CHIN. PHYS. LETT. Vol. 26, No. 5 (2009) 056601

Influence of pH on Nanofluids' Viscosity and Thermal Conductivity *

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(Received 21 November 2008)

Aiming at the dispersion stability of nanoparticles regarded as the guide of heat transfer enhancement, we investigate the viscosity and the thermal conductivity of Cu and Al_2O_3 nanoparticles in water under different pH values. The results show that there exists an optimal pH value for the lowest viscosity and the highest thermal conductivity, and that at the optimal pH value the nanofluids containing a small amount of nanoparticles have noticeably higher thermal conductivity than that of the base fluid without nanoparticles. For the two nanofluids the enhancements of thermal conductivity are observed up to 13% (Al_2O_3-water) or 15% (Cu-water) at 0.4 wt%, respectively. Therefore, adjusting the pH values is suggested to improve the stability and the thermal conductivity for practical applications of nanofluid.

PACS: 66.20.Ej, 82.70.Kj, 47.27.Em

Nanofluid is a kind of new engineering material consisting of nanometer-sized particles dispersed in conventional heat transfer fluids such as water, glycol, or oil based fluid.[1−5] Compared with the conventional heat transfer fluids, nanofluids were found to have substantially higher thermal conductivities than those of base fluids without nanoparticles.[1−7] For example, in the Argonne National Laboratory, researchers studied water- and oil-based nanofluids containing copper oxide nanoparticles, and found a striking 60% enhancement in thermal conductivity for only a 5 vol% of nanoparticles.[2,3] A small amount (< 1 vol%) of Cu nanoparticles or carbon nanotubes dispersed in water or oil was reported to increase the inherently poor thermal conductivity of the liquid by 74% and 150%.[8,9] Furthermore, Philip *et al.*[10] observed the 300% enhancement of thermal conductivity by a Fe_3O_4 nanoparticle loading of 6.3 vol%.

However, due to the high surface energy of nanoparticles, it is easy for nanoparticles to coagulate and difficult to disperse in the base fluid. This leads to changes of the morphology and of volume fraction resulting in low fluidity.[11−13] Therefore, controlling the coagulation of nanoparticles in the nanofluid becomes the primary issue for exploiting their potential benefits and applications. Viscosity describes the internal resistance of a fluid to flow and is a property of crucial importance for all thermal applications involving fluids.[14] In the case of nanofluids, it is an important evaluation for understanding the dispersion stability behavior.[13,14] However, to our knowledge, recent efforts have mainly focused on the thermal conductivity and there are few reports regarding the nanofluid viscosity. In this Letter, by measuring the viscosity and the thermal conductivity of nanofluids, we investigate the effect of pH value on the dispersive stability and the heat transfer enhancement of the nanosuspension. It is expected to provide guidance to design nanofluides with excellent performances.

Commercial Al_2O_3 and Cu particles (from Alfa Aesar, Ward Hill, MA, USA) were chosen as a source material for the nanofluids. They were prepared by the two-step method.[2] The surface area of the particles was determined by the Micromeretic Tristar 3000 and the particle size was measured by an x-ray disk centrifuge particle size analyser (ver 3.49). The average particle size and BET surface area of the powder were found to be 15–50 nm, 100 m^2/g (Al_2O_3), and 25–60 nm, 30–50 m^2/g (Cu), respectively. An anionic surfactant sodium dodecylbenzenesulfonate (SDBS) in chemical grade, from Guangzhou Chemical Reagent Factory, was used to stabilize the suspension. The water was purified by a Milli-Q Academic Millipore system. The pH value of nanofluids was controlled using hydrochloric acid (HCl) and sodium hydroxide (NaOH) in analytical grade. All chemicals were used without any further purification.

Firstly, we measured the viscosities of a series of Al_2O_3-H_2O and Cu-H_2O nanofluids with weight fractions from 0.01% to 0.9% for different pH values by using a capillary viscometer (see Fig. 1(a)). The capillary viscometer was submerged in a glass water tank. The working principle was well established and the specific rules were given in Ref. [14]. Water from a constant-temperature bath entered the bottom of the tank by a pump and returned to the bath through an overflow pipe. The water tank was maintained at a prescribed constant temperature by the water circulation. The vertical angle of the viscometer was accurately controlled by a special tripod.

