Influence of pH and SDBS on the Stability and Thermal Conductivity of Nanofluids

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Aiming at the dispersion of nanoparticles which are regarded as the guide of heat transfer enhancement, we investigated the heat transfer enhancement of two water-based nanofluids, namely, water−Al₂O₃ and water−Cu mixtures. The absorbency, ζ potential, and thermal conductivity of the nanofluids were measured under different pH values and different sodium dodecylbenzene sulfonate (SDBS) dispersant concentrations. The results showed that the stability and thermal conductivity of nanofluids were highly dependent on pH values and SDBS concentrations of nanosuspensions; an optimal pH value and optimal SDBS concentration can result in the highest stability and thermal conductivity of the nanofluids. Therefore, the combined treatment with both the pH and the chemical surfactant concentration was recommended to improve the stability and thermal conductivity for practical applications of nanofluid.

I. Introduction

Nanofluids are a class of heat transfer fluids created by dispersing solid nanoparticles in traditional heat transfer fluids such as water, glycol, or oil base fluid.¹−⁴ The advantages of nanofluids are (1) better stability compared to those fluids containing micro- or millisized particles and (2) higher thermal conductive capability than the base fluids. Such advantages of nanofluids offer important benefits for numerous applications in many fields such as transportation, electronics cooling, nuclear systems cooling, biomedicine, and food of many types.² Since the concept of nanofluid was first introduced by Choi,¹ repeated experiments by several groups around the world demonstrated a striking 60% enhancement in thermal conductivity for only a 5 vol % of nanoparticles.³,⁴ Furthermore, the 300% enhancement of thermal conductivity observed by Philip et al. was achieved by a Fe₃O₄ nanoparticle loading of 6.3 vol %.⁵ Many similar results of anomalous enhancement of the thermal conductivity of various nanofluids were also reported.⁶−¹¹

However, because of the high surface energy of nanoparticles, it is easy for nanoparticles to coagulate and difficult to disperse in water. Therefore, controlling the coagulation of nanoparticles in the nanofluid has become the primary issue for the initial research of nanofluids. It is also important to investigate dispersion and stability of nanofluids to exploit their potential benefits and applications. Many research projects were conducted to enhance the thermal conductivity of nanofluid and also to produce more stable suspensions.⁹−¹² Studies to date have shown that the amount and the charge of nanoparticles in the nanofluid and the interaction between the particles and the dispersant directly affect the stability of the suspension. Agitating,¹³ changing pH values of the suspension, and adding surfactants¹⁴−¹⁸ have been applied to reduce the coagulation of nanoparticles in the nanofluid. Sodium dodecyl benzene sulfonate (SDBS) was widely used to disperse aqueous suspension.¹⁵,¹⁶ ζ potential and UV−vis spectrophotometric measurements have been used to quantitatively characterize colloidal stability of the dispersions.¹⁶−¹⁸ The relationship between the molecular...
structure of low molecular weight organic dispersants and their influence on the properties of nanosuspensions have been studied. These studies have given a good foundation for highly homogeneous, industrially enhanced heat transfer suspension fluids. In this article, we take notice on the suspension stability and attempt to clarify the correlations between the stability characteristics and thermal conductivity of nanofluids.

By changing the pH of the suspension to a control surface potential that can be reflected by \( \zeta \) potential, we systematically investigated the effects of the aqueous suspension pH, SDBS dispersant concentration, and the weight fraction of the dispersed nanoparticles on the suspension stability and enhanced thermal conductivity ratio. \( \zeta \) potential, particle size, and absorbency were measured to show the stability characteristic of the suspension system. The thermal conductivities of nanofluids were measured by a hot disk thermal constants analyzer and by a transient hot wire device. The results showed that the stability and thermal conductivity of nanofluids were highly dependent on pH values and SDBS concentration of nanosuspensions; an optimal pH value and optimal SDBS concentration can result in the highest stability and thermal conductivity of the nanofluids. It is expected to provide guidance to design nanofluids with excellent performance.

