

Is It Important to Measure the Volumetric Mass Density of Nanofluids?

Z. Haddad, C. Abid, O. Rahli, O. Margeat, W. Dachraoui, A. Mataoui

Abstract—The present study aims to measure the volumetric mass density of NiPd-heptane nanofluids synthesized using a one step method known as thermal decomposition of metal-surfactant complexes. The particle concentration is up to 7.55g/l and the temperature range of the experiment is from 20°C to 50°C. The measured values were compared with the mixture theory and good agreement between the theoretical equation and measurement were obtained. Moreover, the available nanofluids volumetric mass density data in the literature is reviewed.

Keywords—NiPd nanoparticles, nanofluids, volumetric mass density, stability.

I. INTRODUCTION

PREPARATION of stable nanofluids is an unavoidable issue that can alter the thermo-physical properties of nanofluids. The stability of nanofluids refers to several aspects: 1) Nanofluids are multi-phase dispersion system with high surface energies and are, therefore, thermodynamic unstable. 2) Nanoparticles dispersed in the nanofluids have strong Brownian motions. The mobility of the nanoparticles can offset their sedimentation caused by the gravity field. 3) Dispersion of nanoparticles in the fluids may deteriorate with time due to the aggregation of nanoparticles, which is caused by van der Waals forces. 4) No chemical reactions either between the suspended nanoparticles or between the base fluid and nanoparticles are desired at working conditions of the nanofluid. Therefore, there are two phenomena that are critical to the stability of nanofluid, aggregation and sedimentation.

In recent years, considerable efforts have been made to prepare stable and durable nanofluids, before it can be fully implemented in the industrial applications [1]-[4]. The nanoparticles that have been mostly used to prepare nanofluids include metallic particles (Al, Au, Ag and Cu) and nonmetallic particles (Al_2O_3 , ZnO, CuO, TiO_2 , Fe_3O_4 , CNTs, SiO_2 and AlN), with an average size varied between 10 and 80 nm. The base fluids commonly used are water and ethylene glycol.

Although research works have shown that changing the pH of suspensions or adding surfactants can prevent coalescence and sedimentation of nanoparticle, the obtained stability was

Zoubida Haddad is with the university of Boumerdes, department of Electronics and Electrical Engineering, Algeria and with Aix-Marseille University, CNRS, IUSTI UMR 7343, 13453 Marseille, France (e-mail: zoubida.haddad@etu.univ-amu.fr).

Walid Dachraoui and Olivier Margeat are with Aix-Marseille University, CNRS, CINaM UMR 7325, 13288 Marseille, France.

Chérifa Abid and Ouamar Rahli are with Aix-Marseille University, CNRS, IUSTI UMR 7343, 13453 Marseille, France.

Amina Mataoui is with the University of Sciences and Technology-Houari Boumediene, department of Fluid Mechanics, Faculty of Physics, Algiers, Algeria.

only for few months [4]. The best way to produce long-term stable nanofluids that exhibits true 'nano' behavior, and measure the thermo-physical properties accurately may be a single-step method. In this way, the chance of agglomeration is reduced. Also, reducing the particle size should remarkably decrease the sedimentation speed of the nanoparticles and improve the stability of nanofluids, since the particle's sedimentation velocity is proportional to the square of the particle size. In this context, a bimetallic nanofluid with high stability is produced.

The purpose of this work is twofold. First, synthesize nickel/palladium (NiPd) nanoparticles by thermal decomposition of metal-surfactant complexes. Then, measure the volumetric mass density of NiPd-heptane nanofluids under various operating temperature and nanofluid concentrations, and compared the results with theoretical prediction of mixture theory.

II. MATERIAL AND METHODS

A. Nickel-Palladium (Ni-Pd)

Bimetallic PdNi nanoparticles are currently attracting a great deal of interest due to their physical and chemical properties. In particular, it is well-known that Pd is a metal with important existing and potential applications as a catalyst in heterogeneous catalysis. The use of Pd as a single active metal component in catalysis has received considerable attention on the basis of its remarkable activity for oxidation reactions and the availability of cleaner fuels, but at the same time it has negative economical aspects due to its high cost [5]. An interesting approach in these respects consists of alloying Pd with lower cost and higher surface energy metals, since it would be economically attractive to design bimetallic catalyst nanoparticles in which the precious and catalytic Pd atoms segregate to the surface. Promising results in this sense have been obtained by using Ni [5]-[7].

