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Thermal Conductivity, Viscosity and Stability of Al_2O_3-Diathermic Oil Nanofluids for Solar Energy Systems.

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Abstract

Nanofluids have excellent potentiality in the field of heat transfer fluids and particularly for solar energy systems such as concentrated solar power plants. However they present many issues to be fixed in order to have a large diffusion. One of these is sedimentation. In this paper, stability, viscosity, FT-IR spectra, cluster size and thermal conductivity of Al_2O_3 – Therminol nanofluids have been investigated as heat transfer fluid in high temperature solar energy systems.

Al_2O_3 – Therminol nanofluids have been prepared to investigate and to improve stability of the suspensions, varying temperature during mixing with magnetic stirrer, amount of surfactant and sonication time with ultrasonic vibrator. Stability of the nanofluid samples was investigated through backscattering technique and for cluster size analysis Dynamic Light Scattering (DLS) was used. Thermal conductivity of the sample was measured in order to evaluate not only the effect of both volume fraction and temperature, but also the influence of the surfactant (oleic acid).

Stability of nanofluids depends on temperature during sample preparation and sedimentation phenomenon is inversely proportional to temperature during mixing with magnetic stirrer.

Influence of concentration of surfactants was studied through preparation of samples having a solid phase particles concentration of 0.3 %vol, 0.7 %vol and 1.0 %vol, respectively. The presence of surfactants creates some bonds with nanoparticles, which mainly helps nanofluids long-term stability.

On the other hand, the presence of surfactants inside the nanofluids does not influence their thermal conductivity. From DLS measurements, a dependence of cluster size on volume fraction was observed for all nanofluid samples.
Experimental data show: viscosity increases by increasing volume concentration; nanofluids with and without surfactants show a non-Newtonian behavior and viscosity of nanofluids increases by increasing cluster size.

Keywords: solar energy system, nanofluids, stability, thermal conductivity, diathermic oil.

Nomenclature

Greek symbols

τ shear stress [Pa]

μ coefficient of viscosity [mPas]

γ shear strain rate [1/s]

ϕ particle volume fraction [%]

μ_{bf} viscosity of the base fluid (diathermic oil) [mPas]

μ_{nf} viscosity of nanofluids [mPas].

Abbreviations

DVLO Derjaguin, Verway, Landau and Overbeek

CNTs Carbon Nanotubes

SN Ratio of surfactants with the nanoparticles

T transmitted light flux

BS Backscattered light flux

TSI TurbiScan Stability Index

DLS Dynamic Light Scattering

ATR Attenuated total reflectance

CMC Critical micelle concentration.

1 Introduction

In the latest past years, the scientific community has revealed great interest in the application of nanofluids in the field of heat transfer, particularly for renewable energy applications. Nanofluids are colloidal suspensions, constituted by two phases: a dispersing one (as oil, water, glycol, etc.) and a dispersed one (nanoparticles of metals or metal-oxides). Lomascolo et al. [1] discussed about the effect of nanoparticles properties on thermal conductivity of nanofluids. Zadeh et al. [2] carried out an hybrid optimization algorithm to analyze a solar parabolic trough collector based on nanofluids. A mathematical model, that describes the thermal performance of a solar pond with nanofluids, has been studied by Al-Nimr et al. [3]. Sardarabadi et al. [4] investigated the effect of SiO_2 water based nanofluid on a PV/T system and Mahian et al. [5] discussed on application of nanofluid in solar energy systems. Besides, Meibodi et al. [6] studied the effects of SiO_2/water-Ethylene Glycol nanofluids on efficiency of a solar thermal collector. Heat transfer as well as pressure drop in energy systems can be influenced by particle size and volume fraction [7] and particle shape [8]. Thermal conductivity of Cu-diathermic oil nanofluids has been investigated by Colangelo et al. [9]. They obtained that thermal conductivity is inversely proportional to the particle size. Sedimentation is one of the most important issues of nanofluids used as heat transfer fluids in solar collectors, highlighted by many papers. Yang et al. [10] investigated on stability of ammonia-water nanofluids and of the influence of surfactants. Experimental results showed that amount of surfactant to reduce sedimentation phenomenon depended on solid phase used in the suspensions. Colangelo et al. [11] proposed a modified flat solar thermal collector to reduce sedimentation phenomenon when nanofluids are employed. Besides an enhancement of thermal efficiency of flat solar thermal collector has been observed using Al_2O_3-water based nanofluids [12].

