolloids was studied with repetitive DLS measurements and zeta-potential measurements (Table 2.) Appearance and particle size of the Ag nanofluids stabilized with surfactants (Ag_1-Ag_3) did not change significantly upon a one month storage period. Also the zeta-potentials of Ag_1-Ag_3 were over or close to 30 mV and thus the fluids can be considered to be electrostatically stable enough to prevent phase separation.

Only PVP stabilized Ag_4 was unstable. Indeed, after a few days of storage, a grey-brown precipitate was formed, indicating formation of Ag₂O. Also the zeta-potential value of Ag_4 is remarkably low, indicating poor stability. Generally, PVP is considered to be a good stabilizer for metallic nanofluids. However, in earlier studies, the metal concentrations were typically smaller [15-17], in which case the steric stabilization of PVP may be more efficient. In addition, the PVP used herein has quite a high molar mass. Smaller polymer chains with higher mobility may be preferable in nanofluid stabilization.

Particle size and stability of copper nanocolloids

The copper nanoparticles are susceptible to oxidation, particularly in an aqueous solution. In order to prevent oxidation, the Cu nanofluid synthesis was carried out in N₂ atmosphere and samples were stored in tightly sealed bottles. Particle sizes and size distributions of Cu nanocolloids are presented in Fig. 3 and Table 3.

Table 3. Particle sizes and size distributions of fresh Cu nanocolloids at 25 °C. Abbreviations: PdI – polydispersity index, Mean number – particle size based on number distribution, Mean volume – particle size based on volume distribution

Sample	Z-avg (nm)	PdI (nm)	Mean numb. (nm)	Mean vol. (nm)	Z-avg, old (nm)
Cu_1	129	0.49	32.8	238	145
Cu_2	104	0.49	27.8	241	118
Cu_3	65.4	0.53	12	42.2	70.4
Cu_4	330	0.49	137	909	-

Particle sizes of Cu nanofluids were notably larger than those of Ag nanocolloids. Indeed, only the particle size of Cu_3 was ~10-40 nm (sizes based on number and volume distributions), although the PdI and Z-average value were relatively high also for this fluid. One factor affecting the particle size is the higher concentration of Cu fluids.

Contrary to Ag nanofluids, the particle number and volume based distributions differ from each other, particularly for Cu_1, Cu_2 and Cu_4. In the volume based particle radii distributions of Cu_1 and Cu_2, a shoulder >100 nm can be observed that is not visible in the particle number based distributions. The particle size distributions of Cu_1 and Cu_2 are close to each other, indicating only minor changes in the Cu formation due to addition of sodium citrate co-stabilizer/-reductant. The greatest difference in the number and volume based distributions can be observed for Cu_4 stabilized with PVP only, for which the volume based particle size is extremely large: ~0.9 μm. The Cu_4 sample was unstable similar to Ag_4; sedimentation was observed in less than an hour of storage at room temperature.

Zeta-potential of Cu nanofluids could not be measured due to oxidation of nanoparticles in the vicinity of the anode. However, the nanofluid stability was assessed by repetitive DLS

measurements (Table 3) after one month storing period. The particle sizes of all nanofluids had increased. The most profound change was observed in Cu_4, for which particle size could not be determined at all due to formation of extremely large agglomerates. The most stable Cu_3 fluid, with also the smallest initial particle size, showed only a slight increase in the particle size. Due to the instability of the Cu samples, the nanofluids were not imaged with TEM.

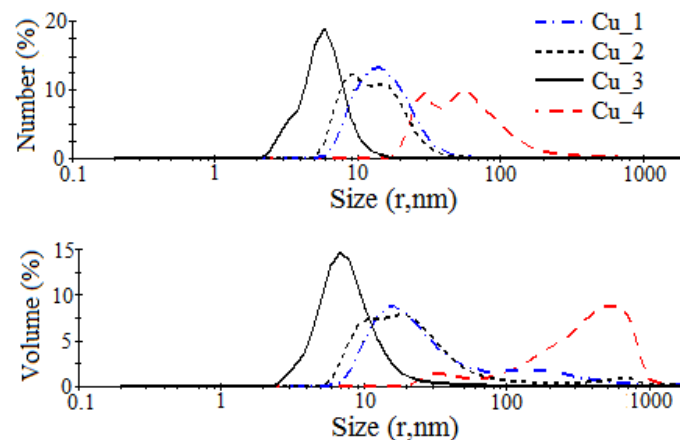


Fig. 3. Top: Number particle size distributions, reported as particle radii. Bottom: Volume particle size distributions of fresh Cu nanofluids. Sample compositions are presented in Table 1.

