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## Preparation of metal oxide-water nanofluids by two-step method

### Introduction

Suspensions of solids in fluids are used to improve thermal properties for more than 100 years. In the 19th century *Maxwell* proposed model for thermal conductivity enhancement in suspensions [*Maxwell, 1881*]. However, application of micro- and larger particles is connected with many disadvantages, e.g. high concentrations of solid phase are needed to achieve satisfying enhancement of thermal properties. Moreover, they are not stable and require continuous recirculation. Additionally, due to high solid content they cause abrasion of installation parts.

These problems may be reduced by application of nanofluids. Nanofluids are the suspensions of nanoparticles (i.e. particles smaller than 100 nm) in base fluids. It is a rather new idea proposed in 1990's, connected with development of nanotechnology [*Choi and Eastman, 1995*]. In the case of nanofluids, satisfying improvement of thermal properties is achieved for much smaller particles concentration. Additionally, they are more stable and can be stored without recirculation.

Nanofluids may be prepared either by one-step or two-step method. In the one-step method nanoparticles are synthesized in base fluid mainly by means of chemical methods [*Eastman et al., 2001; Zhu et al., 2004*]. In the case of two-step method nanoparticles are firstly prepared in a form of powders by physical or chemical methods, e.g. grinding, laser ablation, sol-gel processing, etc. and then suspended in base fluid [*Paul et al., 2011*]. This method of production is cheaper, because nanopowders are produced on large scale. However, due to large and active surface area nanoparticles tend to agglomerate. Therefore, in order to prepare a stable nanosuspension sonication as well as addition of stabilizer or *pH* adjustment may be required. There are many methods to determine nanofluid stability. It may be done visually, by sedimentation tests, centrifugation or UV-VIS analysis. Zeta potential analysis may be also performed. Zeta potential is electric potential at slipping plane, the border between bulk fluid and fluid molecules attached to particle. The value of 25 mV divides low- and highly-charged surfaces. It is assumed that the colloids with zeta potential >40 mV possess good and >60 mV excellent stability [*Yu and Xie, 2012*]. The aim of the study is the investigation of such parameters like sonication time, stabilizer type and suspension *pH* on stability of copper(II) oxide and aluminum(III) oxide water based nanofluids. For the most stable nanofluids particle size distribution and zeta potential analyses were performed.

### Experimental

#### Materials

Nanopowders used for investigation (Tab. 1) were obtained from *Nanostructured & Amorphous Materials, Inc.* Nanopowders were suspended at concentration of 0.5% vol. in water taken from reversed osmosis (*Hydrolab Polska*). The stabilizers used in the experiments were triammonium citrate, diammonium hydrogen citrate, sodium hexametaphosphate (SHMP), sodium dodecyl benzene sulfonate (SDBS), acetic acid and formic acid.

Tab. 1. Properties of nanopowders

	<i>d</i> [nm]	$\rho_{real}$ [g/cm <sup>3</sup> ]
CuO	30–50	6.3–6.49
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	10	3.7

### Procedure

Nanopowders were mixed with water and stabilizers and then sonicated by ultrasonic mixer *Sonix VCX 130* (20 kHz, 130 W) with amplitude of 123  $\mu$ m a set period of time. For selected samples extended preparation procedure was performed. They were prepared for 3 days – between three consecutive sonications nanofluid was mixed for a day. For the best samples PSD (*Malvern Zetasizer Nano S90*) and zeta potential (*Malvern Zetasizer Nano Z*) analyses were performed.

#### CuO nanofluid

In the first part of the experiment, stability of 1% vol. copper(II) oxide in water nanofluids stabilized by triammonium citrate, diammonium hydrogen citrate and sodium hexametaphosphate (SHMP) was investigated. Concentrations of stabilizers were 0.1, 0.2 and 0.3% mas. for citrates and 1, 2 and 3% mas. for SHMP. Suspensions were sonicated for 30 minutes and then left for a day. Then, stability of nanofluids was visually analyzed.