From theoretical studies, the sedimentation rate is due to the possible collisions, which occur among nanoparticles, and to their concentration. Derjaguin, Verway, Landau and Overbeek (DVLO) [13 14] introduced a theory, according to which the stability of nanofluids is due to the combination of the van der Waals force (attractive) and the double layer force (repulsive). Some procedures to stabilize nanofluids are: ultrasonic vibration; utilization of surfactants; variation of the base fluid pH, which influences the Zeta potential around the nanoparticles, as described by Sharma et al. [15] and Ghadimi et al. [16].

Choi et al. [17] used Al_2O_3 and AlN nanoparticles to prepare transformer oil based nanofluids. In order to stabilize suspensions, they tested a technique based on the utilization of surfactant as oleic acid. They found that the excess of surfactant was a disadvantage, due to the creation of reverse micelles, which increased the sedimentation in the nanofluids. They used a membrane filtration to remove the excess of oleic acid inside the suspension, thus proving that only a little concentration of surfactant was sufficient to stabilize the nanofluids. Mahian et al. [18] investigated on stability of ZnO nanoparticles in a mixture of glycol and water. Effects of 2 surfactants, Gum Arabic and DI Ammonium Hydrogen Citrate, have been studied. Better stability has been obtained by using DI Ammonium Hydrogen Citrate with a weight ratio of surfactant to nanoparticles of 1:1.

Xuan et al. [19] presented the results of suspensions of Cu - transformer oil applied to enhance thermal conductivity. In this case, researchers have introduced oleic acid in a percentage related to the concentration of nanoparticles (22 wt%). Nanofluids with surfactants have also been sonicated with ultrasonic vibrator to reduce further sedimentation.

Saeedinia et al. [20] performed an experimental study on CuO suspensions in oil. In this case, no surfactants were added into the suspension, in order not to influence thermal conductivity. The stabilization of these nanofluids was partially achieved by sonicating the nanofluid with an ultrasonic device. The complete sedimentation appeared after one week.

Liu et al. [21] investigated the improvement of thermal conductivity of carbon nanotubes (CNTs) in engine oil suspension. They stabilized CNTs by means of an ultrasonic vibrator, without any surfactant.

Timofeeva et al. [22] studied the thermo-physical properties as thermal conductivity, density, specific heat capacity and viscosity as function of different nanoparticle concentrations of SiO_2 dispersed in Therminol 66, with a cationic surfactant at different temperatures. Silica nanoparticles and surfactants inside the oil enhanced thermal conductivity. The viscosity depended on the nanoparticles concentration and on the ratio of surfactants with the nanoparticles.

Zhang et al [23] measured thermal conductivity and diffusivity of some nanofluids as Al_2O_3, ZrO_2, TiO_2 and CuO in water at different mass fractions (0%, 10%, 20% and 40%), diameters (20, 20, 40 and 33 nm respectively) and temperatures (from 5 to 50°C). They obtained that both thermal conductivity and thermal diffusivity are directly proportional to the volume fraction and a good agreement with Hamilton Crosser model was observed. Different results have been obtained by Hesfe et al. [24] measuring thermal conductivity of Al_2O_3 water based nanofluids with an average diameter of particles of 5 nm. In this case Hamilton-Crosser model does not match with experimental results.

Xie et al. [25] analyzed the thermal conductivity enhancement of alumina-based suspensions with different specific surface areas (from 5 to 124 m^2/g) by means of hot wire method. It has been observed that there is a correlation of thermal conductivity with nanoparticles sizes, thermal conductivity of base fluid and an interaction between liquid and particle.

Li et al. [26] carried out an experimental investigation on the influence of temperature (from 27.5°C to 34.7°C), volume fraction (2%, 4%, 6% and 10%), diameter (29 and 36 nm) and the nanoparticle material on thermal conductivity of CuO and Al_2O_3 suspensions. They found that at a volume fraction of 6% thermal conductivity enhancement was 1.52 times higher than that of the distilled water, while at 10% for Al_2O_3 suspensions, this increase was 1.3 times higher than that of the distilled water at 34 °C.

The purpose of this work is, instead, to study experimentally thermal conductivity, viscosity and stability of Al_2O_3-diathermic oil based nanofluids, used as heat transfer fluid for high-temperature applications such as solar energy systems [9 , 11 , 12], through different methods of sample preparation. Various samples have been prepared in order to identify the effects of ~~the~~ concentration of surfactants, mixing temperature in two-step method on sample preparation procedure. Thanks to this experimental campaign it has been possible to establish a new preparation technique, able to optimize the stability and thus the performance of Al_2O_3-diathermic oil based nanofluids in an economic and easy way.