Viscosity

The viscosities of metal nanofluids were studied in detail since fluid viscosity is an important property in convective heat transfer applications. The relative viscosities of Ag_1-Ag_3, Cu_1 and Cu_2 colloids (filled markers) and surfactant-water solutions (empty markers) used in the preparation of the above-mentioned nanofluids are presented in Fig. 4. The relative viscosity is the ratio of the fluid viscosity to the viscosity of water.

The relative viscosities of nanofluids and corresponding surfactant(aq) solutions do not substantially differ from each other. The viscosities of Cu samples and corresponding surfactant(aq) (Fig. 4B) are naturally higher than those of Ag samples (Fig. 4A) due to the higher solid concentration of Cu fluids. Relative viscosity of Ag samples remains reasonably constant in the whole temperature range, whereas the relative viscosity of Cu fluids increase with temperature.

Anionic SDS ($M = 288$ g/mol) increases the viscosity less than the non-ionic Span85+Tween20 mixtures ($M_{avg} = 1165$ g/mol), probably due to the smaller size of the ionic SDS. Small amount of sodium citrate in SDS(aq) does not impact on the viscosity, whereas a small increase in the viscosity can be observed when citrate is added to the Span85+Tween20(aq).

Altogether, the viscosities of nanofluids with similar surfactant concentrations (Ag or Cu samples) do not greatly differ from each other (maximum difference is about 8%.) The metal nanoparticles studied do not cause additional increase to the relative viscosities of nanofluids. The increase seems to depend solely on the surfactants used here. Indeed, relative viscosities of the nanofluids and the corresponding surfactant-water solutions are remarkably close to each other; the maximum

average difference in the viscosities is only 2%. (The viscosity values are averaged over the measured temperature range of 20-50 °C.)

As expected, the relative viscosities of PVP samples (Fig. 5.) are substantially higher than those of the surfactant stabilized samples (Fig. 4.). Hydrophilic, large PVP ($M_w = 1\,300\text{ kg/mol}$) dissolves well in water and the dispersed polymer chains substantially increase the fluid viscosity. The viscosities of PVP samples increase rapidly with the PVP concentration. Again, the nanoparticles do not cause an additional viscosity increase, but the fluid viscosities depend only on the chemistry and amount of the stabilizers.