II. Experimental Section

A. Chemical. In this work, \( \text{Al}_2\text{O}_3 \) and Cu powder (Shenzhen Junye Nano Material Ltd.) with nanoparticle content \( >99.9\% \) was used in the study. The surface area was determined using the Micromeretic Tristar 3000. The particle size was measured using the X-ray disk centrifuge particle size analyzer v. 3.49. The average particle size and BET surface area of the powder were found to be 15–50 nm, 100 m\(^2\)/g (\( \text{Al}_2\text{O}_3 \)), and 25–60 nm, 30–50 m\(^2\)/g (Cu), respectively. The anionic surfactant SDBS in chemical grade, from Guangzhou Chemical Reagent Factory, was used for stabilizing the suspension. The water was purified by a Milli-Q Academic Millipore system. The pH was controlled using hydrochloric acid (HCl) and sodium hydroxide (NaOH) in analytical grade. All chemicals were used as received without any further purification.

B. Preparation of Nanofluids. Preparation of nanofluids is the first key step in applying nanophase particles to changing the heat transfer performance of conventional fluids. The nanofluid does not simply refer to a liquid–solid mixture. Some special requirements are necessary, such as even suspension, stable suspension, durable suspension, low agglomeration of particles, and no chemical change of the fluid. In this study, a two-step method was selected to prepare the nanofluids and is shown in Figure 1. To minimize particle aggregation and improve dispersion behavior, two effective methods were carried out. (1) Using SDBS as the dispersant. In previous research, we proved that among three dispersants (hexa-decyl trimethyl ammonium bromide (CTAB), poly(oxyethylene) (10) nonyl phenyl ether (TX-10), and SDBS) the most suitable dispersant is SDBS.\(^{15}\) (2) Using ultrasonic vibration. Ultrasonication is an accepted technique for dispersing the highly entangled or aggregated nanoparticle samples, but a longer time of high energy sonication can introduce defects.\(^{15,19}\)

C. Measurement of the Absorbency. The experiments were conducted using the 0.1 wt % alumina and copper nanosuspensions separately to measure the absorbency. Nanoparticles (0.1 g) and a water solution (99.8 g) with different SDBS dispersants (0.01, 0.05, 0.08, 0.1, 0.12, 0.14 g) were directly mixed in two 150-mL beakers. The precision of the electronic balance was \( \pm 0.0001 \) g. Then the two nanosuspensions were stirred thoroughly and ultrasonicated for at least 1 h in an ultrasonic vibrator (KQ2200DE Ultrasonic Cleanser, 100 W, Kunshan of Jiangsu Equipment Company). Twenty milliliters of each suspension was then poured into test tubes, and then the samples were allowed to deposit for seven days. The above solution for 2–3 mL of the suspensions was taken, and then absorbency of the suspensions was measured on a U-3010 spectrophotometer (Hitachi Instrument, Inc.) after depositing for 24 h. The pH value of the system was adjusted with HCl and NaOH solution by precise pH meter (PHS-25).

D. Measurement of \( \zeta \) Potential and Particle Size. In the investigation of the absorbency, 0.1 wt % nanosuspensions were used. However, for measurement of \( \zeta \) potential, a higher content of nanoparticles was not suitable. Instead, dilute 0.05 wt % alumina and Cu were selected. Different concentrations of the SDBS were added to the two suspensions. Then the suspensions were stirred thoroughly and ultrasonicated for at least 15 min, and 2–4 mL of the suspensions was transferred into a measuring cell. Then \( \zeta \) potential and particle size of nanosuspensions were measured by a Malvern ZS Nano S analyzer (Malvern Instrument, Inc.). The measurement was run at voltage \( V = 10 \) V and temperature \( T = 25^\circ \)C with switch time at \( t = 50 \) s. Each experiment was repeated at least six times to calculate the mean value of the experimental data. The pH value of the system was adjusted with HCl and NaOH solution by precise pH meter.