*Supported by the Post-Doctoral Foundation of China under Grant Nos 20060400219 and 200801251.

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The effect of capillary-tube diameter on the apparent viscosity was evaluated using three viscometers with diameters of 0.47 mm, 0.50 mm and 0.55 mm. The mean value obtained using three viscometers is the viscosity of each sample. Before systematic experiments were performed on nanofluids, the experimental system was tested with deionized water as the working fluid. The results with the deionized water were shown in Fig. 1(b). The uncertainty of our measurements is less than about 3.00%.

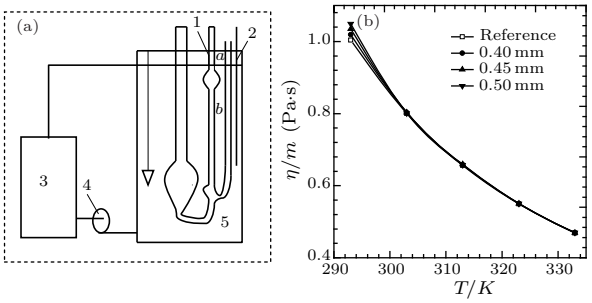

Fig. 1. (a) Experimental scheme for viscosity: (1) viscometer, (2) thermometer, (3) constant-temperature bath, (4) pump, (5) glass water tank, (b) the results of the tested deionized water.

Research to date has shown that the stabilities of alumina and copper powder suspension in an aqueous solution are closely related to their electrokinetic properties. Well-dispersed suspension can be obtained with high surface charge density to generate strong repulsive forces.[13,15] In this work, we used the method of changing suspension pH value to generate strong repulsive forces and to reduce the coagulation of nanoparticles to obtain low viscosity (well-dispersed) suspension. The variations of the nanofluid viscosity with pH and nanoparticles concentration at temperature 30°C are presented in Fig. 2. From Fig. 2(a), it can be seen that both the nanofluids show similar behavior with pH change, and there is an optimized value of pH ($pH_{alumina} \approx 8.0$, $pH_{copper} \approx 9.5$) at which the viscosities of the two nanofluids take their minima $\eta_{alumina} = 0.826$, 0.846, 0.865 mPa·s; $\eta_{copper} = 0.82$, 0.838, 0.860 mPa·s for weight fraction 0.1%, 0.2% and 0.4%, respectively. From Fig. 2(b), we can see that at the optimal pH ($pH_{alumina} \approx 8.0$, $pH_{copper} \approx 9.5$), the nanofluid viscosity increases with an augmentation of particle weight fraction as expected by Einstein's formula.[14] For alumina-water nanofluid, the viscosity increases from nearly 0.82 to 0.84 to 0.86 and then to 0.94 mPa·s with particle concentration increasing from 0.1% to 0.2%, to 0.4% and then to 0.9%. Similar behaviour is found for the copper-water nanofluid: the viscosity increased from 0.81 to 0.83, then to 0.85 and finally to 0.93 mPa·s for particle concentration varying from 0.1% to 0.2%, to 0.4% and then to 0.9%. It is also apparent from Fig. 2(b) that the viscosity of alumina-water is generally higher than that of copper-water nanofluid at the same weight fraction and pH value. This means that the dispersion of alumina powder is poorer than that of copper powder at the same pH value and same weight fraction. The sediment photographs of Al_2O_3–H_2O and Cu–H_2O suspensions at different pH values after depositing for seven days are shown in Figs. 1(c) and 1(d). As shown in this figure, alumina and copper particles tend to form agglomerated structures at pH below 7, which results in rapid sedimentation of particles and instability of the suspension. The alumina suspensions at pH $\simeq$ 7.5–8.9 and copper suspensions at pH $>$ 7.6 show a good dispersion of nano-particles and the dispersion can be maintained for a long period, which is attributed to the higher charge on the surface of nano-particles.

