

Effect of Surface Hydration and Interfusion of Suspended Silica Nanoparticles on Heat Transfer

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ABSTRACT

Experimental results of silica nanofluids consisting of 10nm or 20nm silica particles have been performed. Particle size, zeta potential and the CHF values under different volume concentrations are provided, and agglomeration structures are seen to affect the critical heat flux of NiChrome wire immersed in a pool of water. The critical heat flux (CHF) of the wire does not increase monotonically with concentration. CHF decreases when particle concentration is increased depending on the particle shape and the hydroxylated surface of the nanoparticles.

Keywords: nanofluids, hydration layer, critical heat flux, zeta potential

In recent years, nanofluids, consisting of nanometer sized particles and fibers dispersed in base liquids, have been proven to be effective in enhancing the performance of future energy transport systems. The novel heat transfer fluids exhibit the anomalously enhanced thermal properties. In addition, they have the desirable characteristic of not settling down or clogging up the pores. All these characteristics make nanofluids promising for nanotechnology-based heat transfer applications [1-4]. Three features of nanofluids including anomalously high thermal conductivities at very low nanoparticle concentrations, strongly temperature dependent thermal conductivity and significant increases in critical heat flux (CHF) have been found till now. In addition, the Brownian motion of the nanoparticles, the microconvection around the nanoparticles, layering of liquid molecules at the particle-liquid interface, ballistic nature of heat transport in nanoparticles, and nanoparticle clustering are considered as possible mechanisms responsible for heat transfer enhancement [5-7].

Arguably, the Brownian motion of the nanoparticles and the microconvection around the nanoparticles only play a minor role [9], and the physical structure of layering of liquid molecules at the particle-liquid interface by itself can not contribute to the enhancement of heat transfer [10]. Thus, the mechanisms responsible for the heat transfer enhancement seem to be the chemical structure of solid and liquid interface and the nature of heat transfer inside the nanoparticles and between solid and liquid.

Vassallo et. al. [11]] showed as much as 200% increase in critical heat flux (CHF) over that for the base liquid in silica-water suspension. Here CHF is defined as the point at which the immersed silica wire broke. This tremendous improvement in CHF in water was partially attributed to the formation of wire coating and more nucleation sites for bubble initiation. A more recent paper by Milanova and Kumar [12] reports the effect of the negatively charged silica nanoparticle suspension in boiling conditions in water for different particle size, particle concentration, and under various pH conditions and ionic concentration. All these studies show that the chemical structure of the hydration layer on the particle-liquid interface plays a critical role in addition to the number density of the nanoparticles inside nanofluids and the surface area of nanoparticles. Since the hydration layer on the solid-liquid surface determines the shape of the nanoparticles, the aggregating structure of nanoparticles cluster and the ion density on the surface of the nanoparticle, it determines the way heat is transferred between the solid particles and the liquid.

In this paper, we will report our recent experimental results conducted by silica nanofluids consisting of 10nm or 20nm silica nanoparticles. The zeta potential, the particle size, and the CHF values under different volume concentrations are provided, and the aggregation and agglomeration structures and the effective diameters of silica nanoparticles under various volume concentrations will be discussed. In addition, the hydration layer on the silica-water interface will be presented, and its effect on heat transfer and viscosity of nanofluids will be discussed in detail.

Experimental Procedure

Silica nanofluids are prepared by diluting an aqueous nanosolution with de-ionized (DI) water at concentrations between 0.1% and 2%. An emphasis was put on lower concentrations (<0.5%) because they are of more practical importance. Higher concentrations change some physical properties of the fluid like color, density, viscosity, etc., which is undesirable and are examined only out of scientific interest. Silica nanoparticles are a commercial product of Alfa Aesar and were obtained in a suspension of two concentrations – 15% and 40%, at basic pH (10.5 and 9.5) corresponding to 10nm and 20nm particle sizes, respectively, which were confirmed by TEM analysis. The density of the as received solution is 1.3g/cm³. The

agglomeration characteristics and the diameter of silica nanoparticles at different volume concentrations are systematically determined by zeta potential and particle size analyzer. Electrophoretic Light Scattering (ELS) method and Dynamic Light Scattering (DLS) technique were adopted to characterize the potential and size of the nanoparticles in the fluid.