E. Measurement of the Thermal Conductivity of Nanofluid. Thermal conductivity of nanofluids was measured by means of the transient plane source method\(^{16}\) and a conventional transient hot wire device method. In the TPS method, the TPS element behaves as both temperature sensor and heat source. This novel method offers some advantages such as fast and easy experiments, wide range of thermal conductivities (from 0.02 to 200 W/m K), no sample preparation, and flexible sample size. The TPS element consists of an electrical conducting pattern of thin nickel foil (10 um) in the form of a double spiral, which resembles a hot disk, embedded in an insulating layer made of kapton (70 um). The working principle of the TPS method is a well established and specific rule; see ref 20. A Kapton insulated probe (design 7577) was successively dipped into the different nanosuspensions. 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 um. Then the thermal conductivity was measured by a Hot Disk thermal constants analyzer (Hot Disk, Inc.). The measurement was run at voltage \( V = 0.02 \) V and temperature \( T = 25^\circ \)C with switch time at 5 s.

In the conventional transient hot wire (THW) method, the device was mainly equipped with a homemade wheatstone bridge and the working principle is well established.\(^{3,17,21}\) In our THW apparatus, two platinum wires of 290- and 100-mm length were used (wire radius 0.03 mm and temperature factor 0.003853). The two platinum wires served as both the line source of heat and a thermometer. They were separately immersed in two cells with 30-mm diameter that contained sample nanofluids. The measurement was run at \( I = 100 \) mA, \( T = 25^\circ \)C with switch time at \( t = 5 \) s. If the time were longer, the temperature difference between the hot wire and the sample fluid would increase and free convection would take place, which would result in errors.

Different concentration nanosuspensions were prepared, which were stirred thoroughly and ultrasonicated for half of an hour. The pH value of the system was adjusted with HCl and NaOH solution.


by precise pH meter. Using the above two methods, we repeated each experiment at least six times to calculate the mean value of the experimental data. Before systematic experiments were performed on nanofluids, the two experimental systems were 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. By the TPS method, the experimental thermal conductivities of the deionized water were 0.5700 W/(m K) at 283 K, 0.6020 W/(m K) at 293 K, and 0.6243 W/(m K) at 303 K. By the THW method, the experimental thermal conductivities of the deionized water were 0.5690 W/(m K) at 283 K, 0.5980 W/(m K) at 293 K, and 0.6100 W/(m K) at 303 K. The base values were 0.5741, 0.5985, and 0.6171 W/(m K), respectively. Thus, the uncertainty on thermal conductivities was less than ±3.00%.

III. Results and Discussion

A. Influence of pH and SDBS Concentration on the Stability of Nanosuspensions. The stabilities of alumina and copper powder suspension in 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. Therefore, the study of the electrophoretic behavior through measurement of the ζ potential and the absorbency becomes important for understanding the dispersion behavior of nanoparticles in a liquid medium.15,17 The greater the ζ potential and the absorbency, the more stable the suspension.15 Figure 2 shows the change of ζ potential and absorbency for the two nanofluids as a function of pH with SDBS dispersants. Concentration of nanoparticles and dispersants for the measurement of ζ potential is 0.05 wt %, and concentration of nanoparticles and SDBS for the measurement of absorbency is 0.1 wt %: (a) \(\text{Al}_2\text{O}_3-\text{H}_2\text{O}\), (b) \(\text{Cu-}\text{H}_2\text{O}\).