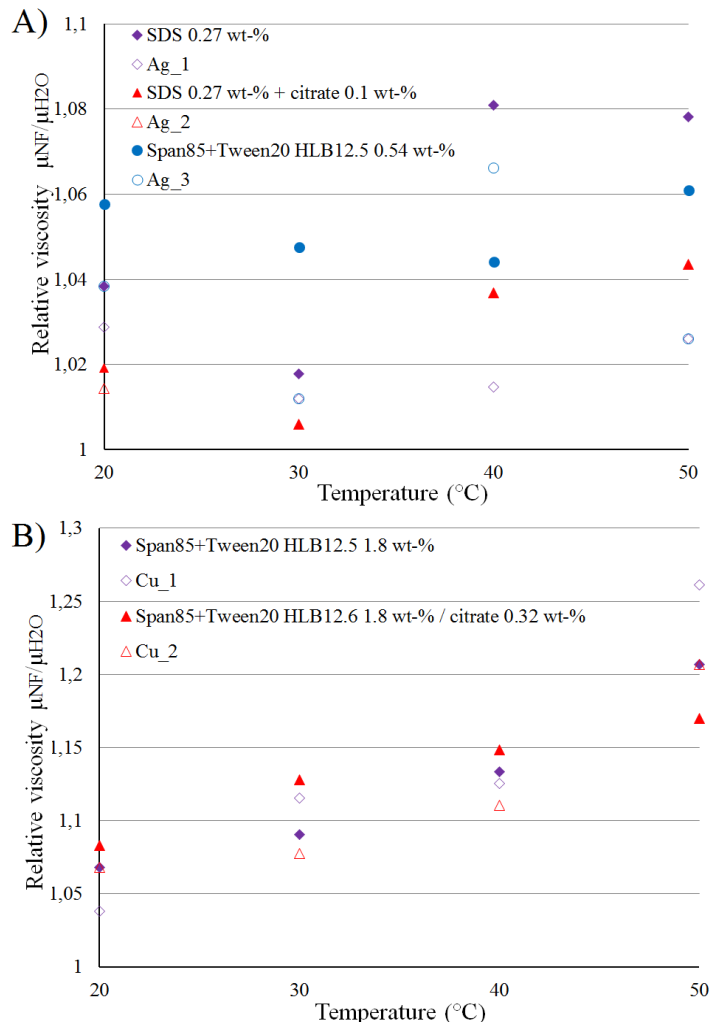


Fig 4. A) Viscosities of Ag_1-Ag_3 nanocolloids (empty markers) and corresponding surfactant-water solutions (filled markers), B) Viscosities of Cu_1 and Cu_2 nanocolloids (empty markers) and corresponding surfactant-water solutions (filled markers). Viscosity of water is presented as solid line for reference. The fluids are measured with 150 rpm shear rate.

The viscosities of Cu_3 and the corresponding stabilizer(aq) are substantially higher than that of Cu_2 and the corresponding surfactant(aq) (Fig 4B.). The only difference between the stabilizer compositions of these nanofluids is the additional 0.14

w-% PVP in Cu_3. Therefore, polymeric PVP heavily dominates the viscosity of the studied nanofluids.

The viscosities of PVP samples are significantly higher than that of water, making practical use of polymer stabilized nanofluids questionable for convective heat transfer. Ag and Cu nanofluids stabilized with smaller surfactants increased the viscosity of water on average by ~3% and ~12.5%, respectively, whereas the viscosities of Cu_3 (0.18 wt-% PVP), Ag_4 (0.4 wt-% PVP) and Cu_4 (1.2 wt-% PVP) were 39%, 69% and 395% higher than that of water, respectively. Therefore, surfactant stabilized nanofluids are considerably more promising for heat transfer applications.

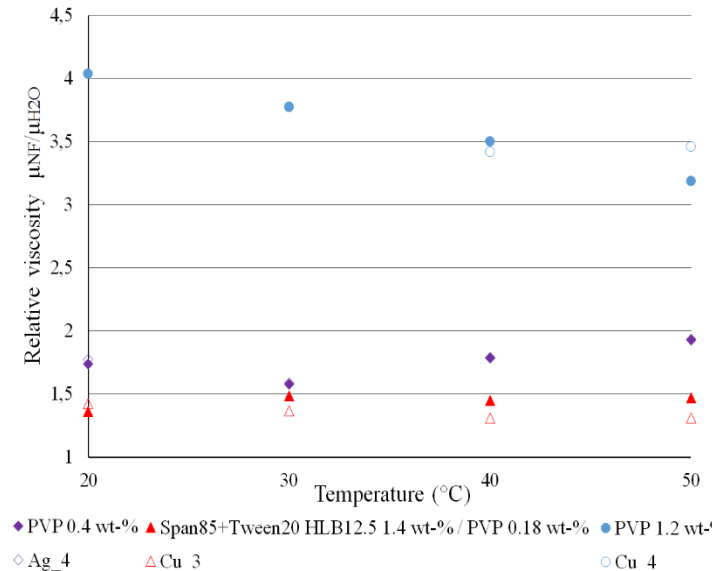


Fig 5. Viscosities of nanofluids stabilized with PVP (empty markers) and corresponding PVP-water solutions (filled markers). Viscosity of water is presented as solid line for reference. The values are reported as averages of viscosities with a 50-150 rpm shear rate.

The shear rate did not influence the viscosities of the fluids without PVP (Ag_1-Ag_3, Cu_1 and Cu_2.) To the contrary, the shear rate did affect the viscosities of the PVP samples, as shown in Table 4. Therefore, the PVP samples can be considered to be non-Newtonian fluids [21]. The viscosities of the PVP samples were measured at 20-50 °C with shear rates varying between 50-200 rpm.

Table 4. The decrease in viscosity of PVP samples due to increase in shear rate is reported as the ratio of fluid viscosity with 200 rpm shear rate to the viscosity with 50 rpm. The viscosities of nanofluids μ_{NF} and corresponding stabilizer(aq) ($\mu_{stabilizer(aq)}$) are reported at 30 °C.