Fig. 1 shows stability of the nanofluids after a day and two days. The most stable suspension was obtained for 1% vol. of SHMP. After a day,

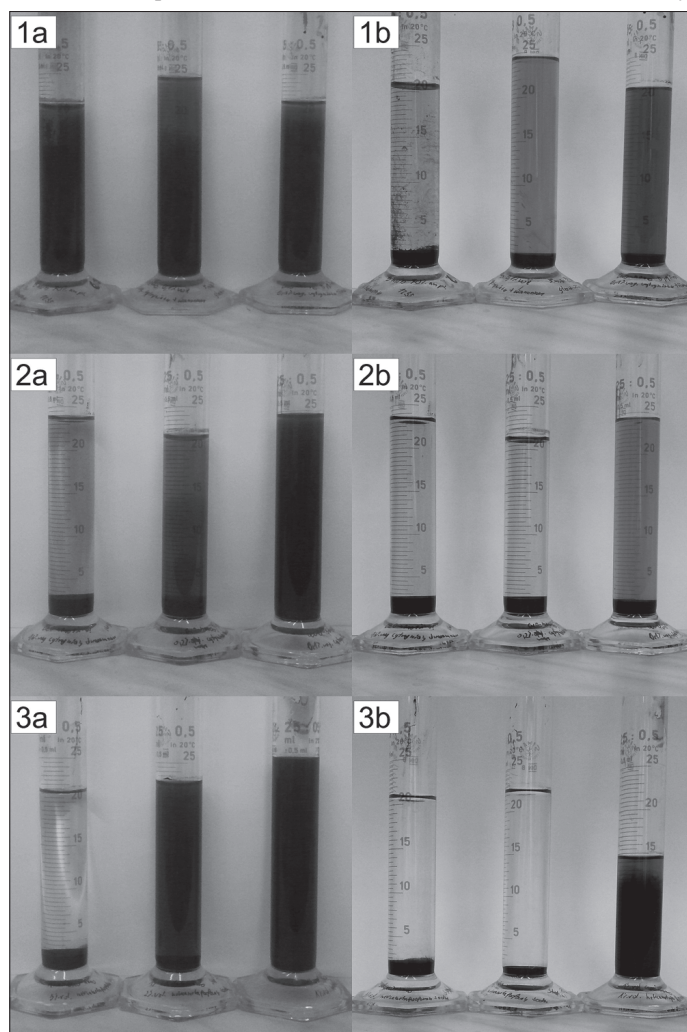


Fig. 1. CuO-water nanofluid after (a) 1 day, (b) 2 days stabilized by (1) triammonium citrate (from left 0.3, 0.2, 0.1% mas.), (2) diammonium hydrogen citrate (from left 0.3, 0.2, 0.1% mas.) and (3) SHMP (from left 3, 2, 1% mas.)

there were no separation zone. After the next day, slight separation zone was noticeable, but the suspension above it was not completely transparent. Brown color characteristic for copper(II) oxide nanoparticles was noticeable. Partial stability of suspensions was also received for 0.1% vol. of tri- and diammonium citrate, but after next day the most of solid phase descended. For 0.1 mas. of triammonium citrate and diammonium hydrogen citrate pale brown color, suggesting a small amount of CuO nanoparticles, was observed above the separation zone. In the case of few samples, i.e. with 0.3% mas. of triammonium citrate, 0.2 and 0.3% mas. of diammonium hydrogen citrate and 3% mas. of SHMP transparent phase above the separation zone had blue color. It is connected with the fact that applied stabilizers altered *pH* in such extend that copper(II) oxide nanoparticles were partially dissolved. Blue color comes from Cu<sup>2+</sup> cations present in water.

For the most stable nanofluid, i.e. stabilized by 1% mas. SHMP, PSD and zeta potential analyses were performed. The results are shown in Fig. 2 and Tab. 2. The PSD by volume shows that almost all particles in suspension were in the range of 100-1000 nm. The maximum was reached for 443 nm. There is also a minor peak with maximum at 70 nm. The reason why a size of the particles is not in the range 30-50 nm is the agglomeration of nanopowder. In order to deagglomerate it the sonication was applied. However, sonication time was not sufficient to break up most of the agglomerates. Power of the ultrasonic mixer may have had also impact on the PSD. Value of zeta potential suggest that nanosuspension stabilized by SHMP should have been very stable. The value of 60 mV is at the border between good and excellent colloid stability. Any instabilities of the suspension might have come from the particle size and not sufficient deagglomeration by sonication.

