Specific heat of metal oxide nanofluids at high concentrations for heat transfer

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ABSTRACT

In this work isobaric specific heat capacity measurements were performed for five different nanofluid sets designed as dispersions up to 15% mass concentrations of MgO, ZnO and ZrO_2 in pure ethylene glycol as well as ZnO and ZrO_2 in an ethylene glycol + water mixture at 50:50% in volume. Isobaric specific heat capacities for the three dry metallic oxide nanopowders and the two base fluids were also studied with the aim of contributing to elucidate on the heat capacity behavior of nanofluids for heat transfer applications. Measurements were carried out by using a quasi-isothermal Temperature-Modulated Differential Scanning Calorimetry (TMDSC) method in the temperature range from 243.15 to 473.15 K. Base fluid results were compared with literature data to validate the measurement procedure. The specific heats for nano-sized materials here presented were also compared with literature data for bulk-sized of the same metallic oxides. In addition, the experimental values were used to evaluate the goodness of different models existing in literature to predict or correlate the specific heat capacities. A new fitting equation was also proposed to correlate specific heats of nanofluids as a function of the base fluid, nanoparticles as well as nanoparticle concentration.

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1. Introduction

Ever since the harmful effects of greenhouse gases were recognized, some scientific communities have focused on methods or technological advances which mitigate the global warming impact. The storage or exchange of thermal energy through a heat transfer fluid is present in most of industrial or domestic applications. It is estimated that about 70% of the energy is produced in or through the form of heat [1]. Therefore, a way to reduce the carbon footprints would be to limit energy consumption by enhancing the performance of heat exchange systems and minimizing energy loss [2,3]. Typical methods to enhance passively the heat exchange capacity include using micro-structures to increase the effective interchange area of the heat exchanger, employing materials with high thermal conductivity to manufacture the heat exchangers, raising the flow rate, increasing the temperature or using thermal fluids with a high heat-transfer performance [4–6]. However, most exchangers are usually made of aluminum, cooper or other metals so little improvement can be done in this feature, while the harsh working conditions of industrial applications prevent the use of micro-structures to modify the interchange area. The rise in flow

rate involves increasing the pumping power which sometimes reduces the overall efficiency. Thus, obtaining heat thermal fluids with improved properties is one of the best methods to enhance exchange performance in real thermal installations [6–8].

Nanoparticle suspensions in conventional fluids, nanofluids, have emerged as a new generation of thermal fluids due to their developed heat transfer capabilities. Unlike the millimeter- or micrometer-sized particle slurries studied in the past, the nanoparticles used to design nanofluids are "similar" in size to the molecules of base fluid, and so exhibit a higher stability with little gravitation settling over relatively long periods of time [9]. Proof of the interest raised by nanofluids as new heat transfer fluids is the high number of works carried out in this field during the last years [1,10–14]. Up to now, many studies on the effect of nanoparticle properties (shape, size, volume fraction, etc.) and the thermal conductivity of carrier fluids were reported. In convective heat transference using nanofluids, the heat transfer coefficient depends not only on the thermal conductivity but also on other properties, such as the specific heat, density and dynamic viscosity, which influences strongly the heat transfer characteristics. However, reports on density or isobaric heat capacity, C_p, of the carrier fluid are still limited in the literature [7,15–17].

Basically the specific heat capacity of a material represents its ability to exchange sensible thermal energy to a temperature

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Nomenclature

A, B, C	fit parameters for specific heat capacity correlations
$AAD\%$	percentual Average Absolute Deviation
$A_{dh/dt}$	amplitude of modulated heat flow, J/(g s)
$A_{dT/dt}$	amplitude of dT/dt rate, K/s
A_T	amplitude of modulate temperature, K
C_p	isobaric specific heat capacity, J/(K g)
C_{pv}	isobaric volumetric heat capacity, J/(K cm^3)
DSC	Differential Scanning Calorimetry
EG	ethylene glycol
h	enthalpy, J/g
k_{Cp}	calibration constant for specific heat capacity measurements
$\dot{q}$	heat transfer rate, J/s
T	temperature, K
t	time, s
T'	nominal MDSC temperature
T_0	reference temperature from Vajjha and Das correlation
TMDSC	quasi-isothermal Temperature Modulated Differential Scanning Calorimetry

$\dot{V}$	volumetric flow rate, cm^3/s
vol%	volume fraction
W	water
wt.%	percentual nanoparticle mass concentration

Greek symbols

ρ	density, g/cm^3
ϕ	nanoparticle volume concentration
φ	nanoparticle mass concentration
λ	wavelength, nm
ω	angular frequency, 1/s