2 Experimental setup

2.1 Preparation of nanofluid

Nanofluid samples were prepared and stability, average cluster size, viscosity and thermal conductivity were analyzed. Figure 1 shows the flowchart of the procedure to prepare samples of nanofluids and to investigate their properties.

Both liquid phase and solid phase are weighed with a precision balance with a resolution of 0.01 g. A magnetic homogenizer is equipped with a heating plate to mix the two phases at a fixed temperature and velocity. After this step the suspensions undergo to sonication with an ultrasonic vibrator with a power of 70 W at a frequency of 20 kHz.

Figure 1 – Flowchart of the procedure of sample preparation and properties analysis

Al_2O_3 nanoparticles (Nanophase Corporation) with average diameter of 45 nm and spherical shape have been used as solid phase (Figure 2). Microstructure and surface morphology of the nanoparticles have been observed using a scanning electron microscope SEM (model ZEISS-ΣIGMA with a GEMINI column). After a pre-treatment in centrifuge of nanofluids at 4000 rpm for 30 seconds, some SEM images of alumina-based nanofluids in oil have been recorded at different magnifications: 100000X and 25000X with a voltage of 15 kV and a work distance of 7.4 mm. Images showed the spherical shape of alumina nanoparticles with an average size of 40-50 nm.

Figure 2 - SEM images at 25000X and 100000X magnification of Al_2O_3 nanoparticles (1% vol.).

Therminol 66 has been used as base fluid, that is a diathermic oil with an operating temperature range between 10 °C and 345 °C, typically used in high temperature solar energy systems. Oleic acid with 90% purity (Alfa Aesar) has been used as surfactant. A hydrophilic head and a hydrophobic tail constitute surfactant molecules. In polar solvent, the hydrophobic section is oriented towards the particle, while the hydrophilic one is positioned outside. In apolar solvent, as in diathermic oil, orientation of the surfactant molecules is opposite (Figure 3).

Figure 3 – Orientation of surfactant molecules inside polar and apolar solvent

Samples of nanofluids with 0.3 %vol, 0.7 %vol and 1.0 %vol were prepared. Table 1 shows all samples that have been prepared in this investigation. Amount of oleic acid is indicated as multiple of Critical Micelle Concentration (CMC). A codification of the samples has been used to facilitate the presentation of the results (third column of Table 1).

Table 1– Nanofluid samples used in this investigation

2.2 Characterization of nanofluids (instruments and measurement procedure)

Stability has been analyzed through Turbiscan LabExpert (Figure 4). Turbiscan LabExpert has a near infrared light source (880 nm) and two synchronous detectors. The transmission detector receives the light flux transmitted (T) through the sample; the backscattering detector captures the backscattered light (BS). The reading head acquires transmission and backscattering data either at a chosen position on the sample cell, or every 40 μm, while moving along the 55 mm cell height. The recorded backscattering intensity of radiation is proportional to particles concentration. An important factor obtained by the TurbiScan instrument is related to the TurbiScan Stability Index (TSI). It monitors the destabilization kinetics versus ageing time. It sums all the variations detected in the sample (size and/or concentration) at a given ageing time. The higher the TSI is, the worse the stability of the sample is. These stability index results have been used to compare the stability of many samples. The formula related to the TSI is reported in equation (1):

$$TSI = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{BS})^2}{n-1}} \qquad (1)$$

where x_i is the mean backscattering for every minute of measurement, x_{BS} is the mean x_i, and n is the number of scans [27 , 28].

Solid phase inside nanofluid is in form of aggregates (clusters). To measure their average size, DLS (Dynamic Light Scattering) technique has been used through Zetasizer Nano ZS (Malvern Instruments), shown in Figure 4b. The size range of this instrument is between 0.6 nm and 6 μm, with an accuracy of ±2%. DLS measures Brownian motion and relates this phenomenon to the size of clusters. A laser illuminates the sample, placed in a cuvette, and a detector analyzes the fluctuations of the scattered light.

To investigate rheological properties of all samples, the Newtonian or non-Newtonian behavior of the nanofluids of Al_2O_3 nanoparticles in diathermic oil has been analyzed by means of a Bohlin CVO rheometer (Malvern Instruments, UK), shown in Figure 4c. The rheometer has a torque range from 0.5μNm to 100 mNm and a speed range from 50 mrad/s to 320 rad/s. The Newtonian fluid is characterized by the following relation: τ = μγ, where τ is the shear stress, μ is the coefficient of viscosity, and γ is the shear strain rate [29].