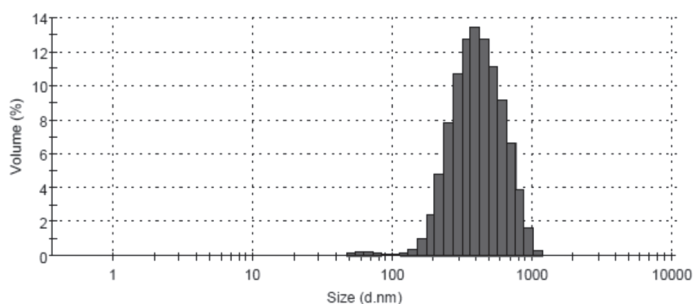


Fig. 2. PSD by volume of CuO-water nanofluid stabilized by 1% mas. SHMP

Tab. 2. Zeta potentials of selected samples

particles	stabilizer	ζ [mV]
CuO (1% vol.)	SHMP (1% mas.)	-60.2
γ-Al <sub>2</sub> O <sub>3</sub> (0.5% vol.)	acetic acid ( <i>pH</i> 3.9)	33.4
γ-Al <sub>2</sub> O <sub>3</sub> (0.5% vol.)	acetic acid ( <i>pH</i> 3.4)	43.5
γ-Al <sub>2</sub> O <sub>3</sub> * (0.5% vol.)	SHMP (0.5% mas.)	-44.6
γ-Al <sub>2</sub> O <sub>3</sub> * (0.5% vol.)	acetic acid ( <i>pH</i> 3.4)	52.4

\* samples prepared for 3 days

**Al<sub>2</sub>O<sub>3</sub> nanofluids**

The second part of experiment was the investigation of stability of 0.5% vol. γ-alumina in water nanofluids. The nanosuspensions were stabilized by sodium dodecyl benzene sulfonate (SDBS), sodium hexametafosfate (SHMP), acetic acid and formic acid. Mixtures of stabilizers were also applied.

In the first stage, sight analysis of samples stability obtained by 30-minutes sonication of mixture containing water, stabilizer and nanoparticles was performed. As the stabilizers SDBS, acetic acid, formic acid and SHMP were used. The SDBS-acetic acid, acetic-formic acid and acetic-formic acid-SHMP mixtures were also applied. Fig. 3 a-g shows stability of γ-alumina-water nanofluids after a day. Generally, neither of the methods gave satisfactory results. In all cases most of the solid phase descended. In the case of SDBS liquid phase was completely transparent for all applied stabilizer concentrations (0.03, 0.075 and 0.1% mas.). No result was also observed for SDBS-acetic acid mixture.

For 0.1% mas. of SDBS and acetic acid adjusted to *pH* 3.4, 4.2, 6 and 7 no suspension was noticed. Better results were obtained for application of acids as stabilizers. For acetic acid turbidity of liquid phase was obtained for *pH* of 3.9. For higher *pH*, i.e. 4.5, 5.5 and 6.7 liquid phase was transparent. When formic acid was applied the turbidity of liquid phase was also get for *pH* below 4, i.e. 3.0, 3.4 and 3.9. For *pH* of 4.9 liquid phase was partially transparent. In the case when equimolar mixture of acetic and formic acid was applied the best result was obtained for *pH* of 3.9. Liquid phase was also somewhat turbid for *pH* of 3.1 and 4.5 and 5.5. Part of γ-alumina nanoparticles were also suspended when SHMP and SHMP with equimolar acetic and formic acids were used. In the case of pure SHMP the best results were obtained for 0.5% mas. But for other investigated concentrations, i.e. 1 and 2.45% mas. result were comparable. In the case of the 0.5% mas. SHMP and acetic-formic acids mixture there was no evident difference between stability for all investigated *pH*, i.e. 3.5, 4.6 and 6.0.