Subscripts

bf	base fluid
exp	experimental
nf	nanoparticle
nf	nanofluid
pred	predicted

change. Thus, precise C_p values are necessary in energy balances since, for example, the heat-exchanged in a heat exchanger can be assessed through the temperature difference between the inlet and outlet, the mass flow rate and the specific heat capacity of the working fluid [18,19]. Moreover, this thermophysical property is one of the key parameters for describing nanofluid performance in a thermal installation. The conventional correlations for laminar and turbulent flow conditions usually include the Prandtl dimensionless number which depends on C_p value [20–22]. Precise specific heat capacity data are also needed to calculate other related properties like diffusivity or dynamic thermal conductivity [23,24]. At low volume fractions, the heat capacities (and densities) of nanofluids are expected and have been experimentally observed to be similar to those characterizing the base fluid [25]. However, a better understanding of the solid nanoparticles effect on nanofluid heat capacities is needed, especially at high volume fractions for which scarce studies were carried out.

Although some researchers [19,24,26,27] use setups based on own designs to perform nanofluid specific heat capacity measurements, Differential Scanning Calorimetry (DSC) techniques are predominant in literature [28]. The Temperature-Modulated Differential Scanning Calorimetry (TMDSC) technique, included within DSC methods, has as main advantages its ability to measure the absolute specific heat capacity without the need of making multiple runs as well as inferior distortions from experimental parameters [2]. Most of the reported works on specific heat capacity use nanofluids based on metallic oxides, as it occurs with other thermophysical properties. Those heat capacity studies of Al$_2$O$_3$ [4,7,15,16,18,19,24,26,27,29–32], SiO$_2$ [7,19,33–35], CuO [20,36–39] or TiO$_2$ [30,40] nanofluids should be highlighted. This is due to the fact that metallic oxides are relatively cheap and can be produced more easily than other nanoparticles which would warrant a more direct consideration for practical applications [41,42]. Even so, there are also nanofluid heat capacity reports on multi-wall carbon nanotubes [6,23,43] or metallic nanoparticles [2,7]. Regarding studied base fluids, it is a common practice to use water [6,15,19,24,29,36,37,39,44], ethylene glycol [2,7,15,27,36,38] or ethylene glycol + water mixtures [6,7,19,20,26,30,33]. They are the heat transfer mediums more widely used in industrial applications. In addition, there are other works reporting isobaric heat capacities of nanofluids based on ionic liquids [23,45], mineral oils [7], or eutectic mixtures [16,34,46–49]. According to Timofeeva

et al. [50] the nanoparticle and base fluid parameters with a higher influence on nanofluid isobaric heat capacity are nanoparticle concentration, nanoparticle material and base fluid type, while other parameters such as shape or size of nanoparticles, or Zeta potential do not affect this property.

In the absence of available experimental data, different equations based on mixing theory for ideal gas mixtures and classical-statistical mechanism have been applied in literature to estimate the isobaric heat capacities of nanofluids [29]. Recently, some authors [16,21,43] have also proposed different models to describe nanofluid isobaric specific heat capacity behavior. Vajjha et al. [21] and Pakdaman et al. [43] equations correlate nanofluid heat capacities as function of temperature and nanoparticle concentration, after experimentally studying nanofluids based on different metallic oxides in an ethylene glycol + water mixture [21] and multi walled carbon nanotubes in a heat transfer oil [43]. Otherwise, Shin et al. [16] studied nanofluids using an eutectic salt as base fluid and suggested a new model which takes into consideration the effect that the chain-like nanostructure formation have on the specific heat capacity of salt-based nanofluids.

Materials with high thermal conductivity, specific heat, and density are generally beneficial to increase heat transfer performance [29,50]. However, since solids typically exhibit inferior specific heat capacity than those of liquids, nanofluids are also expected to present lower heat capacities than their corresponding base fluids [29,51]. Thus, nanofluid specific heat decreases as the nanoparticle concentration rises based on existing experimental [4,7,19,26,29,30,33,36,37,40,43] and theoretical [52,53] results. Nevertheless, some studies [7,23,30,34,39,49] found the contrary behavior, i.e. isobaric heat capacity increases with the concentration of nanoparticles, which can be attributed to the addition of dispersants into the dispersions as pointed out by Sharul et al. [28] or the formation of chain-like structures between base fluid and nanoparticles as suggested by Shin et al. [16,35]. The conclusion drawn from the literature review is that more studies are necessary to determine well the volume concentration and temperature dependences on nanofluid heat capacities.

The objective of the present work is to determine the heat capacity of nanoparticles and nanofluids, and compare the obtained results with available theories. The nanofluids were designed as dispersions up to 15% in mass of three different metallic oxide nanoparticles, MgO, ZnO and ZrO$_2$, in pure ethylene glycol