Sample	μ_{NF}	$\mu_{stabilizer(aq)}$
	200 rpm/50 rpm	200 rpm/50 rpm
Ag_4	0.977	0.971
Cu_3	0.964	0.928
Cu_4	0.818	0.810

The viscosities of all the PVP samples decreased as the shear rate increased from 50 to 200 rpm, indicating shear thinning behaviour. [21] Shear thinning increases with the PVP concentration. The large polymeric PVP molecules may entangle

together at low shear rates. As the shear rate increases, the polymers disentangle and the fluid viscosity decreases. The shear thinning is more profound for stabilizer(aq) than for nanofluids. This unexpected behaviour may be due to more compact packing of PVP in the vicinity of metal nanoparticles: flexible polymer chains fold around the particles, resulting in decrease in the viscosity. Without the nanoparticles, the hydrophilic PVP molecules maintain more straight-chain configurations. Shear thinning is more significant at lower temperatures, when the kinetic mobility of the molecules is slower.

Thermal properties

Table 5 presents the thermal properties of stable nanofluids.

Table 5. Specific heats and thermal conductivities of fresh nanocolloids at 30-50 °C and 30 °C, respectively. Abbreviations: c_p – specific heat, λ_{NF} – thermal conductivity of nanofluids, λ_{H_2O} – thermal conductivity of water

Sample	c_p (J/gK)	λ_{NF} (W/mK)	$\lambda_{NF}/\lambda_{H_2O}$ (W/mK)
Ag_1	4.05	1.36±0.29	2.20
Ag_2	4.09	1.34±0.14	2.17
Ag_3	4.11	1.85±0.37	2.99
Cu_1	3.96	0.96±0.32	1.55
Cu_2	3.92	0.97±0.35	1.57
Cu_3	3.99	1.06±0.26	1.72

The specific heats are reported as average values of three heating and cooling cycles in a temperature range of 30-50 °C. The specific heats of Ag and Cu nanocolloids are 2-3% and 4-5 % lower than that of water (4.18 J/gK at 30-50 °C), respectively. The lower c_p of Cu fluids is due to a higher concentration of metal particles and stabilizers.

Thermal conductivities of both Ag and Cu fluids are notably higher than that of water (0.618 W/mK at 30 °C.) Similar enhancements have been reported by other research groups [1,2,13,14]. The mechanism behind the thermal conductivity of metallic nanofluids is still under debate, although some theories have been suggested [22]. The anomalous conductivities of the nanofluids should be treated with caution. The measured λ varied notably between the subsequent measurements, particularly for instable Cu fluids, causing large measurement uncertainties. In addition, the measurement accuracy is somewhat weakened due to the limited calibration range (0-0.6 W/mK) of the device.

However, some general trends may be deduced from the results. Conductivities of Ag fluids were substantially larger than those of Cu samples, despite the higher metal volume fraction of Cu fluids. Within the silver fluids, Ag_3 had the highest λ . One explanation could be the smaller size of the Ag particles, particularly those of Ag_3. As the particle size decreases, the number of particles increases rapidly. The nanoparticles are in a close distance, particularly for fluids with a high volume fraction (φ) and small particle size. For instance, for Ag_3 type fluid with $\varphi=0.02\%$ and radius, $r= \sim 0.8$ nm the surface-to-surface particle distance, given by $d_s = 0.893r\varphi^{-1/3}$ [23], is only ~ 12 nm. Within these short-range distances, formation of local, loosely packed particle clusters is possible. Heat may be efficiently conducted inside such assemblies. However, these loose clusters do not settle out from the fluid since agglomeration does not happen due to strong repulsion of surfactant covered particles at very short particle distances. Another effect that may enhance λ

is liquid layering into a more ordered structure in the vicinity of crystalline nanoparticles. This ordering occurs in the range of ~ 1 nm within the surfaces, being already significant at these small interparticle distances. [22]

CONCLUSIONS

Concentrated metal nanocolloids (Ag: 2000 ppm, Cu: 5000 ppm) with small particle sizes were prepared in a robust method utilizing Tollen's reagent and reduction of metal ions in micellar microreactors by strong NaBH_4 . Different stabilizers were tested for nanofluid preparation; ionic SDS and sodium citrate, non-ionic sorbitan trioleate (Span85) and polysorbate 20 (Tween20), and polymeric PVP and mixtures of these. It has to be acknowledged that albeit preparation of metal nanofluids have been reported in several publications before [1-4,14-19], this method differs from the existing ones by combination of the strong reductant and utilization of the Tollen's reagents. Furthermore, the recipe is optimized in order to obtain nanofluids optimal for heat transfer applications, i.e. fluids with small particle sizes, high concentrations but moderate viscosities.