Mid-infrared spectra have been acquired with a Perkin-Elmer Spectrum One FTIR spectrometer, as shown in Figure 4d, equipped with ATR (Attenuated Total Reflectance) accessory. The wavelength range is between 7800 cm^{-1} and 350 cm^{-1}, with a resolution from 0.5 cm^{-1} to 64 cm^{-1}. The spectral resolution used for all measurements was 4 cm^{-1}. This accessory operates by measuring the changes that occur in a totally internally reflected infrared beam, when the beam comes in contact with a sample.

Figure 4 – Turbican LabExpert (a), Zetasizer Nano ZS (b), Bohlin rheometer (c) PerkinElmer Spectrum Two FT-IR spectrometer (d).

Nanofluids thermal conductivity has been measured by means of an instrument based on the hot-wire technique, compliant to ASTM D 2717 – 95 standard [30].

Hot-wire method is based on the measurement of electric resistance variation as a function of temperature. The ideal apparatus is made with an infinitely long metallic wire, with negligible diameter and negligible specific heat, embedded in the sample, which has a temperature rise due to Joule effect and, consequently, an electric resistance variation. The temperature rise is due to the thermal conductivity of the fluid surrounding the wire. Thus, measuring the variation of the electric resistance, it is possible to determine the thermal conductivity. The presence of a localized heat source (the wire) yields, inevitably, temperature gradients, responsible for convection motions within the fluid, which depend on the intensity and duration of the heat flow that passes through the wire. To avoid these physical phenomena, thermal conductivity measurements should have short duration and for this aim, the transient hot wire method has been used in this investigation. It is based on the following heat equation (2) solution, for two coaxial cylinders system in transient mode, with a heat flux, q:

$$\Delta T = T(r,t) - T_0 = \frac{q}{4\pi k}\left(\ln t + \ln(\frac{4\alpha}{r^2})\right) - 0.5772 \quad (2)$$

Where k is the thermal conductivity, α is the thermal diffusivity of the fluid, T_0 is the reference temperature, r is the distance from the axis of the cylinder and 0.5772 is the Eulero-Mascheroni constant [31].

Plotting equation (2) on the plane [ln t; ΔT], it is linear and its slope is equal to:

$$\frac{d\Delta T}{dlnt} = \frac{q}{4\pi k} \quad (3)$$

In this way, the thermal conductivity k can be calculated from the slope of the line, which, in ideal conditions, is constant throughout the time, without reference to any specific value of temperature and geometry of the system. The real experimental setup is made with a platinum wire (with a diameter of 0.1 mm and length of 35 mm), welded on a holder and immersed in a cylindrical cell, where nanofluid is placed. A thermocouple measures the average temperature inside the cell. Boundary effects, generated by the welds at the ends of the wire and its finite length, could affect thermal conductivity measurements. However, boundary effects are negligible and errors that generate are taken into account through the uncertainty of the measuring instrument. The experimental apparatus was calibrated to measure fluid having a temperature between 20 °C and 150 °C and a thermal conductivity in the range between 10 and 1000 mW/mK. The average temperature of the samples was assured by a thermostatic system. Figure 5 shows hot wire apparatus used in this investigation.

Figure 5 - Hot wire apparatus

2.3 Accuracy of the instruments and uncertainty analyses in measurements

The uncertainty of nanoparticles average size measurements was estimated with the standard deviation of the experimental data. For all the samples, 5 measurements have been carried out and standard deviation of average values has been calculated to obtain 95% confidence interval. For samples with surfactant, uncertainty was between 3.8% and 6.8%, while values between 16.9% and 38.9% have been obtained for samples without surfactant. These high uncertainties (without surfactant) are due to polydispersed suspension and the presence of large aggregates. Accuracy of Zetasizer Nano ZS is lower than 2%.

Backscattering accuracy of Turbiscan LabExpert was calculated by the average value obtained with 3 scans on a white Teflon standard sample and it was lower than 0.7%. Also in this case uncertainty was calculated by the standard deviation of the experimental data. In particular backscattering at two fixed positions along sample cell (at 15 mm and 40 mm respectively from the bottom of the cell) were measured and 95% confidence interval was calculated. Uncertainty was about 8%.

