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An investigation of thermal characteristics of eutectic molten salt-based nanofluids

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ABSTRACT

The thermal properties of the eutectic molten salt-based nanofluids are characterized in this work. A robust correlation describing the effects of nanoparticle concentration, temperature and nanoparticle diameter on the specific heat is established for both the Solar Salt-based nanofluid ($NaNO_3$-KNO_3) and the binary eutectic carbonate salt (Li_2CO_3-K_2CO_3) with Silica nanoparticles. Moreover, other properties are investigated using the available data in the literature. Additional experimental works are necessary to clarify the behavior of the molten salt-based nanofluids. The established correlations given here are presented for the first time in the literature.

1. Introduction

Addition of nano-size particles in common fluids increases the thermal characteristics of these mixtures. These innovative classes of fluids referred to as Nanofluids [1], are colloidal suspension of dispersing nanoparticles (2–100 nm). The most studied nanofluids have been the aqueous-nanofluids, where the base fluid is water or glycols. Various works have been published regarding their enhanced thermal characteristics [2–3] and their application [4]. More recently it has been proposed that the addition of nanoparticles can improve the thermal characteristics of molten salts [5]. These new class of molten salt-based nanofluids are sometimes referred to as nanosalts. The molten salts are very useful for high-temperature thermal energy storage systems (TES), principally for concentrated solar power (CSP) systems [6], because they are very stable at high temperatures and they can store thermal energy and release it when required. Typical molten salts used in CSP are Alkali-Nitrate, Alkali-Carbonate or Alkali-Chloride. Among these, the most common molten inorganic salt used in CSP applications is a binary eutectic mixture of sodium nitrate salt and potassium nitrate salt ($NaNO_3$-KNO_3 as 60:40 ratio by weight), which is commonly called the Solar Salt. The addition of nanoparticles in molten salts is essential to increase the thermal performance of the thermal energy storage system and enhancing their thermophysical characteristics.

The most recent works in enhancing the thermal properties of molten salt are related to the specific heat [7]. When the nanoparticles are added, the specific heat shows a variation in its value. For an aqueous nanofluid with Alumina Nanoparticles [1], it is commonly accepted in literature that the addition of nanoparticles to the water reduces the effective specific heat of the nanofluid while the value of the effective thermal conductivity increases. For example, Zhou and Ni [8] have presented an experimental investigation of the specific heat of an aqueous nanofluid with alumina nanoparticles using a Differential Scanning Calorimeter (DSC). Their results have demonstrated that the specific heat decreases while the volume fraction increases up to 21.7% and that there is a good agreement with the thermal equilibrium analytical model. Khanafer et al. [9] have demonstrated a robust correlation for an effective specific heat for water-based nanofluid with Alumina nanoparticles. A critical synthesis of thermophysical properties of aqueous nanofluid was performed by Khanafer and Vafai [10], where they compared the discrepancies between various experimental works and theoretical models in describing the heat transfer enhancement characteristics of nanofluids.

While for aqueous nanofluid the specific heat is well understood, several works in literature have shown controversial results regarding the effective specific heat capacity of nanosalts [5,11–17]. The most studied nanosalts in the literature are the Solar Salt and the eutectic salt of Li_2CO_3-K_2CO_3 (62:38%wt ratio). The experimental investigation of Shin and Banerjee [11] is one of the early studies of the effective specific heat of a nanosalt. The nanosalt was prepared within a two-step process. A DSC instrument was used to measure the specific heat of the molten salt. Their results have shown an enhancement of the effective specific heat by 24% compared to the pure salt.

Transmission and scanning electron microscopy (TEM and SEM) has

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Nomenclature

c_p	Specific heat
d_p	Nanoparticle diameter
T	Temperature

Greek symbols

Φ	Mass fraction

Subscripts

p	Nanoparticle

been employed to verify the dispersion uniformity after the addition of nanoparticles. The SEM and TEM images of nanosalts, have revealed that uniform needle-like nanostructures have been formed within the nanosalts. Hu et al. [15] experimentally analyzed the specific heat capacity of Solar Salt with different mass fractions of alumina nanoparticles. They used the same preparation technique of Shin and Banerjee [11] to compose the nanosalt. A Differential Scanning Calorimeter based on the sapphire method was employed to measure the specific heat capacity and the results have shown an enhancement between 2% (lowest concentration of alumina nanoparticles) and 8.3% (highest concentration). Moreover, the SEM images have shown the formation of needle-like structures, which can be responsible for the specific heat enhancement.

Qiao et al. [16] studied both experimentally and numerically the specific heat capacity of three molten salts, sodium nitrate, potassium nitrate and lithium nitrate using Silica nanoparticles at different concentrations (0.5%wt up to 4%wt). They have shown that the specific heat of the nanosalt is lower than the results obtained by the MD simulations. Moreover, the SEM images have shown that the nanosalt at 0.5%wt presents some nanostructures similar to sticks near the nanoparticles, while the nanosalt at 4%wt presents the phenomenon of agglomeration. This aspect could explain why the highest value of specific heat is reached at 1% concentration of Silica nanoparticles.