B. Synthesis of Nanofluids

The synthesis is slightly modified from ref [8]. In a typical experiment, a solution mixture of 1:1 nickel acetylacetonate ($\text{Ni}(\text{acac})_2 \cdot 0.082\text{g}$, 0.328 mmol) and palladium acetylacetonate ($\text{Pd}(\text{acac})_2 \cdot 0.1\text{g}$, 0.328 mmol) in 2mL of trioctylphosphine, was injected into a 3-neck flask containing 7mL of oleylamine at 205°C. After aging at 205°C for 30 minutes, the temperature was increased to 235°C in 30 minutes and kept at this temperature for one hour. Washing of the nanoparticles was done through three cycles using ethanol for flocculation and centrifugation to remove the supernatant. Finally, the nanoparticles were redispersed in pure heptane.

C. Characterization of Nanoparticles

The morphological characterization of NiPd nanoparticles deposited on a carbon-coated copper grid was carried using a high resolution Transmission Electron Microscopy (HRTEM JEOL 3010).

D. Formulation of Nanofluids

NiPd-heptane nanofluids with concentrations of 16 g/l and 4g/l were first produced (Fig. 1). Then, five concentrations of 7.55 g/l, 5.95 g/l, 4.5 g/l, 2.95 g/l and 1 g/l were obtained by dilution with heptane under magnetic stirring for 1min at 220 rpm (Fisher Scientific/FB15038). The produced samples of 16 g/l and 4 g/l were stable for one year and a half without any visible sedimentation. It should be noted that the other dilutions were prepared after that period.



Fig. 1 Photograph of NiPd-Heptane Nanofluids

III. RESULTS AND DISCUSSION

A. Morphology and Crystalline Structure of Nanoparticles

Figs. 2 (a) and (b) show the transmission electron microscopy and high resolution transmission electron microscopy of NiPd nanoparticles, respectively. A high resolution TEM (HRTEM) image of the nanoparticles revealed the highly crystalline nature of the nanoparticles with a diameter of about 5 nm. Moreover, the image shows that nanoparticles are uniform and monodispersed. In Fig. 3, the histogram of TEM image confirms that NiPd nanoparticles have an average diameter of 4.5nm +/- 0.6nm (standard deviation).

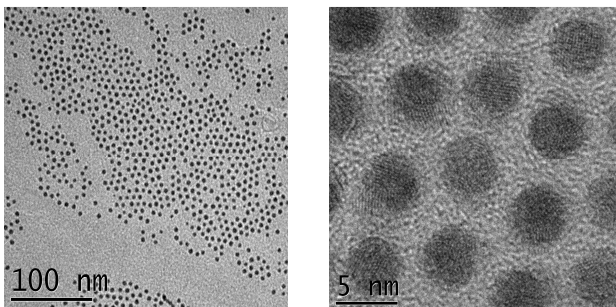


Fig. 2 (a) TEM image, (b) HRTEM image

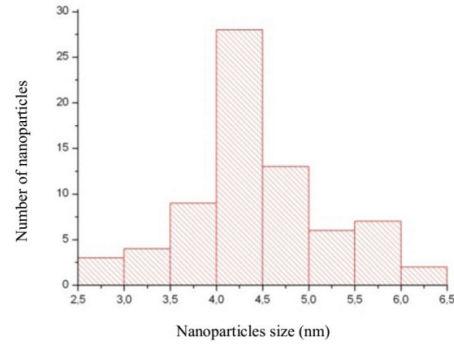


Fig. 3 Histogram of TEM image of NiPd nanoparticles.

B. Volumetric Mass Density Measurement

Nanofluid volumetric mass density is measured using the portable DMA 35 according to the oscillating U-tube principle. The sample is introduced into a U-shaped borosilicate glass tube that is being excited to vibrate at its characteristic frequency electronically. The characteristic frequency changes depending on the volumetric mass density of the sample. Through determination of the characteristic frequency the sample can be calculated. Due to the temperature dependency of the density value, the temperature of the sample has to be determined precisely.

To validate the measurements, the volumetric mass density of distilled water was measured at four temperatures 20°C, 30°C, 40°C, and 50°C. The results were compared with the data provided by A. Bejan [9]. Table I shows the measured and reference values. It can be seen that the deviation between measured data and standard reference for the limited temperature range considered in this study is less than 0.2%.

T(°C)	ρ_{meas} (g/cm ³)	ρ_{ref} (g/cm ³)	$(\rho_{\text{meas}} - \rho_{\text{ref}}) / \rho_{\text{ref}}$ (%)
20	0.9992	0.9982	0.10
30	0.9967	0.9952	0.15
40	0.9925	0.9922	0.03
50	0.9882	0.9877	0.051

C. Volumetric Mass Density of Nanofluids

Because density is an important property of nanofluids that affects the Reynolds number, friction factors, pressure loss and Nusselt number, we focus our attention in this paper on accurately measuring the density of NiPd-heptane nanofluids. The equation for the density of two-phase mixtures for particles of micrometer size is available in the literature on slurry flows [10]. Pak and Cho [11] measured the volumetric mass density of γ -Al₂O₃ and TiO₂ at a volume concentration of 4.5%. They confirmed that the mixture theory of micrometer particle is valid for nanometer size particles, which is expressed by the following expression

$$\rho_{nf} = (1 - \phi)\rho_f + \phi\rho_s \quad (1)$$

where ρ_{nf} is the density of the nanofluid, ρ_s is the density of the particle, ϕ is the particle volume concentration, ρ_f and is the density of the base fluid.