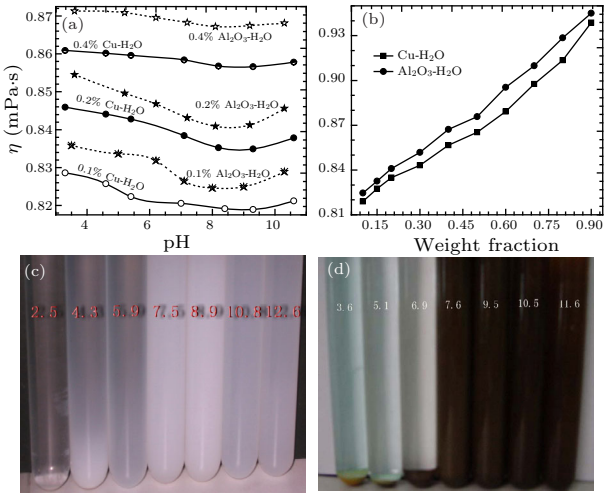

Fig. 2. Variation of the nanofluids viscosity with pH and nanoparticles weight fraction at temperature 303 K: (a) the variation of the viscosity with pH, (b) the variation of the viscosity with nanoparticles concentration, (c) the sediment photograph of Al_2O_3-H_2O suspensions after depositing for seven days, (d) the sediment photograph of Cu-H_2O suspensions after depositing for seven days.

Secondly, we measured the thermal conductivity of a series of Al_2O_3-H_2O and Cu-H_2O nanofluids with weight fractions from 0.01% to 0.4% at different pH values by means of the transient plane source (TPS) method.[2,15] In this method, the TPS element behaves as both temperature sensor and heat source. This novel method offers some advantages such as fast and easy experiments, a wide range of thermal conductivities (from 0.02 to 200 $W \cdot m^{-1} \cdot K^{-1}$), no sample preparation and flexible sample size. The TPS element consists of an electrical conducting pattern of thin nickel foil (10 μm) in the form of a double spiral, which resembles a hot disk, embedded in an insulating layer made of kapton (70 μm)(see Fig. 3). The working principle of the TPS method is well established and the specific rules can be seen in Ref. [2]. A Kapton insulated probe (design 7577) was successively dipped into different nano-suspensions. The diameter of the sensing spiral in the probe was about 2.001 mm and

the Kapton insulation on both sides of the spiral had a thickness of 13 μm. Then, the thermal conductivity was measured by a Hot Disk Thermal Constants Anlyser (Hot Disk Inc., Uppsala, Sweden). The measurement was run at voltage $V = 0.02$ V and temperature $T = 25°$C with a switch time at 5 s. Each experiment was repeated at least ten times to calculate the mean value of the experimental data. Before systematic experiments were performed on nanofluids, the experimental system was tested with deionized water as the working fluid. The results with the deionized water will also serve as the basis for comparison with the results of nanofluids (see Table 1). The uncertainty of our measurements is less than 1.00%.

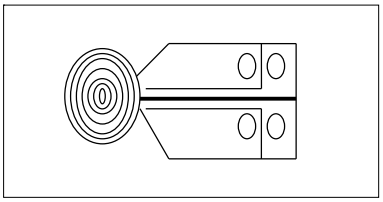

Fig. 3. Schematic diagram of the transient plane source (TPS) sensor.

Table 1. Thermal conductivity of deionized water.

T (K)	$k_{\rm exp}$ (W/mK)	$k_{\rm ref}$ (W/mK)	$(k_{\rm exp} - k_{\rm ref})/k_{\rm ref}$(%)
283	0.5706	0.5741	−0.61
293	0.6010	0.5985	0.42
303	0.6233	0.6171	1.00

Thermal conductivity ratios of the two suspensions and the base fluid as a function of pH were presented in Fig. 4. From the similarity of data obtained in Al_2O_3-H_2O and Cu-H_2O suspensions, one can see that the thermal conductivities for the nanofluids with different pH values follow the trends similar to those observed in the viscosity measurement. This means that for the fluids the highest thermal conductivity corresponds to the lowest viscosity at the same pH value, and there exists an optimized value of pH ($\rm pH_{alumina} \approx 8.0$, $\rm pH_{copper} \approx 9.5$) at which the thermal conductivity ratios take their maximum values $(\rm K/K_{\it f})_{Al_2O_3} = 1.09, 1.1$, $(\rm K/K_{\it f})_{Cu} = 1.12, 1.13$, at weight fractions 0.1% and 0.2%, respectively.