As pH increases, the absolute value of ζ potential and absorbency reach the maximum value of \(\zeta_{\text{alumina}} = -40.1\ \text{mV}, \zeta_{\text{copper}} = -43.8\ \text{mV},\) and \(\zeta_{\text{alumina}} = 1.18, \zeta_{\text{copper}} = 0.95\). The electrostatic repulsion force between particles is the strongest, and the coagulated particles can be redispersed through mechanical force, and thus the dispersion stability of nanoparticles is the best. As the pH value continues to further increase, the concentration of the pH adjustment reagent (NaOH) in the system increases, which causes the compression of electrical double layer, thus lowering the absolute value of ζ potential of the particle surface and electrostatic repulsion force, and the suspension exhibits a poorer dispersion than in the cases of \(\text{pH}_{\text{Al}_2\text{O}_3} \approx 8.0\) and \(\text{pH}_{\text{Cu}} \approx 9.5\). Compared with the two nanofluids, both of them show similar behavior with pH change, and there exists an optimized value of pH (\(\text{pH}_{\text{alumina}} \approx 8.0\), \(\text{pH}_{\text{copper}} \approx 9.5\)) at which the ζ values and absorbency take their maximum value. In the region of \(2 < \text{pH} < 8.0\), \(\zeta_{\text{alumina}} > \zeta_{\text{copper}},\) the dispersion of alumina powder is better than that of copper powder at the same pH, but in the region of \(\text{pH} > 8.0\), \(\zeta_{\text{alumina}} < \zeta_{\text{copper}},\) the dispersion of alumina powder is poorer than that of copper powder at the same pH.

The effects of SDBS dispersant concentration on the stability of nanoparticles at pH \(\approx 8.0\) (alumina) and pH \(\approx 9.5\) (copper) are shown in Figure 3. It can be seen that, as the SDBS concentration increases, the absolute value of ζ potential and absorbency increase to the maximal value at SDBS-alumina \(\approx 0.10\%\) and SDBS-copper \(\approx 0.07\%\) weight fraction, yielding a well-dispersed system. As shown in Figure 3, a plausible dispersion mechanism of SDBS on both nanosuspension was as follows: SDBS can partially ionize in water and give anionic species, whereas alumina and copper nanoparticles carry positive charge in a neutral aqueous medium, having a strong affinity for anionic groups. When the SDBS concentration is lower, the negatively charged dodecylbenzene sulfonate formed by dissociation of SDBS is adsorbed on the positively charged surfaces of the nanoparticles and consequently the surfaces are negatively charged, and this leads to an electrostatic stabilization effect. With the increase of SDBS, on the one hand, the anion groups pushed into the adsorbed layer makes the absolute value of ζ potential increase, resulting in increasing the repulsive forces between the particles, thereby increasing the thickness of electrical double layer; on the other hand, large numbers of anion groups in the aqueous suspension hinder the particles from colliding and then reduce the collision probability between the particles. Here, the adsorbed phenyl sulfonic group and a significant electrical double layer were simultaneously presented. When more SDBS is added into the suspension, the concentration of Na⁺ increases with SDBS concentration increase, and...
the Na$^+$ group entering into the absorbed layer reduces the net charge of powder surface and makes the absolute value of $\zeta$ potential decrease, resulting in weak dispersion system. Our results agree with those described in ref 22, where the authors developed dispersants with molecular architecture tailored to the amphoteric alumina surface to control the dispersion stability.

Meanwhile, the values of particle size can really reflect the dispersion of nanoparticles in water. Therefore, the measurements of the particle size of the two nanofluids were also performed in the same process of $\zeta$ potential measuring. The results are shown in Figure 4. Compared with the two nanofluids, both of them show similar behavior with pH and SDBS concentration change, and there exists optimized values of pH (pH$_{\text{Alumina}} \approx 8.0$, pH$_{\text{Copper}} \approx 9.5$) and SDBS concentration (SDBS$_{\text{Alumina}} \approx 0.10\%$, SDBS$_{\text{Copper}} \approx 0.07\%$) at which the values of particle size take their minimum value $D_{\text{Alumina}} \approx 240$ nm, $D_{\text{Copper}} \approx 320$ nm, respectively. According to results of the $\zeta$ potential, particle size, and absorbency, for the two nanofluids pH$_{\text{Alumina}} \approx 8.0$ and pH$_{\text{Copper}} \approx 9.5$, SDBS$_{\text{Alumina}} \approx 0.10\%$ and SDBS$_{\text{Copper}} \approx 0.07\%$ could be selected as the operating pH and SDBS concentration.