Fig. 4 displays the measured volumetric mass density of NiPd-heptane nanofluids for different concentrations and within a temperature range of 20°C to 50°C. The general observation is that volumetric density decreases with temperature and increases with an increase of particle concentrations, which agree well with the behavior of pure and dispersed fluids. Comparison of the measured volumetric mass density values and those calculated from (1) are also presented. The maximum deviation is 1.12% at a particle concentration of 5.95 g/l. Therefore, we conclude that mixture theory predicts well the volumetric mass density of nanofluids.

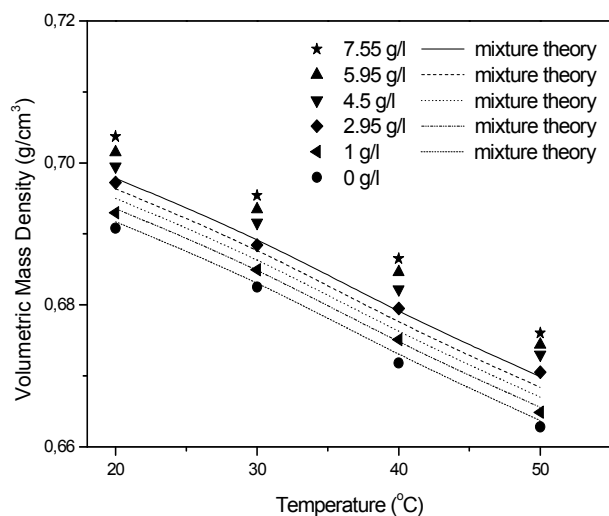


Fig. 4 Volumetric Mass Density of NiPd Nanofluids

Table II summarizes experimental data of nanofluids volumetric mass density reported by previous authors and their deviation from the proposed theoretical model [12]-[19]. Most of experimental findings show that mixture theory predicts well the volumetric mass density of nanofluids, which is not a new finding since this theory is based on the mass conservation. However, only a few authors that reported contradictory results; Kumaresan and Velraj [16] showed that the mixture theory could not predict the volumetric mass density of the nanofluids with the presence of MWCNT nanoparticles. They attributed this difference to the spontaneous filling of nanotubes with water in a confined way which increases the mass of the nanofluid for a given volume. Mahbulul et al. [19] explained this difference to be mainly due to the fact that pack and cho model was derived for water based nanofluids.

IV. CONCLUSION

Well dispersed heptanes based NiPd nanofluids with average particle size of 4.5nm were synthesized using thermal decomposition of metal-surfactant complexes. The samples were stable at least one year and a half and there was no visible sedimentation. As results show, the nanofluid volumetric mass density can be determined using mixture theory since it is based on mass conservation. However, the contradictory results reported in literature can be due to the fact that nanofluids can not be prepared precisely at a desired volume or mass concentrations.

TABLE II
SUMMARY OF LITERATURE REVIEW OF VOLUMETRIC MASS
DENSITY OF NANOFUIDS

Authors	Nanofluids /parameters	Comparison with theory
Ho et al. [12]	Al ₂ O ₃ -water, $\Phi=0.1-4\text{vol.}\%$, $D=33\text{ nm}$, $T=5-40\text{ }^\circ\text{C}$	Agree well
Ravikanth et al. [13]	Al ₂ O ₃ -water/EG, $\Phi=2-10\text{vol.}\%$, $D=53\text{ nm}$, $T=0-50\text{ }^\circ\text{C}$	Agree well
Mohamed Ali et al. [14]	Al ₂ O ₃ -water, $\Phi=0.21-0.75\text{vol.}\%$, $D=10\text{ nm}$, $T=25.5\text{ }^\circ\text{C}$	Agree well
Fakoor Pakdaman et al. [15]	MWCNT-oil, $\Phi=0.1, 0.2\text{ and }0.4\text{ wt.}\%$, $D \times H=2-6\text{ nm} \times 1-10\text{ }\mu\text{m}$	satisfactorily agreement
Kumaresan and Velraj [16]	CNT-water/EG, $\Phi=0.15, 0.3\text{ and }0.45\text{ wt.}\%$, $D \times H=30-50\text{ nm} \times 10-20\text{ }\mu\text{m}$	Overestimated
Heyhat et al. [17]	Al ₂ O ₃ -water, $\Phi=0.1-2\text{vol.}\%$, $D=40\text{ nm}$, $T=20-60\text{ }^\circ\text{C}$	Agree well
Saeedinia et al. [18]	CuO-oil, $\Phi=0.2-2\text{wt.}\%$, $D=50\text{ nm}$, $T=20-60\text{ }^\circ\text{C}$	Agree well
Mahbulul et al. [19]	Al ₂ O ₃ - R141b, $\Phi=0.1-0.4\text{ vol.}\%$, $D=13\text{ nm}$, $T=5-20\text{ }^\circ\text{C}$	underestimated