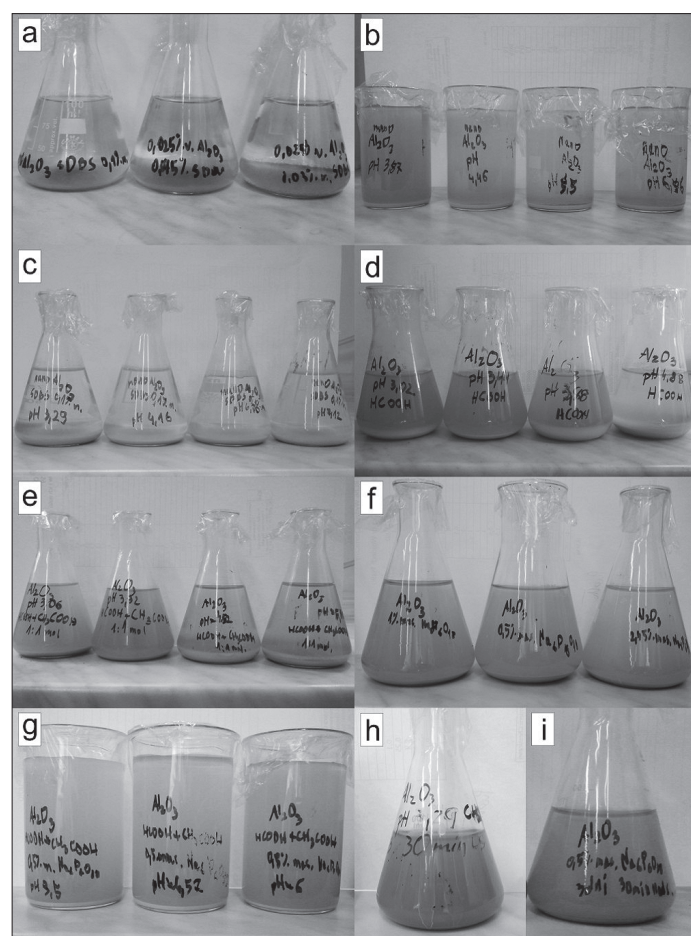


Fig. 3. γ-Al<sub>2</sub>O<sub>3</sub>-water nanofluid after a day, prepared in (a-g) 1 day (h-i) 3 day preparation procedure stabilized by (a) SDBS (from the left 0.1, 0.075, 0.03% mas.), (b) acetic acid (*pH* 3.9, 4.5, 5.5, 6.8), (c) acetic acid-0.1% mas. SDBS mixture (*pH* 3.4, 4.2, 4.5, 5.5), (d) formic acid (*pH* 3.0, 3.4, 3.9, 4.9), (e) equimolar acetic-formic acids mixture (*pH* 3.1, 3.9, 4.5, 5.5), (f) SHMP (1, 0.5, 2.45% mas.), (g) acetic-formic acids-0.5% mas. SHMP mixture (*pH* 3.5, 4.5, 6.0), (h) acetic acid (*pH* 3.4) and (i) SHMP (0.5% mas.)

For two samples stabilized by acetic acid, i.e. for *pH* of 3.4 and 3.9 DLS (Fig. 4) and zeta potential analyses (Tab. 2) were performed. DLS analysis showed that *pH* of the suspension had minor influence on size of particles. For lower *pH* the first peak maximum was observed for slightly smaller particles i.e. 404 nm, while for *pH* of 3.9 it was 448 nm. Peaks at ~5 μm are connected with impurities – larger agglomerates from the sediment, which were present in the sample. Zeta potentials for both investigated acetic acid concentrations were in the range of moderate and good stability. Higher absolute value of zeta potential, and therefore better stability was obtained for lower *pH* (i.e. 3.4).

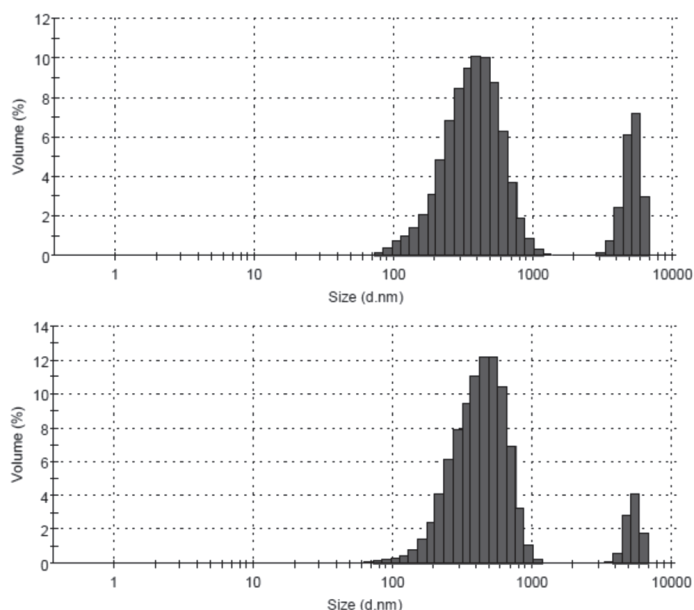


Fig. 4. PSD by volume of  $\gamma\text{-Al}_2\text{O}_3$ -water nanofluids stabilized by acetic acid ( $\text{pH}$  3.4-upper and 3.9-lower) prepared in 1-day procedure

One of reasons why no stable nanosuspension of  $\gamma$ -alumina in water was obtained is the size of the particles. Although, the size of the particles given by producer was 10 nm, they agglomerated and formed larger particles. The applied power and sonication time could have been not sufficient to deagglomerate the particles. Suspensions of larger particles are not as stable as that of lower ones. It might have been the reason why despite application of different stabilizers no satisfactory results were obtained. Also the absolute value of zeta potential is not high enough. Stabilization of  $\gamma$ -alumina only by acetic acid might have not been sufficient.