**B. Influence of pH and SDBS Concentration on Thermal Conductivity of Nanosuspensions.** Surface chemical effects have only recently been considered as factors in the thermal conductivity of nanofluids. Studart et al. showed that simple acid treatment of carbon nanotubes enhanced their suspension stability and thermal conductivity in water. In our work, the effects of pH and SDBS on the thermal conductivity were also investigated. The thermal conductivity ratios of the two suspensions and the base fluid with SDBS dispersant as a function of pH with 0.1 wt % nanoparticles were presented in Figure 5. From the similarity data obtained from Al$_2$O$_3$ and Cu suspensions, one can see that for the both nanofluids at lower pH (pH$_{\text{Al}_2\text{O}_3} < 7.5$, pH$_{\text{Cu}} < 9.0$) the thermal conductivity ratio increases as pH increases, whereas at higher pH (pH$_{\text{Al}_2\text{O}_3} > 8.0$, pH$_{\text{Cu}} > 9.5$), the thermal conductivity ratio decreases as pH increases. Similar to the stability test, there also exists an optimized value region of pH (pH$_{\text{Al}_2\text{O}_3} \approx 8.0$, pH$_{\text{Copper}} \approx 9.5$) at which the thermal conductivity ratios take their maximum value ($K/K_{\text{Base}} = 1.07$, $K/K_{\text{Cu}} = 1.09$). 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 particles. When the nanoparticles are dispersed into water, the overall behavior of the particle–water

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interaction depends on the properties of the particle surface, which is one of the primary factors controlling nanoparticle aggregation. In the case of adding SDBS, the lower or higher pH values result in the lower surface charge and weaker repulsion between particles, which leads to the stronger agglomeration. On the other hand, as observed by \( \zeta \) potential, particle size, and absorbency measurement when the pH is close to the optimized value, the surface charge increases, leading to an increase in the \( \zeta \) potential on the nanoparticle surface, and the suspensions show significantly enhanced mobility of nanoparticles as a result of reduced agglomeration. The microscopic motions of the nanoparticles cause microconvection that enhances the heat transport process, which was also reported in ref 7. Therefore, we also attempt to link the concept of surface charges to the change in thermal conductivity ratio of nanofluids. The point to mention is that the charged surface sites seemingly provide much more effective passages through which heats or phonons go more efficiently. This conclusion was also presented by Lee et al. They showed that as the pH value diverged from the isoelectric point (PZC), the particles acquired larger charge and particle–particle repulsion increased, thus making the suspension more stable and resulting in high thermal conductivity.

Figure 6 presents the thermal conductivity ratio of the nanosuspensions and the base fluid with respect to the concentration of SDBS dispersant at pH\(_{\text{alumina}} \approx 8.0\), pH\(_{\text{copper}} \approx 9.5\) with 0.1% nanoparticles. For the base fluid, the thermal conductivity ratio starts to increase after a certain value of the dispersant concentration. In the present experiments, the highest thermal conductivity appears at 0.03% SDBS in deionized water solution, which means the thermal conductivity with SDBS 0.03% deionized water solution is higher than that of pure water. In the 0.1% Al\(_2\)O\(_3\) nanosuspensions, the thermal conductivity ratio increases slowly as SDBS concentration increases from 0 to 0.03%, and then decreases slowly at the region of 0.03% < SDB% < 0.1%, but in the region of SDB > 0.1% the thermal conductivity ratio decreases very quickly with an increase in the SDBS concentration. Obviously, for the Al\(_2\)O\(_3\) nanosuspensions and the base fluid, when more SDBS is added into the systems, the thermal conductivity ratios decrease very quickly. Owing to this trend, the addition of dispersant seems more noneffective in the nanosuspensions. This is because the heat transfer area becomes narrower because of the amount of the surfactants on the particle surface. Taking into account the combined effect of dispersion behavior and thermal conductivity, for the 0.1% Al\(_2\)O\(_3\) nanosuspensions the SDBS weight fraction 0.1% can be selected as an optimizing concentration. For the 0.1% Cu nanosuspensions, the trend of the variation of the thermal conductivity is very similar to those in the base fluid and Al\(_2\)O\(_3\) nanosuspensions with dispersant, and the 0.07% SDBS can be selected as an optimizing concentration.