REFERENCES

- [1] Y. Li, J. Zhou, S. Tung, E. Schneider, S. Xi, A review on development of nanofluid preparation and characterization, Powder Technol, vol. 196, pp. 89-101, 2009.
- [2] A. Ghadimi, R. Saidur, H.S.C. Metselaar, A review of nanofluid stability properties and characterization in stationary conditions, Int. J. Heat Mass Transfer, vol. 54, pp. 4051-4068, 2011.
- [3] W. Yu, H. Xie, A review on nanofluids: preparation, stability mechanisms, and applications, J. Nanomater, vol. 2012, pp. 1-17, 2012.
- [4] Z. Haddad, C. Abid, H.F. Oztop, A. Mataoui, A review on how the researchers prepare their nanofluids, International Journal of Thermal Sciences, vol. 76, pp. 168-189, 2014.
- [5] A.B. Hungria, J.J. Calvino, J.A. Anderson, A. Martínez-Arias, Appl. Catal, vol. B62, pp. 359, 2006.
- [6] P. Miegge, J.L. Rousset, B. Tardy, J. Massardier, J.C. Bertolini, J. Catal, vol. 149, pp. 404, 1994.
- [7] L. Porte, M. Phaner-Goutorbe, J.M. Guigner, J.C. Bertolini, Surf. Sci, vol. 424, pp. 262, 1999.
- [8] S.U. Son et al., J. Am. Chem. Soc., 2004, 126, 5026.
- [9] A.Bejan, "Convection Heat Transfer", John Wiley & Sons, 3rd ed, 2004.

- [10] N.P.Cheremisinoff, Encyclopedia of Fluid Mechanics, vol. 5, Slurry Flow Technology. Houston, TX: Gulf Publishing, 1986.
- [11] B.C. Pak and Y.L. Cho, Hydrodynamic and heat transfer study of dispersed fluids with submicron metallic oxide particles. *Exp. Heat Transfer*, vol. 11, pp. 151-170, 1998.
- [12] C.J. Ho, W.K. Liu, Y.S. Chang, C.C. Lin, Natural convection heat transfer of alumina-water nanofluid in vertical square enclosures: An experimental study, *International Journal of Thermal Sciences*, vol. 94, pp. 1345-1353, 2010.
- [13] S. Ravikanth, S. Vajjha and D.K. Das, Measurements of Specific Heat and Density of Al_2O_3 Nanofluid, *Nanoscope, and Macroscopic Materials*, CPI 063, Me505cop/c.
- [14] M. Ali, O. Zeitoun, S. Almotairi, Natural convection heat transfer inside vertical circular enclosure filled with water-based Al_2O_3 nanofluids, *International Journal of Thermal Sciences*, vol. 63, pp. 115-124, 2013.
- [15] M. Fakoor Pakdaman, M.A. Akhavan-Behabadi, P. Razi, An experimental investigation on thermo-physical properties and overall performance of MWCNT/heat transfer oil nanofluid flow inside vertical helically coiled tubes, *Experimental Thermal and Fluid Science*, vol. 40, pp. 103-111, 2012.
- [16] V. Kumaresan, R. Velraj, Experimental investigation of the thermo-physical properties of water-ethylene glycol mixture based CNT nanofluids, *Thermochimica Acta*, vol. 545, pp. 180-186, 2014.
- [17] M.M. Heyhat, F. Kowsary, A.M. Rashidi, S. Alem Varzane Esfehiani, A. Amrollahi, Experimental investigation of turbulent flow and convective heat transfer characteristics of alumina water nanofluids in fully developed flow regime, *International Communications in Heat and Mass Transfer*, vol. 39, pp. 1272-1278, 2012.
- [18] M. Saeedinia, M.A. Akhavan-Behabadi, P. Ra, Thermal and rheological characteristics of CuO-Base oil nanofluid flow inside a circular tube, *International Communications in Heat and Mass Transfer*, vol. 39, pp. 152-159, 2012.
- [19] I.M. Mahbubul, R. Saidura, M.A. Amalina, Thermal conductivity, viscosity and density of R141b refrigerant based Nanofluid, *Procedia. Engineering*, vol. 56, pp. 310-315, 2013.