The effect of nanoparticle morphology on the specific heat of nanosalts

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A B S T R A C T

Enhancing the specific heat capacity of molten salts by nanoparticle dispersion has emerged as a means to reduce the capital costs of thermal storage for concentrating solar thermal power plants, enabling cheaper solar electricity. Although several studies have shown near 30% enhancement in the specific heat of nanosalts other studies have reported a decrease of similar magnitude. In order to explain discrepancies reported in the literature, this study investigates the influence of various nanoparticle morphologies and preparation methods on the specific heat of nanosalts, which has not been systematically explored. To date, the extent of initial dispersion and the dispersion stability have only been reported on an ad-hoc basis in the literature. In the present study surface chemistry and sonication energy are controlled independently during preparation. By controlling both of these factors, the change of specific heat in nanosalts, results of this study present achieving up to 18% enhancement in specific heat of nanosalts by preparing an optimal nanosalt with distinctive nanoparticles.

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1. Background

Nanoparticles dispersed in salts, or nanosalts, have emerged as a means to enhance the liquidus specific heat capacity of molten salts, which are commonly used in medium-to-high temperature thermal energy storage (TES) systems. The TES system plays an important role in solar concentrated thermal (CST) plants as it provides dispatchability – allowing excess heat to be stored during daytime – thereby profitably extending peak production after peak sunshine. This both enhances the economic feasibility of CST and better aligns renewable energy supply with demand. Depending on the capacity of the system, thermal storage can represent 10–30% of total plant capital cost [1,2]. At present, thermal storage is the least developed solar thermal component with only a few CST systems incorporating a TES world-wide [3]. As such, it is a major area for research and development and for potential cost reduction [1]. Since 2010 researchers have proposed that it may be possible to enhance the specific heat capacity of molten salts by adding nanoparticles to create more efficient TES systems [4].

Simple analytical models, based on mixing theory, have been proposed for calculating the effective specific heat of nanofluids. Based on these it is clear that lower effective specific heat values should result for most base fluids when nanoparticles are added. This is because most solids (including nanoparticles) have relatively low specific heat values when compared to fluids. Experimental studies on molecular liquids, water and oils, have

confirmed this behaviour and have showed a decrease in the specific heat of water and ethylene glycol based nanofluids varying between 2–45% reductions, depending the type and concentration of the nanoparticles used [5–12]. However, several recent studies, summarized in Table 1, have shown enhancement are indeed possible when nanoparticles are mixed with liquidus salts since these have some of the lowest specific heat capacities found in fluids.

Shin and Banerjee [13] proposed a new model to calculate the specific heat of nanosalts based on their suggested specific heat enhancement mechanism [14]. This model takes into account mass fractions and specific heat values for the base fluid, i.e. the molten salt, the nanoparticle, and the semi-solid layer of liquid molecules surrounding the nanoparticles. The semi-solid layer, or compressed layer, is believed to have several times higher specific heat values than the bulk molten salt. Due to the high nanoparticle surface area found in the nanosalt, the total contribution of the semi-solid layer creates a considerable enhancement on the overall effective specific heat of nanosalt. This model is written as [13]:

$$C_{p,nf} = \frac{\rho_{np}V_{np}C_{p,np} + \rho_c V_c C_{p,c} + \rho_f V_f C_{p,f}}{\rho_{np}V_{np} + \rho_c V_c + \rho_f V_f} \qquad (1)$$

where C_p is specific heat, ρ is the density, and V is the volume fraction. Subscripts ns, np, c, and f represent property values of the nanosalt, nanoparticle, compressed layer, and bulk phase of the molten salt. The thermophysical property values (density and the specific heat capacity) of the molten salt and the nanoparticles can be obtained from the literature. Values for the compressed layer are yet to be confirmed, but Shin and Banerjee [13] have proposed

Nomenclature

C_P	specific heat capacity	V	volume fraction
CST	concentrated solar thermal	ρ	density
DCS	differential scanning calorimetry		
DLS	dynamic light scattering	*Subscripts*	
IL	ionic liquid	ns	nanosalt
MD	molecular dynamics	np	nanoparticle
TEM	transmission electron microscopy	c	compressed layer
TES	thermal energy storage	f	fluid

that the specific heat of compressed layer should be assumed to be near 4 times higher the specific heat of molten salt – corresponding to the specific heat value of the solid salt at its melting point. However, this value was represented by the measurement of specific heat of molten salt by an adiabatic scanning calorimeter, which may also account for the heat of fusion during melting phase. In the same study, Molecular Dynamics (MD) simulations indicated that an average thickness for this layer was approximately 1 nm which is used to calculate the compressed layer volume, although it can vary significantly for different particles and molten salts. Using these values, Shin and Banerjee [13] showed that Eq. (1) to be in good agreement with their experimental results. In order to be able to use Eq. (1) for different nanosalts a good understanding of the extent of dispersion and the characteristics of the compressed layer (its thickness and specific heat) is required.