Therefore, one more investigation was performed. The suspensions of  $\gamma\text{-Al}_2\text{O}_3$  in water stabilized by SHMP and acetic acid were sonicated three times for 30 minutes. Between sonications 24 h of mixing by magnetic stirrer (400 rpm) was applied. Optical analysis of suspensions obtained by this procedure showed that they are more turbid than in the case of samples sonicated only once for 30 minutes.

For these samples PSD and zeta analyses were also performed. Particle size distributions by volume are shown in Fig. 5. For 0.5% mas. SHMP three diameter peaks were obtained. The most significant for 311

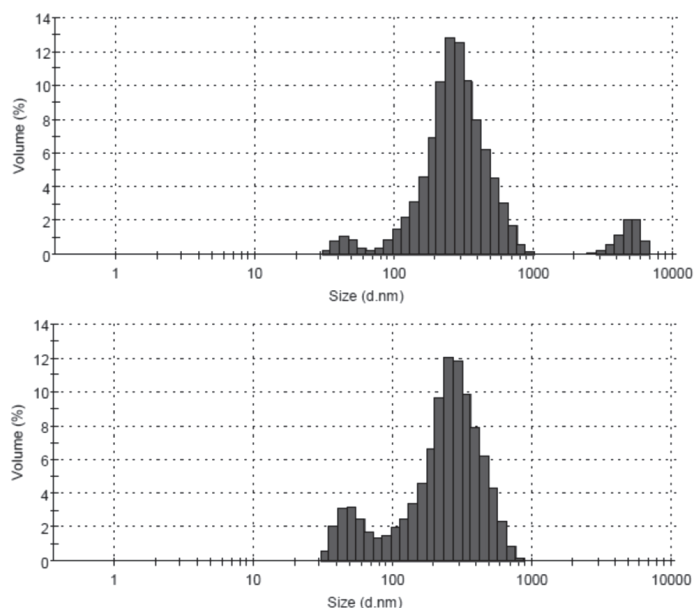


Fig. 5. PSD by volume of  $\gamma\text{-Al}_2\text{O}_3$ -water nanofluids stabilized by 0.5% mas. SHMP (upper) and acetic acid  $\text{pH}$  3.4 (lower) prepared in 3-day procedure

nm and two smaller for 47 and 4900 nm. For suspension stabilized by acetic acid at  $\text{pH}$  3.4 two maxima – at 53 and 295 nm were obtained. Fraction of particles  $<100$  nm is higher than in the 1-day procedure. Moreover, no particles  $>1000$  nm were observed, but in the case of suspension stabilized by SHMP that peak might have been the result of impurity. Absolute values of zeta potential for both investigated stabilizers were in the range of good stability. Better results were obtained for acetic acid, which may have suggested that it was better stabilizer.

Comparing zeta potential values for suspension stabilized by acetic acid ( $\text{pH}$  3.4) prepared for 1 and 3 days it might have been noticed that in the later case higher absolute value and therefore better stability was obtained.

Sonication time had positive influence on deagglomeration of  $\gamma$ -alumina particles. In the case of 3-day preparation the maximum peak had shifted from  $\sim 400$  nm to  $\sim 300$  nm. Additionally, small peak at  $\sim 50$  nm appeared. Decrease of average particle size had influence on stability of suspension, because smaller particles sediment slower than larger ones. Moreover, longer preparation had positive influence on zeta potential, which is also responsible for better suspension stability. However, obtained results were not satisfying, because most of the  $\gamma$ -alumina was in the form of sediment at the flask bottom. But, other researchers also mention that it is very difficult to suspend 10 nm  $\gamma\text{-Al}_2\text{O}_3$  particles [Gowda *et al.*, 2010].

## Conclusions

In the study stability of nanofluids obtained by suspending 30–50 nm copper(II) oxide and 10 nm  $\gamma$ -aluminum(III) oxide nanopowders in water with different stabilizers was analyzed. Following conclusion arise from the presented results:

- good stability of CuO-water nanofluid was obtained for 1% mas. SHMP,
- instability of CuO-water nanofluid might have been connected with the average size of particles ( $\sim 400$  nm) and not sufficient deagglomeration by sonication,
- poor stability of  $\gamma\text{-Al}_2\text{O}_3$ -water nanofluid was received for all investigated stabilizers,
- instability might have been connected with the average size of particles ( $\sim 400$  nm) and not sufficient deagglomeration by sonication.
- longer time of sonication decreased average particle diameter (to  $\sim 250$  nm), significant fraction of  $<100$  nm particles was also noticed, but 10 nm was not reached.

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