In addition to the particle size measurement, zeta potential also was measured. When the thickness of the diffuse layer declines, the particles exhibit near-zero zeta potential and a subsequent particle-particle contact occurs. Hence, zeta potential conveys information on the possible behavior of the particles within the solution.

Good dispersion of the solid phase was achieved by magnetic stirring for half an hour and ultra-sonicating for fifteen minutes. Viscosity readings of the prepared nanofluid were taken with a digital Brookfield viscometer before and after sonication in order to determine the effect of the ultrasound on the surface chemistry and agglomeration characteristics of nanosilica.

The heat transfer characteristics of silica nanofluid were systematically examined through pool boiling experiment, following the procedure given in [12]. A NiChrome wire (NiCr), serving as a thermocouple, was completely immersed in a glass container and current was applied at equal increments and time intervals. The temperature of the wire surface was maintained above the saturated temperature for water. The pool boiling curve was generated by plotting the heat flux q in kW/m^2 obtained from the current and resistance. The wall superheat was obtained from the resistance of the NiCr material [13]. CHF is the point at which the burning gradually progresses to a critical point when the wire breaks.

Results and Discussion

The surface chemistry and electrostatic potential of silica nanoparticles will be studied in detail because of their influence on agglomeration rate, distortion in shape, formation of an ordered second fixed layer (hydration layer). The high pH at which SiO_2 naturally exists implies high charge on the particles surface, mutual repulsion and attraction, and directed motion in the presence of electric current. A number of studies reveal a hydroxylated surface [14-16] with OH groups bond to SiO_2 skeleton. The ability of the silanol groups to form hydrogen bonds with water molecules, i.e. adsorb water molecules at the interface will prove significant in viscosity effects and heat transfer enhancement, which will be discussed later. The size and curvature of the particles are aspects that determine the extent of hydration, dehydration, and recombining of the functional groups at the surface. The density distribution and the number of the silanol groups determine the overall charge of the particles, their repulsion potentials, and the overall stability of the solution. Figure 2 shows a model of a charged silica nanoparticle with OH groups attached to surface silicon atoms. Bigger diameter particles intrinsically possess more silanol groups which provide greater repulsive forces and less agglomeration. This study reveals

higher zeta potential value for 20nm-size particles ($\zeta_{20\text{nm}} = -27\text{mV}$) compared to the one for 10nm-particles ($\zeta_{10\text{nm}} = -23.5\text{mV}$), where both are at 0.2% concentration. At this loading, no agglomeration effect are observed based on the particle size measurement results, therefore the difference in the electrostatic potential is solely due to the particle size and curvature.

At concentrations as low as 0.1, 0.2, 0.3% the shape of nanosilica is spherical but with increase in the loading, the potential barriers weaken (fig.1A), which leads to increase in the effective diameter. The particle size with further increase in concentration doubles (from 10nm it goes up to 18nm, and 20nm for 1% and 2%). The dynamic light scattering technique gives us an accurate Gaussian distribution of the particles in the sample with a narrow variance. The shape of the particles plays an important role in the redistribution of the surface charge and TEM analysis was done in order to confirm the already obtained particle size and shed light to the change in the shape of the agglomerates (fig.1C.) As the silanol groups are farther apart (small positive radius of curvature) they form fewer hydrogen bonds between them, which make them more readily removable at elevated temperatures. Therefore 10nm-size particles are generally expected to have lower zeta potential in absolute value. At concentrations greater than 0.4% the zeta potential is not high enough to provide repulsion and particles start to form agglomerates of two (as viewed by the TEM micrographs). At 0.5% a mutual interfusion (of 2-3particles) is observed which leads to a change in curvature from positive to negative at certain locations (fig.2A, B). The surface OH groups are brought together by the concave curvature, water is formed and retained in these crevices which results in an overall discharging. This statement is in accordance with the experimental values for the zeta potential, which was seen to absolutely increase asymptotically. This trend is followed by the particle size, which after a concentration of 0.5% is constant. Although the average diameter does not change, the shape undergoes distortions and reduction in the total surface area, which could impact the heat transfer properties of the nanofluid, as analyzed further.