The particle sizes of surfactant stabilized Ag fluids (without PVP) were <20 nm. The smallest particle size, ~ 1.5 nm, was obtained for Ag fluid using Span85+Tween20 non-ionic surfactant mixture (HLB 12.5.) Surfactant stabilized Ag fluids were stable over a month. The viscosities of surfactant stabilized Ag fluids were slightly higher than that of water (relative viscosity 1.02-1.04.) Therefore, only minor additional pressure losses can be expected in the convective heat transfer of these fluids.

The particle sizes of Cu fluids were substantially larger, and the size distributions were also wider as compared to those of Ag fluids. The stability of aqueous Cu fluids is questionable due to the strong oxidation tendency of copper. Indeed, the particle size of most of the Cu fluids was notably increased during a one month storage. Non-ionic Span85+Tween20 (HLB 12.5) surfactant mixture together with small amount of PVP produced the most stable Cu fluid.

Silver nanoparticles increased the thermal conductivity (λ) of water by factor of two, making them highly promising for heat transfer applications. Thermal conductivities of Cu fluids were approximately one and a half times larger than that of water. Based on these preliminary tests, the smaller particle size and better nanofluid stability seem to increase λ . However, the results should be treated with caution due to the high measurement errors ($\pm 10-36$ %.) Thermal conductivities of metal nanofluids should be studied more detail in the future.

Polymeric PVP alone did not provide enough stabilization for either Ag or Cu nanofluids. Indeed, both Ag and Cu fluid samples stabilized with PVP only were instable, despite that PVP has been used frequently for stabilization of metal nanofluids in earlier studies [2-4,13,19]. The high metal concentration and high molar mass of the PVP ($M_w = 1300$ kg/mol) may influence the stability of the samples here.

In addition to poor stability of the PVP samples, polymer stabilized nanofluids had extremely high viscosities. The viscosities of the PVP fluids were 1.5-4 times higher than that of water, being problematic considering pressure losses in forced

convective heat transfer. Also, shear thinning behaviour of polymeric stabilizers may cause problems in convective heat transfer applications.

