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Experimental and theoretical analysis of NiO nanofluids in presence of surfactants

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ABSTRACT

This study presents a combined experimental and theoretical analysis of the stability of NiO nanofluid systems based on a base fluid composed of the eutectic mixture of diphenyl oxide and biphenyl in presence of surfactants. The base fluid is used as a heat transfer fluid in concentrated solar energy and the surfactants were used to analyse the stability of the nanofluids: Benzalkonium Chloride (BAC) and 1-Octadecanethiol (ODT). The stability was analysed experimentally by using UV–vis spectroscopy, particle size and ζ potential measurements. The experimental results indicate that the presence of BAC as surfactant enhance the stability of the nanofluids. Molecular dynamic calculations were performed for three systems (75% BAC, 75% ODT and 75% BAC-75% ODT) to understand the behaviour of both surfactants in the stability of the nanofluid. The analysis of the radial distribution functions (RDFs) and spatial distribution functions (SDFs) revealed a competition of ODT with both base fluid and NiO nanoparticles that explains why the BAC surfactant favoured the formation of stable NiO nanofluid over that with ODT.

1. Introduction

The colloidal suspension of nanomaterials in a fluid, named as nanofluid, is known to improve several properties of the fluid, such as isobaric specific heat [1–6] or thermal conductivity [2,3,7–14]. These nanofluids show different applications, typically related with heat transfer process. One of these applications is in Concentrating Solar Power (CSP) plants. CSP is an emerging technology of renewable energy for the objective established by society of confronting the growing demand for energy while minimizing environmental harm. The main problem with CSP is its high cost compared with conventional energy sources. For this, one of the option for reducing costs or for improving the global efficiency of the plants is the improvements of the efficiency of the heat transfer processes that take place in these plants. In this sense, the use of nanofluids which improve the thermal properties of the heat transfer fluid (HTF) typically used is of great interest.

An important property of the nanofluids is their physical stability, related with agglomeration of sedimentation of the nanoparticles. Nanoparticles in a base fluid tend to agglomerate because of the van der Waals attractive forces and after can sediment [15]. But, it is also well-known that the thermal conductivity of nanofluids is higher for those nanofluids with higher stability [16–22].

In this sense, in this work, an experimental and theoretical analysis of the physical stability of NiO nanofluids is shown. The main objective of the work is focused both on the study of the physical stability and to scrutinize the interactions between the NiO with the surfactants in the non-polar HTF at room temperature that explain the stability through molecular dynamics. The nanofluids studied were prepared using commercial NiO nanoparticles and a base fluid composed of the eutectic mixture of biphenyl and diphenyl oxide, which is a typical HTF used in CSP plants. The effect of the addition of two surfactants, benzalkonium chloride (BAC) and 1-octadecanethiol (ODT), individual and combined in equal parts (75%), on the physical stability of the nanofluids was analysed from an experimental and theoretical perspective. So, the physical stability was analysed experimentally from UV–vis spectroscopy, particle size and ζ potential measurements. Experimental results indicated the presence of BAC stabilized the systems as compared to the ODT. Thus, from a theoretical viewpoint, a theoretical study was performed based on molecular dynamics calculations focused on trying to explain why the presence of BAC stabilizes the NiO nanofluid systems. Therefore, three nanofluid systems (75% BAC, 75% ODT and 75% BAC-75% ODT) were analysed for comparison purposes at the same

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temperature (300 K). The structural properties of the systems were obtained by analysing their radial distribution function (RDF) and spatial distribution function (SDF). The analysis of these functions enabled us to identify the sites of the interaction between the NiO and the two surfactants and the base fluid. The theoretical results show the existence of a competition between ODT with both base fluid and the metal oxide nanoparticle that explains why the presence of BAC favoured the formation of stable nanofluids. As a novelty, it is worth of mention that the analysis of the theoretical results shows the presence of an inner layer around the NiO where the incorporation of BAC molecules play an important role in stabilizing the systems.

2. Materials and methods

2.1. Experimental

The nanofluids analysed in this study were prepared using the two-step method [23]. The first step involves the synthesis of nanoparticles and the second is the dispersion of the nanomaterial into the base fluid. In this study, the base fluid was a commercial heat transfer fluid composed of the eutectic mixture of biphenyl ($C_{12}H_{10}$, 26.5%) and diphenyl oxide ($C_{12}H_{10}O$, 73.5%), supplied by The Dow Chemical Company©, model Dowtherm A. Both compounds show practically the same vapour pressure so the mixture is usually treated as a single compound. The nanomaterial added to the base fluid was commercial NiO nanoparticles (purity ~99.8%, density 6670 kg m^{-3} at 298.15 K, Sigma-Aldrich).

An initial colloidal suspension of NiO nanoparticles in the base fluid was prepared with a nanoparticle mass concentration of 0.01 wt%. Also, Benzalkonium chloride (BAC, Sigma-Aldrich©) or 1-Octadecanethiol (ODT, purity: 98%, density 0.847 kg m^{-3} at 298.15 K, Sigma-Aldrich©) was added in order to analyse the effect of the surfactants and the nature of them in the stability of the nanofluids. The proportion of surfactant added was 75% with regard to the nanoparticle mass concentration. Also, a nanofluid adding a mixture of both surfactants (75% of each) was prepared. In all cases, the complete mixture was homogenized for 20 min using a Sonics Vibra Cell VCX 750 sonicator (~50 W output power) in a bath at 288 K. Aliquot of the initial solution was extracted to prepare a nanofluid with the NiO nanoparticle mass concentration of $1 \cdot 10^{-4}$ wt%, adding the base fluid necessary to obtain 100 mL of nanofluid. The new nanofluids underwent sonication under the same conditions as the initial nanofluid. So, in this work we tested the stability of nanofluids based on NiO nanoparticles adding 75 wt% of BAC (75% BAC), 75 wt% ODT (75% ODT) and an mixture of 75 wt% BAC and 75 wt% ODT (75% BAC-75% ODT).