Note that the thermal conductivity of base fluid is nearly constant at different doses of electrolyte salt and acid or base. The enhancement seems to be related only to the particles. When the nanoparticles are dispersed into water, the overall behavior of the particle-water interaction depends on the properties of the particle surface. As observed by the viscosity measurement when the pH is increased to the optimized value, the surface charge increases because of the more frequent attacking of the surface hydroxyl groups and phenyl sulfonic group by potential-determining ions (H^+, OH^- and phenyl sulfonic group). This leads to an increase of the electrostatic repulsion force between the particles, and the suspensions show significantly reduced agglomeration and enhanced mobility, ultimately improving the heat transport. When the pH is too large, the concentration of the pH adjustment reagent (NaOH) in the system increases, which causes the compression of the electrical double-layer. This leads to an decrease of the electrostatic repulsion force, and the suspension exhibits a poorer dispersion. Thus we also attempt to link the concept of surface charges to the change in thermal conductivity ratio of nanofluids. This conclusion was also presented by Lee *et al.*[11] They showed that as the pH value diverges from the isoelectric point (PZC), the particles acquire larger charge and the particle-particle repulsion increases, thus making the suspension more stable and resulting in high thermal conductivity. Therefore, it looks reasonable to infer that optimizing pH or high surface charge facilitates phonon transport through increases of transport efficiency.

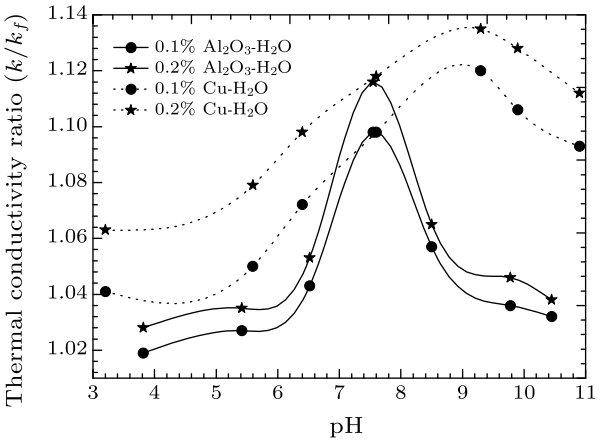

Fig. 4. Thermal conductivity ratios of nano-suspensions at different pH values.

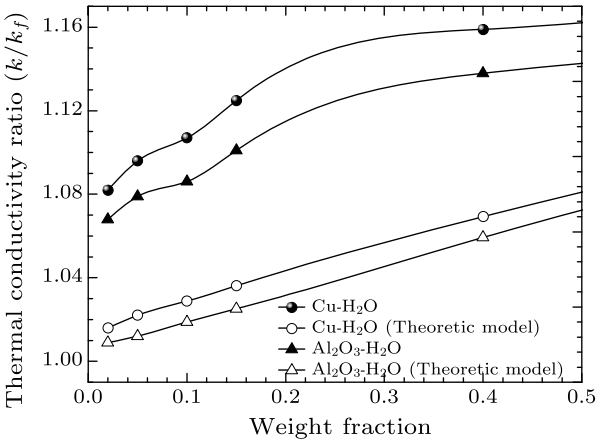

Fig. 5. Thermal conductivity ratios of nano-suspensions as a function of the solid weight fraction.

Figure 5 presents the thermal conductivity ratio of the nano-suspensions and the base fluid as the function of nanoparticles concentrations at $\rm pH_{alumina} \approx 8.0$, $\rm pH_{copper} \approx 9.5$. From the figure we can see that