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REFERENCES

1. Khoshvaght-Aliabadi, M., Hormozi, F., and Zamzamin, A., Experimental study of Cu-water nanofluid forced convective flow inside a louvered channel, *Heat Mass Transfer*, Vol- 51, 2015, pp. 423-432.
2. MingZheng, Z., GuoDong, X., Lei, C., Jian, L., and LiJun, Z., Analysis of flow and heat transfer characteristics of micro-pin fin heat sink using silver nanofluids, *Science China Technology Series*, Vol. 55, No. 1, 2012, pp. 155-162
3. Dzido, G., Chmiel- Kurowska, K., Gierczyki, A., and Jarzebski, A. B., Convective heat transfer to Ag- and Cu- ethylene glycol nanofluids in the minichannel flow, *NSTI-Nanotech*, Vol. 1, 2008, pp. 778-781
4. Madhesh, D., and Klaiselvam, S., Experimental study on the heat transfer and flow properties of Ag-ethylene glycol nanofluid as a coolant, *Heat Mass transfer*, Vol. 50, 2014, pp. 1597-1607
5. Godson, L., Raja, B., Mohan Lan, D., and Wongwises, S., Convective heat transfer characteristics of silver-water nanofluid under laminar and turbulent flow conditions, *Journal of Thermal Science and Engineering Applications*, Vol. 4, 2012, 031001-1-8
6. Chehade, A. A., Gualous, H. L., Le Masson, S., Fardoun, F., and Besq, A., Boiling local heat transfer enhancement in minichannels using nanofluids, *Nanoscale Research Letters*, Vol-. 8:130, 2013, pp. 1-20
7. Polvongsri, S., and Kiatsiriroat, T., Performance analysis of flate plate solar collector having silver nanofluid as a working fluid, *Heat Transfer Engineering*, Vol. 35:13, 2014, pp. 1183-1191
8. Qiang, L., and Yimin, X., Convective heat transfer and flow characteristics of Cu-water nanofluid, *Science in China (Series E)*, Vol. 45, 2002, pp. 408-416
9. Heris, S. Z., Etemad, S. Gh., and Esfahany, M. N., Convective heat transfer of Cu/water nanofluid flowing through a circular tube, *Experimental Heat Transfer*, Vol. 22, 2009, pp. 217-227
10. Li, Q., Xuan, Y., and Yu, F., Eperimental investigation of submerged single jet impingement using Cu-water nanofluid, *Applied Thermal Engineering*, Vol. 36, 2012, pp. 426-433
11. Meriläinen, A., Seppälä, A., Saari, K., Seitsonen, J., Ruokolainen, J., Puisto, S., Rostedt, N., and Ala-Nissila, T., Influence of particle size and shape on turbulent heat transfer characteristics and pressure losses in water-based nanofluids, *International Journal of Heat and Mass Transfer*, Vol. 61, 2013 439-448
12. Kakac, S., and Pramuanjaroenkij, A., Review on convective heat transfer enhancement with nanofluids, *International Journal of Heat and Mass Transfer*, Vol. 52, 2009, pp. 3187-3196
13. Salehi, J. M., Heyhat, M. M., and Rajabpour, A., Enhancement of thermal conductivity of silver nanofluid synthesized by a one-step method with the effect of polyvinylpyrrolidone on thermal behavior, *Applied Physics Letters*, Vol. 102, 2013, pp. 231907-1-3
14. Eastman, J. A., Choi, S. U. S., Li, W. Yu., and Thompson, L. J., Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles, *Applied Physics Letters*, Vol. 78, 2001, pp. 718-720
15. Soukupová, J., Kvitek, L., Panáček, A., Nevečná, T., Zboril, R., Comprehensive study on surfactant role on silver nanoparticles (NPs) prepared via modified Tollens process, *Materials Chemistry and Physics*, Vol. 111, 2008, pp. 77-81.
16. Kvitek, L., Pucek, R., Panáček, A., Novotný, R., Hrbác, J., and Zboril, R., The influence of complexing agent concentration on particle size in the process of SERS active silver colloid synthesis, *Journal of Materials Chemistry*, Vol. 15, 2005, pp. 1099-1105
17. Panáček, A., Kvitek, L., Pucek, R., Kolár, M., Vecerova, R., Pizúrová, N., Sharma, V. K., Nevečná, T., and Zboril, R., Silver colloid nanoparticles: synthesis, characterization, and their antimicrobial activity, *The Journal of Physical Chemistry B*, Vol. 110, 2006, pp. 16248-16253.
18. Le, A.-T., Pharm, H., Dinh Tam, P., Quang Huy, T., Dac Cam, P., and Kudrinskiy, A. A., Green synthesis of finely-dispersed highly bactericidal silver nanoparticles via modified Tollens technique, *Current Applied Physics*, Vol. 10, 2010, pp. 910-916.
19. Park, B. K., Jeong, S., Kim, D., Moon, J., Lin, S., Kim, J. S., Synthesis and size control of monodisperse copper nanoparticles by polyol method, *Journal of Colloid and Interface Science*, Vol. 311, 2008, pp. 417-424.
20. Nakai, T., Murakami, Y., Sasaki, Y., Fujiwara, I., and Tagashira, S., Ion-pair formation of copper(II)-ammine complex with an anionic surfactant and the recovery of copper(II) from ammonia medium by the surfactant-gel extraction method, *Analytical Sciences*, Vol. 20(1), 2004, pp. 235-237.
21. Phuoc, T. X., Massoudi, M., Experimental observations of the effects of shear rates and particle concentration on the viscosity of Fe₂O₃-deionized water nanofluids, *International Journal of Thermal Sciences*, Vol. 48(7) 1294-1301.
22. Keblinski, P., Phillpot, S. R., Choi, S. U. S., and Eastman, J. A., Mechanisms of heat flow in suspensions of nano-sized particles (nanofluids), *International Journal of Heat and Mass Transfer*, Vol. 45, 2002, pp. 855-863.
23. Russel, W. B., Saville, D. A., Schowalter, W. R., Colloidal dispersions, Cambridge University Press, Cambridge, UK, 1989.