With Bohlin CVO rheometer (Malvern Instruments, UK) it is possible to measure viscosity of the samples with an accuracy of 5% while for Perkin-Elmer Spectrum One FTIR spectrometer accuracy is 1.6 cm^{-1}.

Hot wire device has an accuracy of 1% and for thermal conductivity measurements 95% confidence interval, for all samples, was calculated and it was less than 0.6% (section 3.5).

3. Results and discussion

3.1 Analysis of stability of samples by means of Turbiscan

A10OA1 sample was prepared with the procedure indicated in the previous section and stability analysis at 60 °C was made with Turbiscan LabExpert for 1 hour. Results are shown in Figure 6a, where a marked sedimentation inside A10OA1 after the first sonication is evident. The black line on sample A10OA1 after the first sonication indicates the boundary of the clarified zone. When a second sonication was made on the A10OA1 sample, it was more stable, as it appears by a comparison between Figure 6a and Figure 6b. From the first graph, the process of sedimentation is clear, because the backscattering flux increases at the bottom of the cuvette and it decreases at the top; instead in the second graph the curve basically is unchanged over the time. This behavior can be explained considering that ultrasonic vibration breaks nanoparticle clusters and many supernatants are present in the sample.

Figure 6 – Delta backscattering of a) A10OA1 after the first sonication, b) A10OA1 after the second sonication

To avoid this phenomenon inside samples with surfactants, the procedure of preparation of nanofluids was modified. In particular mixing with magnetic stirrer was made at 40 °C, 80 °C and 120 °C and then the suspension was vibrated for ten minutes. Figure 7 shows delta backscattering (at 60 °C, which is the maximum possible test temperature of TurbiscanLab Expert) for each sample and a better stability was obtained with sample mixed at 120 °C, as it will be explained in the following section.

Figure 7 – Delta backscattering of A10OA after a mixing at room temperature, 40 °C, 80 °C and 120 °C.

3.2 Analysis of stability of samples by means of FIT-IR measurements

To explain the best stability of nanofluids at 120ºC, FT-IR spectra (as shown in Figure 8) have been acquired to analyze all different functional groups inside the samples.

Figure 8 – FT-IR spectra of: a) A10OA1 after the second sonication, A10OA1 after the first sonication, b) A10OA1 at 120°C, nanoparticles of alumina, and diathermic oil plus oleic acid

An important result, deduced by the spectra for all the samples, is the absence of water and, consequently, of the functional groups of O-H at 3500 cm^{-1}. The first hypothesis, that water molecules, due to relative humidity of air and humidity of the nanoparticles, were trapped inside the sample during mixing with magnetic stirrer, was excluded by this analysis.

The FT-IR spectra of the diathermic oil plus oleic acid (called OIL+OA1), of A10OA1 after the second sonication (called A10OA1 S2), of A10OA1 after the first sonication (called A10OA1 S1), of A10OA1 at 120°C (called A10OA1 120C) are characterized by vibrational frequencies at 2852 cm^{-1} and 2923 cm^{-1}, derived from functional groups of C-H, at 1448 cm^{-1} and 1602 cm^{-1} from functional groups of C═O, and a zone of the fingerprint at 697 cm^{-1}.

Al_2O_3 nanoparticles have a FT-IR spectrum characterized only by the zone of the fingerprint above 1000 cm^{-1}. The intensity of the peak related to the zone of the fingerprints for the sample A10OA1 S2 is higher than that related to the sample A10OA1 S1 and with the same trend of the sample A10OA1120C. This behavior confirms the graphs of the Turbiscan reported in Figure 7.

This physical behavior is due to the combination of three physical processes:

- The samples mixed at 120 °C have lower viscosity than those mixed at room temperature, 40 °C and 80 °C;
- Increasing temperature, the surface tension of the nanofluids decreases, thus the wettability of the nanofluids' solid phase improves [32] and this causes the most stable sample, obtained at 120 °C;
- When temperature increases, a tensional elongation of nanoparticles is produced inside the nanofluid and then they are more easily broken by means of the mixing of the magnetic stirred and by means of the mechanical power generated by the sonication [33].

3.3 Influence of surfactant

In this investigation, oleic acid is used as surfactant to improve stability of nanofluids.

Due to the strong effect of the preparation procedure, as explained in section 3.1, the detailed procedure to prepare samples of nanofluids was modified as follows:

– Weighting of both liquid and solid phases to obtain a sample of 50 ml;

- Mixing with magnetic stirrer for 30 minutes at 120°C;
- Sonication of 25 ml of the sample for 10 minutes.

