

## Research Paper

# Experimental study of the interactivity, specific heat, and latent heat of fusion of water based nanofluids



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## HIGHLIGHTS

- The increase in corrosion due to the presence of nanoparticles is characterized.
- Experimental difficulties in previous studies are discussed in relation to the identified corrosion reaction.
- The latent heat of fusion is reported for alumina and titania nanofluids.

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## ABSTRACT

In this paper, the unsuitability of water-based nanofluids in aluminum environments is demonstrated. In addition, the specific heat capacity ( $c_p$ ) of water-based nanofluids with alumina or titania nanoparticles is investigated, with the  $c_p$  reported for these frozen nanofluids. The results confirm the accuracy of the oft referenced Model II in determining the  $c_p$  of these nanofluids. The latent heat of fusion for the nanofluids is also reported. Alodined-aluminum sample pans were used to reduce the rate of the water-aluminum reaction enough such that reliable data was obtained. Initial measurements of nanofluids were performed in aluminum sample pans; the nanoparticles are hypothesized to have catalyzed the aluminum and water reaction which resulted in unrepeatable data. The synthesis of the byproduct of this reaction, the mineral bayerite, is confirmed. Room temperature electrochemical studies confirm that the presence of nanoparticles increases the corrosion rate.

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## 1. Introduction

As engineering solutions become more optimized, new materials are needed to continue to improve our technology. In particular, nano-scale materials design has moved to the forefront of materials engineering.

In many industrial or mechanical processes fluids perform vital cooling or lubrication functions. Nanofluids consist of nanometer sized particles suspended in a base fluid. The suspended particles, because of their small size, have physical properties dominated by the electric field of the atoms on the surface. These nanoscale effects can cause large shifts in the bulk properties of the nanofluids. For example, CuO nanoparticles suspended in water by 20 wt% have demonstrated heat conductivity 60% higher than water alone [1]. This vast increase in heat conductivity theoretically increases

the transfer of heat into and out of the fluid, allowing for less fluid to perform the same amount of cooling. This theoretical benefit has led to nanofluids being investigated as nano-scale cooling fluids or replacements for large scale coolants. In addition, nanofluids have been investigated for use as coolants in spacecraft [2].

Several previous studies have investigated the specific heat capacity ( $c_p$ ) of various nanofluids. Zhou and Ni [8] reported the  $c_p$  of eight different concentrations of alumina and water nanofluids between 20 and 45 °C, but his experimental section indicates DSC scans were performed to 70 °C. Zhou et al. describes the results of their experiments above 40 °C as relatively scattered, or unrepeatable, suggesting some experimental difficulties. They found that the  $c_p$  decreased exponentially with increasing volume concentration of nanoparticles.

Murshed [10] used the double hot wire technique to measure the  $c_p$  of alumina, titania, and carbon nanotube nanofluids in 15 concentrations at room temperature. This is in contrast to Zhou and Ni, who used differential scanning calorimetry (DSC). Murshed's correlated well with the previous studies, although they

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were only conducted at one temperature. O'Hanley et al. [9] used DSC to measure the  $c_p$  of CuO, SiO, and Al<sub>2</sub>O<sub>3</sub> nanofluids in 12 concentrations and found comparable results for temperatures between 35 and 55 °C. They measured the  $c_p$  up to 70 °C, however, and did not report results above 55 °C. Finally, Barbes et al. [7] studied the  $c_p$  between 23 and 63 °C and results which correlate with the previous authors. They did not cite any technical difficulties and reported all of their results.

For applications in which heat loss to the environment is a possibility, understanding the behavior of the coolant as it freezes is necessary for the proper engineering of the application. In addition, the specific heat while frozen and the latent heat are required to understand the performance of nanofluids as heat storage media. These properties have not been measured and reported in the literature.

In this study, the latent heat of fusion and frozen specific heat are reported for two nanofluids. The frozen specific heat is found to follow a similar pattern as for liquids, were the specific heat decreases linearly with increasing mass concentration of nanoparticles. In addition, the latent heat of fusion is found to exponentially decrease with increasing concentration of nanoparticles. Finally, during initial testing, anomalous results were acquired which were similar to anomalies experienced by other authors. The anomalies were due to the water and aluminum reaction being catalyzed by the presence of nanoparticles. This reaction between aluminum and the nanofluids is confirmed and discussed.

## 2. Experimental procedure

Alumina (Al<sub>2</sub>O<sub>3</sub>) nanofluids were provided by Nanostructured & Amorphous Materials, Inc in 20 wt% concentration. The 10 wt%, 5 wt%, and 2 wt% concentrations were created by mixing 20 wt% concentration nanofluid and deionized water. Titania (TiO<sub>2</sub>) nanofluids were provided in 1 wt% and 3 wt% concentration. Samples were verified to maintain dispersion after repeated fast cooling cycles in a liquid nitrogen bath, and slow cooling cycles in ice. No sedimentation was observed after samples melted. Dynamic light scattering was used to verify particle size (30 nm ±) before and after testing. Particle size did not change.