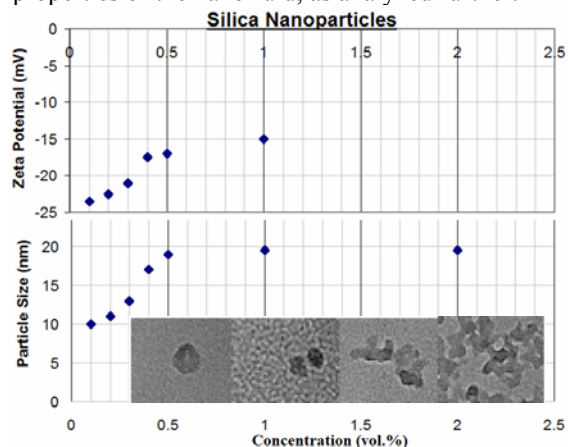


Figure 1: A. Zeta potential measurements; B. Particles size analysis; C. TEM micrographs.

Silica nanoparticles have been diluted in de-ionized water without the addition of any additives or stabilizers. The water molecules selectively orient towards the silanol groups with their oxygen atoms towards the surface. The process of water adsorption takes place simultaneously with the redistribution of the OH groups at the interface, i.e. places where curvature effects contribute to the formation of water. It has been shown [17] that $\text{Si}_s\text{OH}:\text{OH}_2$ bond is weaker compared to $\text{SiOH}:\text{OH}_2(\text{OH}_2)$. The following interactions are given by the equations with the corresponding bonding energy:

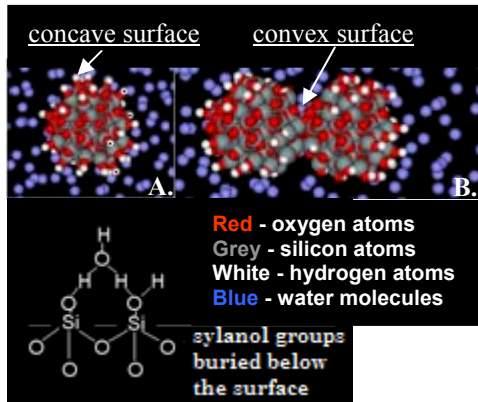
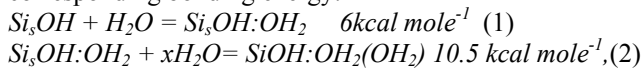


Figure 2: A. Silica nanoparticle built using the crystallographic method; B. Two silica nanoparticles simulating agglomeration just before a critical concentration.

Where Si_s represents silicon atom at the surface. The higher bonding energy between the water molecules within the ordered liquid layer compared to the one at the particle-liquid adsorption state is contributed to fact that water is intrinsically stable in a cluster of 4-5 molecules as it is in bulk. This ordering is approximately 3 molecular units and does not exceed 0.3nm. [18] The thickness is not expected to change with particle size, although it has greater influence on the smaller particle diameters due to the relative ratio of liquid and solid. Similar increase in the density profile at the solid interface was observed by [19] through Molecular Dynamics Simulations (MD) and numerically found to be in the order of 1-3nm.

The viscosity of 10nm- and 20nm- sized silica at varying concentrations is experimentally determined (fig. 3A) and shows an increase of up to 17% at concentration as high as 1% and 2%. However, if we apply ultrasound prior to the measurements, the viscosity drastically decreases by approximately 5 to 10%. It hasn't been determined if this is a direct result of removal of the hydration layer at some places on the surface, breaking of the formed clustered (as viewed by the TEM analysis), or both. These results conducted for 10nm and 20nm silica nanoparticles are representative of the extent of agglomeration, surface charging, and hydration and their combined effect. At lower

loadings the viscosity increases solely due to the fixed water layer, which tends to move along with the particle. Particles are not agglomerated at this stage and they exhibit non-Newtonian behavior, due to their small size and negligible weight. The applied ultrasound could not only serve as a source of good dispersion, but also as a continuous “breaker” of the hydrogen bonds between the solid surface and the liquid layer, due to the difference in the bonding energy between liquid-liquid and liquid solid interactions. The breakage of the immobilized layer is attributed to the smaller energy barriers for the silanol – water bond.