the thermal conductivity of nanofluid is enhanced approximately nonlinearly with the weight fraction of the nanoparticle, the maximum thermal conductivity enhancements of nanofluids up to 13% for Al_2O_3 and 15% for Cu are observed at the 0.4% suspension. These results are in good agreement with those of the maximal enhancement for alumina or copper nanofluids observed in previous reports.[5–8] In the case of optimizing the pH value for the both nanofluids, the electrostatic repulsion force between particles becomes sufficient to prevent attraction and collision between particles caused by Brownian motions. Greater electrostatic force can also lead to the production of more free particles by increasing the particle-particle distance, and further reduce the probability of particle coagulation, enhance the mobility of nanoparticles, and eventually enhance the heat transport. Also shown in Fig. 5 is the comparison between the experimental data for nanofluids and the values calculated from the Hamilton–Crosser model.[16] The comparison results show that the measured thermal conductivities are greater than those calculated from the Hamilton–Crosser model. This is because the mechanisms behind the exceptionally enhanced thermal conductivity of nanofluids are still under scrutiny. The Hamilton–Crosser model did not consider many other factors that can significantly effect the nanoparticles heat transport in nanofluids, such as surface chemical effect, particle size and particle Brownian motion. Here, we also suggest that surface charge states adjusted by pH can change the effective thermal conductivity of nanofluids, which has been presented in Refs. [11,2,15].

In conclusion, we have investigated the viscosity and thermal conductivity of Al_2O_3-H_2O and Cu-H_2O nanofluids under different pH values. From the experimental results it is shown that the viscosity of nanofluids is closely related to the enhancement of thermal conductivity, the nanofluids have lower viscosity, better dispersion behavior, and higher thermal conductivity. An optimal pH value can result in the lowest viscosity and the highest thermal conductivity of the nanofluids. The maximum thermal conductivity enhancements of up to 13% for Al_2O_3 and 15% for Cu are observed at the weight fraction 0.4% suspension. Thus, adjusting the nanofluids pH value is recommended to improve the dispersive stability and the thermal conductivity for practical applications of nanofluid. The experimental results are also compared with the Hamilton–Crosser model and show that the experimental results are remarkably higher than those predicted by the Hamilton–Crosser model for solid-liquid mixtures. The differences indicate that we must take into account several possible factors in enhancing the heat transfer performance of nanofluids, for example, high surface charge facilitates phonon transport through increases of effective sites and transport efficiency.

References

[1] Prasher R 2005 *Phys. Rev. Lett.* **94** 025901
[2] Li X F, Zhu D S, Wang X J, Gao J W and Li H 2008 *Thermochimica Acta* **469** 98
[3] Timofeeva E V, Gavrilov A N, McCloskey J M and Tolmachev Y V 2007 *Phy. Rev.* E **76** 061203
[4] Eastman J A, Choi U S, Li S, Thompson L J and Lee S 1996 *Fall Meeting of the Materials Research Society* (MRS, Pittsburgh, Boston, 2–6 December 1996) p 1
[5] Eastman J A, Phillpot S R, Choi S U S and Keblinski P 2004 *Annu. Rev. Mater. Res.* **34** 219
[6] Assael M J, Metaxs I N, Kakosimos K and Constantinou D 2006 *Int. J. Thermophys.* **27** 999
[7] Jana S, Khojin A S and Zhong W H 2007 *Thermochim. Acta* **462** 45
[8] Choi S U S, Zhang Z G and Yu W 2001 *Appl. Phys. Lett.* **79** 2252
[9] Philip J, Shima P D and Raj B 2007 *Appl. Phys. Lett.* **91** 203108
[10] Kumar D H, Patel H E, Kumar V R R, Sundararajan T, Pradeep T and Das S K 2004 *Phys. Rev. Lett.* **93** 144301
[11] Lee D, Kim J W and Kim B G 2006 *J. Phys. Chem.* B **110** 94323
[12] Keblinski P and Thomin J 2006 *Phys. Rev.* E **73** 010502
[13] Li X F, Zhu D S and Wang X J 2007 *J. Colloid Interface Sci.* **310** 456
[14] Nguyen C T, Desgranges F, Roy G, Galanis N, Mare T, Boucher S and Angue M H 2007 *Int. J. Heat and Fluid Flow* **28** 1492
[15] Li X F and Zhu D S 2006 *Chem. Ind. Eng. Progress* **25** 875 (in Chinese)
[16] Hamilton R L and Crosser O K 1962 *Ind. Eng. Chem. Fundam.* **1** 187
Hamilton R L and Crosser O K 1962 *Ind. Eng. Chem. Fundam.* **1** 91