From Figures 5 and 6, compared with the two results of TPS and THW, it was noted that both of them showed similar behavior with pH and SDBS concentration change, and the values of TPS were higher than those of THW. This may be caused by experimental errors. Figures 5 and 6 also show that, because of the higher thermal conductivity of copper nanoparticles than that of aluminum nanoparticles, thermal conductivity enhancement of copper–water nanofluids was greater than that of aluminum–water nanofluids.

C. Influence of the Weight Fraction of Nanoparticle on Thermal Conductivity of Al\(_2\)O\(_3\) Nanosuspensions. Figure 7 shows the enhanced thermal conductivity ratio of both nanofluids with the optimizing SDBS concentration as a function of nanoparticle concentration at pH\(_{\text{Al}}\) \( \approx 9.0\) and pH\(_{\text{Cu}}\) \( \approx 9.5\). The results showed that the thermal conductivity of nanofluid is enhanced approximately nonlinearly with the concentration of the nanoparticle, and the maximum thermal conductivity enhancements of nanofluids up to 11% for Al\(_2\)O\(_3\) and 13% for Cu were observed at the 0.4 wt% suspension. This enhancement of nanofluid thermal conductivity at low particle concentration was also reported recently by Keblinski et al. They showed that thermal conductivity enhancement in the nanofluid containing 20-nm Al\(_2\)O\(_3\) nanoparticles reached about 16% at 0.5 vol%. Figure 7 also shows the comparison between the experimental data for nanofluids and the values calculated from the theoretical model that considered the form of aggregates and other 3D shapes proposed by Landau and Lifshitz. The comparison result shows that the measured thermal conductivities were greater than those calculated from the theoretical model, because the theoretical model had not considered other factors that can significantly affect the nanoparticles heat transport in nanofluids, such as surface chemical effect, particle size, and particle Brownian motion. Thus, new assessments and mathematical models of the effective thermal conductivity for nanofluids will need to be proposed. Here, we also suggested linking the concept of surface charge states that can be adjusted by pH or surfactant to the change in effective thermal conductivity of nanofluids, which had been presented in refs 23.
17, 22, and 23. In this way, we can infer that the stability of nanofluids has good corresponding relation with the enhancement of thermal conductivity: at low concentration, the better dispersion behavior and the higher thermal conductivity.

**IV. Conclusions**

This article was concerned with the stability and thermal conductivity of Al$_2$O$_3$–H$_2$O and Cu–H$_2$O nanofluids under different pH values and SDBS concentration. The experimental results showed that the stability of nanofluids have good corresponding relation with the enhancement of thermal conductivity: at low concentration, the better dispersion behavior and the higher thermal conductivity. The stability of nanofluids could be improved by adding optimizing SDBS dispersant. As the pH and dispersant concentration of the nanofluid become closer to the optimized value, the surface charge increases because of more frequent attacks to the surface hydroxyl groups and phenyl sulfonic group by potential-determining ions (H$^+$, OH$^-$, and phenyl sulfonic group), and the colloidal particles get more stable and eventually alter the thermal conductivity of the fluid. Moreover, the use of Al$_2$O$_3$ and Cu nanoparticles as the dispersed phase in water can significantly enhance the thermal conductivity, and the enhancement increases with particle concentration under the optimized pH and SDBS concentration. The maximum thermal conductivity enhancements of up to 11% for Al$_2$O$_3$ and 13% for Cu were observed at the nanoparticle 0.4 wt % suspension. Thus, the combined treatment with both the pH and chemical dispersant was recommended to improve the thermal conductivity for practical applications of nanofluid. The experimental results were also compared with the theoretical model and showed that the experimental results were remarkably higher than predicted by the theoretical model for solid–liquid mixtures. Although the mechanisms behind the exceptionally enhanced thermal conductivity of nanoscale colloidal solutions nanofluids are still not clear, we hypothesize that, at low concentration of nanoparticles, nanoscale convection induced by the Brownian motion of the nanoparticles causes enhanced mixing and hence increased heat transfer beyond what simple conduction-based theories predict.

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