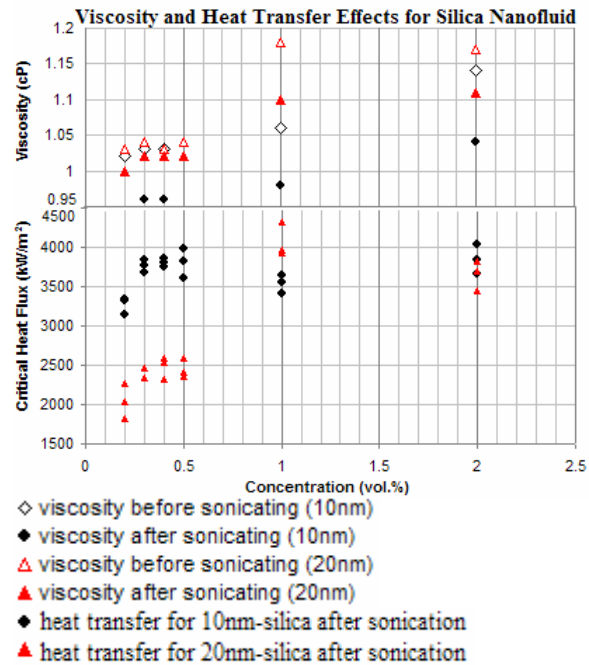


Figure 3: A. Viscosity; B. Critical Heat Transfer for Silica nanofluid.

At higher concentrations, agglomerations of 2-3 nanoparticles start to evolve and the viscosity increases drastically. After the process of ultra-sonication, these aggregates seem to be broken, because at 1% and 2% both 10nm and 20nm silica steadily shows a decrease in viscosity in the order of 7-8%. The effect of sonication on heat transfer and CHF of nanofluids is not known. Although the ultrasound waves break particle aggregates, they also break the hydration layer, which improves the heat transfer due to its ordered structure. The sites where desorption of water layer has taken place become discharged which may possibly lead to further agglomeration during the pool boiling experiment. So when current is applied, the particles tend to collapse onto the NiCr wire. It has been experimentally observed that the lower the zeta potential of the particles, the thicker the deposition on the thermocouple. The effect of thickness and porosity of the deposition on bubble size and intensity of growth on heat transfer has been discussed in another work. [21]

Although it has been shown that smaller particles – 10nm vs. 20nm generally exhibit better heat transfer characteristics [12] due to the smaller surface area to volume ratio for the later, clusters of a few particles are theoretically postulated [20] to increase the thermal transport due to the thermal resistance of the voids. Therefore not only the size of the formed agglomerations, but also the shape of the clusters determines the heat transfer properties of the nanofluid. The surface area of the particles considerably reduces when two particles fuse into one another, compared to the case when they merely touch.

Referring to Fig. 3, it has been established that the increase in nanoparticle size will decrease the heat transfer and the critical heat flux at the point of wire breaking. It is also known that the critical heat flux can also increase due to an increase in concentration. Thus, two opposing effects on CHF are taking place, one due to the change in the surface area and another due to the increase in the number of particles in the suspension, i.e., particle number density. The change in CHF at different ranges of concentrations can be explained using the following table.

Table 1: Effect of concentration on CHF for 10nm particles

Region	Conc, %	Particle size, nm	Surface area	Number density	CHF
1	0.1 - 0.2	10	Maintains	Increases	Increases
2	0.2 - 0.5	10 - 20	Increases	Decreases	Increases
3	0.5 - 1.0	20	Increases/ maintains	Decreases	Decreases
4	1.0 - 2.0	20	Maintains	Increases	Increases

Referring to Table 1, in Region 1, the particle size and the surface area stay constant, but the number density doubles due to the doubling of concentration and CHF slightly increases. In Region 2, the average particle size increases to twice the original diameter due to agglomeration, the surface area increases, and the number density decreases. The rate of increase in surface area is higher than the rate of decrease in number density, and hence the CHF increases first sharply up to 0.3% concentration, and stays approximately constant in the rest of the region. In Region 3, as more particles start agglomerating, although the surface area either maintains or increases, the number density drops drastically. The cumulative effect is that the CHF decreases in this region. Finally, in Region 4, the surface area does not increase any further, but the number density increases with further concentration, so the CHF increases.

In summary, the critical heat flux of the wire does not increase monotonically with concentration as theory predicts. CHF depends on the agglomeration characteristics, particle shape and the hydroxylated surface of the nanoparticles.

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