Chieruzzi et al. [17] have investigated the thermal properties of the potassium nitrate with 1.0%wt for three different types of nanoparticles: Silica, alumina and a mixture of Silica-alumina. Their results have shown that different nanoparticles induce a change in the shape of the heat flow curve obtained from a DSC, modifying the value of the onset melting temperature of about 3 °C and the value of latent heat (enhanced by 9.5%). The addition of Silica nanoparticles increases the specific heat while the addition of alumina nanoparticles decreases its value. The SEM images have shown that Silica nanoparticles disperse more effectively than the alumina nanoparticles. Pertinent aspects of specific heat capacity of high-temperature nanosalts are summarized in Table 1.

Our investigation, shows that there are substantial disagreements within the existing experimental data in the literature. Sanchez et al. [18], have mentioned that the procedure for the preparation of the molten salt and the method of measurement profoundly affects the experimental results for the specific heat. In particular, they have analyzed the influence of the type of crucible, the sample weight and the ambient humidity. They have shown that the highest precision occurs when using a large amount of the sample (more than 30 mg), prepared inside an inert atmosphere and using a T-zero hermetic crucible during the measurements. Despite the substantial variation in the experimental data, it is possible to find an accurate correlation when employing the Silica nanoparticles. The aim of this work is to develop a robust empirical correlation based on the latest available experimental data for the specific heat for both solid and liquid phases for the molten salt-based nanofluids as a function of nanoparticles diameters, temperature and mass fraction.

2. Results and discussion

The data given in Table 1 is utilized to come up with an effective correlation for eutectic molten salts seeded with Silica nanoparticles. At this time it is not possible to perform a proper investigation for the other nanoparticles due to the lack of data and disagreements within the existing data.

2.1. Specific heat of Solar Salt with silica nanoparticles (liquid phase)

Table 2 displays the attributes for the available literature where the Solar Salt at liquid phase with Silica nanoparticles has been studied. The works of Chieruzzi et al. [14] and Riazi et al. [19] have been used for the cross-validation procedure. Effect of variations in nanoparticle diameter and mass fraction on the temperature averaged specific heat is displayed in Fig. 1. It can be seen that the maximum enhancement for the average specific heat occurs at 1% mass fraction. The temperature averaged specific heats at different diameters and mass fractions are shown in Table 3 [18–21]. We have utilized the MATHEMATICA software to obtain an empirical correlation relating the specific heat of a liquid solar salt for different nanoparticle diameters, mass fractions and temperatures through a multiple regression analysis. The correlation for the specific heat for the Solar Salt with SiO_2 nanoparticles in the liquid phase is established as:

$$c_p = \begin{pmatrix} -2.470\times10^{-4}d_p - 1.797\times10^{-6}d_p^2 + 1.775\times10^{-8}d_p^3 + \\ 7.299\times10^{-1}\phi + 3.067\times10^{-2}\phi d_p - 9.012\times10^{1}\phi^2 + 2.215\times10^{3}\phi^3 \end{pmatrix} T + 1.615T^{-5.497\phi+2.12\times10^2\phi^2} \tag{1}$$

The specific heat c_p is evaluated in J/g °C, the nanoparticle diameter d_p is in nanometer and the mass fraction ϕ is non-dimensional. This correlation covers the following range of variations in mass fraction, temperature and nanoparticle diameters:

$$0.005 \le \phi \le 0.02,\ 250 \le T(^\circ C) \le 450,\ 5 \le d_p(nm) \le 60$$

The properties of the regression coefficients are given in Table 4. This correlation has 10 Degrees of Freedom and a R^2 regression of 99%. The Akaike information criterion (AIC) [23] has a value of − 2870 and the standard error of regression is 0.016. It consists of a power law equation, where the exponent depends only on the mass fraction; a linear dependence with the temperature with a third order polynomial for both the particle diameter and the mass fraction. The results for this correlation are shown in Fig. 2.

It should be mentioned that there is relatively limited data available for obtaining the correlations. As such a cross-validation procedure is useful in detecting if a model is overfitted. This procedure assesses how well a model fits new data that has not been used in the model estimation process. When a model is not capable of predicting the new data, it will be an indication that the model is probably tailored to the specific data points that are included in the sample and not generalizable outside the sample. To see if our data is overfitted, we proceed with a cross-fitting procedure using Riazi et al.'s [19] data. They found that the specific heat in liquid phase for Solar Salt with Silica Nanoparticle at 1% and 20 nm in a range of 250–350 °C is 1.74 ± 0.026 J/g °C. For the same set of parameters, our correlation returns a value of 1.66738 at 300 °C (midway temperature value in the considered range). The error between Riazi et al. [19] data and the model is 4%. Therefore, the reliability of our model is acceptable. Another experimental work by Chieruzzi et al. [14] was used to make yet another cross-validation check. Our correlation provided a good estimation of the experimental data by Chieruzzi et al. [14] as well. For example, from their work [14], for a temperature range between 250 and 300 °C the temperature-