Table 1 summarizes all the specific heat measurements of nanosalts reported to date in the literature. Although most of the studies have shown enhancements in specific heat are possible, some have reported reductions compared to the pure molten salt.

Most studies have used the two-step aqueous mixing method proposed by Shin and Banerjee [15] to synthesize nanosalts. In this method nanoparticles are first mixed with the salt(s) in distilled water, which is then sonicated (via bath or probe sonicator) to ensure a homogenous dispersion. After 100–120 min sonication the aqueous solution is placed on a hot plate to evaporate the water. After heating at temperatures between 70–200 °C, dry powder samples of nanosalts are obtained.

Although this general process has been followed in the literature, a wide range of (sometimes contradictory) results have been reported. There are several important steps in the preparation, including the initial particle synthesis method, which were either overlooked or inconsistently controlled in some of the literature which could play a significant role in the effective specific heat of nanosalts. For example, different researchers have procured nanoparticles from several different manufacturers which indicates that the studies began with a diverse set of morphological characteristics, which would impact their dispersibility and specific heat results. We also hypothesize that several other preparation steps including sonication time/intensity and drying time/temperatures are critical to control to achieve consistent results. Ultimately, the aim is to prepare a stable, homogenous dispersion of nanoparticles in nanosalts, and it is not clear all previous studies have succeeded. This study investigates the effect of various preparation issues with respect to the resulting nanosalt morphology to demonstrate how big of a role these have on the effective medium's specific heat as compared to reported results.

1.1. Nanoparticle stability in nanosalts

Above their liquidus temperature, salts are non-volatile liquids that consist of a cation coupled with an anion [25,26]. Their ionic bonds are much stronger than the Van der Waals forces found in molecular fluids, giving them a different structure on the nanoscale [27]. Salts that are used for preparing nanosalts have smaller ions, as compared to the low-temperature Ionic Liquids (IL) often discussed in research literature, which result in higher melting points and decomposition temperatures, which are beneficial for TES systems.

While the operational temperatures of these liquids are very desirable, their high ionic strengths screen off the electrostatic charge stabilization forces which are generally used to make nanoparticles stable in molecular liquids [28,29]. This creates a stability challenge for nanosalts, since common aqueous dispersion methods are not necessarily applicable. Despite the fact that electrostatic forces are not available for dispersion stability in ILs, there are other forces which may be utilised [30,27]. Colloidal stabilisation in ILs was discussed by Ueno and Watanabe [27] who identified two forces which can be harnessed at the IL-solid interface: (a) IL-based steric force and (b) IL-based solvation force.

The steric force is due to strong adsorption of bulky IL ions to a particle surface, preventing close approach and aggregation. The steric force is expected to be strongest for highly charged or polarisable particle surfaces. The IL-based solvation force is analogous to the hydration forces [31], but extends over greater distances. These forces are able to stabilise particles against attractive van der Waals forces in ILs. However, studies by Smith et al. [32,33] (using static and temperature-dependent light scattering measurements) have shown that the long-term stability of silica particles in ILs is mainly due to solvation forces. Thus, solvation forces could also play a significant role in particle stability in nanosalts. However, to date the effectiveness of solvation force on particle stabilisation in molten salts with smaller ions, compared to ILs, at high temperatures has not been explored. Fig. 1 illustrates schematic comparison of colloidal stabilisation in molecular liquids and molten salts.

The stability of nanoparticle dispersion in nanosalts could explain some of the discrepancies found in the literature on the measured specific heat of nanosalts. Based on Eq. (1), smaller nanoparticles should cause higher enhancement due to their higher surface area. However, results reported by Dudda and Shin [21] contradicts that as they found larger nanoparticles have resulted in higher enhancements. On the other hand, Tiznobaik and Shin [18] report a fixed percentage of enhancement regardless of the nanoparticle size. Since nanoparticle cluster size cannot be measured in the molten phase for high melting temperature salts, the degree of nanoparticle dispersion is not clear in these studies. Clustering could result in significantly different compressed layer volumes, causing different enhancements. Another difference can be seen in two other studies [20,22] where $NaNO_3$–KNO_3 (60:40) eutectic salt have been studied with 13 nm Al_2O_3 nanoparticles. The first study reveals 5.9% enhancement in specific heat by addition of 1wt.% Al_2O_3 nanoparticles and the latter shows −1.25% reduction. One main difference between these two studies is the manufacturer of the nanoparticles that were procured – as seen in Table 1 – which could also cause different stability performance