Specific heat capacity and latent heat was measured by differential scanning calorimetry, utilizing a TA Q20 DSC. Samples were weighed by a Mettler-Toledo Xp2U Micro Balance to a precision of one µg. Samples were processed in hermetically sealed alodined aluminum sample pans. Experiments were run according to the method outlined in ASTM E1269, using sapphire and ice as standards [3]. Nitrogen was used as a purge gas for the alumina and water nanofluids. Helium was used as a purge gas for the titania and water nanofluids.

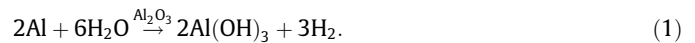
A Kaiser Optical RXN-1 Raman microscope system was used to acquire Raman spectra. The excitation wavelength is 785 nm, with a power of 5 mW at the sample. The low wavenumber detection limit of the system is 150 cm<sup>-1</sup>.

Electrochemical studies were undertaken by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) using an 88 mm<sup>2</sup> aluminum (99.9999% pure) working electrode, platinum counter and a standard calomel electrode as reference. Polarization studies were performed after EIS tests at room temperature at a sweep rate of 0.5 mV/s in the range of 250 mV relative to the open circuit corrosion potential using a Bio-Logic instrument Model VSP 0508 potentiostat. Electrochemical impedance spectroscopy measurements were conducted with the same electrode arrangement in the frequency range 10 kHz–100 mHz at an amplitude of 10 mV vs open-circuit. The results obtained from EIS were analyzed and fitted to equivalent circuit using Z Fit contained in the EC-Lab [23]. Polarisation data was analyzed by in-

house software referred to as Symadec. De-ionized water was mixed with sodium sulfate to produce a 0.1 M solution. This was used as a reference for the corrosion of aluminum in water. Alumina nanofluid in 20 wt% was diluted to 10 wt% with 0.1 M sodium sulfate solution.

## 3. Results and discussion

Initial DSC experiments were undertaken with aluminum sample pans. Our investigation revealed that the nanoparticles had catalyzed the reaction [4]:



This reaction produced a powder residue and released hydrogen gas. This gas was responsible for the release of the hermetic seals causing initial results to be unreliable. Raman scattering spectra of the residue is presented in Fig. 1. This spectrum closely matches the spectra for the mineral bayerite (Al(OH)<sub>3</sub>) [5], with the addition of a peak at 361 cm<sup>-1</sup>, characteristic of alumina nanoparticles, confirming that the nanofluid was reacting with the sample pans. Use of alodined aluminum pans slowed the reaction sufficiently for reliable and repeatable measurements to be taken.

No articles have been found which report the reaction between the aluminum sample pans and the nanofluids. Several authors have reported results for alumina nanofluids in the temperature range which accelerates the reaction [6–10]. Zhou et al. describes the results of their experiments above 40 °C as relatively scattered, or unrepeatable, suggesting that a reaction may have been occurring in their samples. In addition, Narvaez [11] reported observing nanoparticle settling after several hours of operation in an environment containing aluminum. Narvaez also reported evidence of the nanofluids boiling during testing, with higher concentrations of nanofluids exhibiting increased evidence for boiling. Nanoparticle settling combined with evidence of a gas being produced suggests that their experiment may have suffered from a nanofluid catalyzed aluminum and water reaction. Studies which did not report anomalies in their results used Hastelloy sample chambers [7], or reported incomplete results without comment [9].

As shown in Fig. 2, EIS experiments demonstrated that the presence of nanoparticles dramatically decreased the charge transfer resistance. In addition, the corrosion potential (E<sub>corr</sub>) shifts to more negative values with the addition of nanoparticles. Together these suggest that the corrosion rate of aluminum in the nanofluid is at least ten times greater than in pure water. This further con-

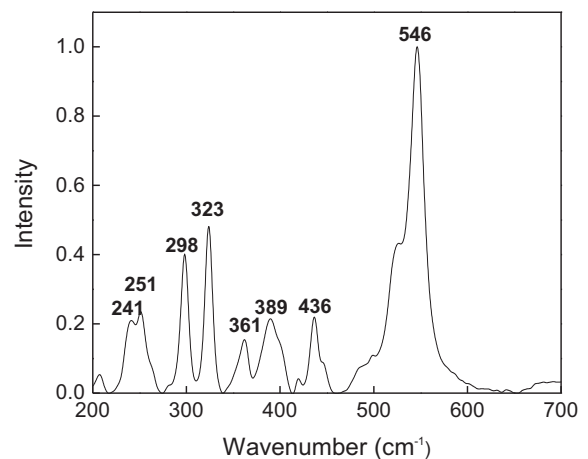


Fig. 1. Raman spectra of oxidation residue in sample pans containing nanofluids. Note that the 361 peak is the signature peak for alumina nanoparticles. Other peaks are characteristic of the mineral bayerite.

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