The nanoparticles used were characterized using x-ray diffraction (XRD) to determine the crystalline and Transmission Electron Microscopy (TEM) to observe the size and shape of the nanoparticles. XRD pattern was recorded using a D8 Advance diffractometer supplied by Bruker® with Cu-Kα radiation. The scan conditions were from 10 to 75° in 2θ with a resolution of 0.02°, 40 kV and 40 mA. TEM analysis was performed using a JEM-2100F microscope supplied by Jeol©. On the other hand, the nanofluids were characterized to analyse their stability. Stability is one of the key concepts in colloidal suspensions due to the thermal properties depending on it. UV–vis spectroscopy (UV–vis) can provide a measurable characterization of stability by evaluating the extinction coefficient of a suspension [24]. To this end, UV–vis spectra were recorded using an OceanOptics© DH-2000-Bal halogen lamp and an OceanOptics© USB-2000 + monochromator operating in the 400–880 nm wavelength range, using a glass cuvette at room temperature. The sedimentation process can be analysed from particle size measurements. Particle size and size distribution was measured at room temperature by Zetasizer Nano ZS using the dynamic light scattering (DLS) principle as a simple method for analysing suspension stability and particle size measurements in solution [15,25]. Also, ζ potential measurements were performed using a Zetasizer Nano ZS supplied by Malvern Instruments Ltd. This system uses the principle of Electrophoresis Light Scattering (ELS), in which charged particles suspended in a fluid are attracted toward the oppositely charged electrode when an electric field is applied. The ζ potential measurements were performed applying a potential of 120 V at 313 K, and the results were analysed using the Huckel model, typical for low dielectric constant fluids.

2.2. Computational framework

2.2.1. Force field

The TraPPE-EH force field [26,27] was used to describe the intra and intermolecular interactions of the HTF fluid (diphenyl oxide/biphenyl blend). The TraPPE-EH force field treats aromatic rings and the directly connected atoms as rigid entities. The phenyl rings were treated as rigid but were allowed to rotate with regard to each other around the C1—C1′ bond of the biphenyls.

The intra and intermolecular interactions of the BAC and ODT surfactant were described by using the TraPPE-UA force field [28–30]. For the alkyl groups, a fully flexible model based on single interaction sites (pseudo-atoms) was used to represent a carbon atom together with all of its bonded hydrogen atoms (CH_3 and CH_2). The polar nitrogen and sulphur atoms, and the carbon atoms bonded to them, were treated as explicit interaction sites in a rigid unit.

TraPPE-EH and TraPPE-UA potentials use Lennard-Jones (LJ) and Coulomb potentials to represent non-bonded interactions

$$u_{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{1}$$

where r_{ij}, ε_{ij}, σ_{ij}, q_i, q_j, and ε_0 are the distance between interaction sites i and j, the LJ well depth, the LJ diameter, the partial charges on interaction sites i and j, and the permittivity of vacuum, respectively.

The simulation of the metal oxide nanoparticle was performed using a rigid unit cell of 27 atoms (14 nickel atoms and 13 oxygen atoms) with point group Fm-3 m. The non-bonded force field was described using the setting parameters of Buckingham (B) and Coulomb potentials for this metal oxide nanoparticle [31,32]

$$u_B(r_{ij}) = A_{ij}\ exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{2}$$

where A_{ij}, ρ_{ij} and C_{ij} are parameters for interactions between sites i and j. An alignment of Buckingham parameters to Lennard-Jones potential functions was performed to combine the Buckingham parameters of the nanoparticle and the Lennard-Jones parameters of the HTF fluid, BAC and ODT surfactants. The parameter relationship between both potentials (Eqs. (3) and (4)) was adopted from [33] and applied by simultaneously imposing an equal force constant at the well depth minimum (R) and an equal mean inter-atomic energy from the point of equilibrium to the point of total separation (D).

$$\frac{u_B}{D}(r_{ij}) = 0.6471\ exp\left(14.3863\left(1-\frac{r_{ij}}{R}\right)\right) - 1.6471\left(\frac{R}{r_{ij}}\right)^{5.6518} \tag{3}$$

$$\frac{u_{LJ}}{D}(r_{ij}) = \left(\frac{R}{r_{ij}}\right)^{12} - 2\left(\frac{R}{r_{ij}}\right)^{6} \tag{4}$$

2.2.2. Simulation details

Molecular dynamics simulations were performed with the DLPOLY code [34] in the canonical ensemble (NVT) using a Nose-Hoover thermostat and periodic boundary conditions. The initial configurations were built with the PACKMOL code [35] providing cubic boxes in which the length of the box sides was chosen to keep the density of the experimental HTF at 298 K (1059 kg m^{-3}). A time step of 0.5 fs