In this step, the effect of surfactant on stability of Al_2O_3 – oil based nanofluids was investigated. Sample with 0.3 %vol of solid phase and oleic acid at CMC (A03OA1) was prepared and compared with one with the same volume fraction of nanoparticles and a higher amount of oleic acid, 22 %wt (about 7xCMC). This value is the same that was chosen by Xuan et al. [19] to prepare oil-Cu nanoparticles suspension with a volume fraction of solid phase between 2.0 and 5.0%. Al_2O_3 – diathermic oil based nanofluid, with 0.3% of solid phase and 22 %wt of oleic acid called A03OA7, was prepared and tested.

Figure 9a shows samples after nine days from preparation. It is possible to note that amount of solid phase on the bottom of the cuvette with A03OA7 is higher than that of A03OA1. This behavior, as explained by Choi et al. [17], is due to excess of surfactant that forms a double chain on the clusters of nanoparticles (Figure 9b). In these conditions, surface of the clusters is hydrophilic and therefore sedimentation phenomenon occurs.

Figure 9 – a) A03OA1 and A03OA7 after nine days from sample preparation, b) double chain due to excess of surfactant, c) A10OA2 and A10OA3 after five days of sample preparation

On the basis of these results, three samples of oil based nanofluids were prepared with an oleic acid concentration directly proportional to volume fraction of solid phase. In particular CMC was added to diathermic oil for 0.3 %vol (A03OA1), 2x CMC for 0.7 %vol (A07OA2) and 3xCMC for 1.0 %vol (A10OA3), respectively. However Figure 9 shows that sedimentation phenomenon, after five days form preparation, in A10OA3 is higher than that in a sample with the same volume fraction, 1.0 %vol, and oleic acid at 2xCMC. Therefore samples for the next step of analysis were A03OA1, A07OA2 and A10OA2.

3.4 Investigation on the stability of nanofluids of Al_2O_3 nanoparticles in oil with and without oleic acid.

A03XX, A03OA1, A07XX, A07OA2, A10XX and A10OA2 nanofluid samples were prepared to analyze the stability of the suspensions. Figure 10 shows the trend of the TSI as function of time (2 hours), for each sample, at 60 °C. In Figure 11 the pictures of the samples after eight days (a) and after one month (b) from preparation are shown. The sample A030A1 (0.3% in volume fraction with oleic acid) doesn't present much sedimentation after eight days and one month from preparation (a and b).

The second and third samples, A03XX and A07XX (0.3% and 0.7% in volume fraction without oleic acid) are not stable; since after one month (b) they have greater sedimented phase than after eight days form preparation (a). The fourth sample after one month from preparation (A07OA2, characterized by 0.7% volume fraction with oleic acid and double CMC) presents as well a greater quantity of sedimentation on the bottom of the cuvette than that after eight days from preparation. In the second last sample A10XX (1% in volume fraction without oleic acid) after one month (a) the clarified zone is evidently higher than that after eight days. In the last sample A100A2 (1% in volume fraction with oleic acid and double CMC) both clarified zone and sedimented materials appear mostly clear on the cuvette after one month than after eight days from preparation.

From these figures it is possible to assert that effect of surfactants is negligible at the beginning of the stability measurements. The value of the TSI is in a range between 0.4 and 0.5. The effect of surfactants is more marked at the long term. At the same volume fraction, samples with surfactants are more stable than those without. However oleic acid is only a limiting factor of the sedimentation phenomenon, which also depends on gravity force. In Figure 11b another phenomenon can be noted inside sample with surfactants, that is the height of clarified zone on the top of the cuvette, which is directly proportional to volume fraction of the solid phase. This is due to the weight force of the nanoparticle clusters, as suggested by measurements reported in the next section.

Figure 10 – TSI for Al_2O_3 – diathermic oil based nanofluids at 60 °C for 2 hours

Figure 11 – Sedimentation of solid phase inside samples of Al_2O_3 – diathermic oil based nanofluids after a) eight days and b) one month from preparation.

Nanofluids without surfactants, instead, show greater sedimentation than those with surfactants. The presence of surfactants creates some bonds between nanoparticle and base fluid, which make them more stable. This physical process is due to surfactants' molecules that cover the nanoparticles' surface, reducing their aggregation. In this way, surfactants play their role to stabilize the nanofluids [34 35].

3.5 Thermal conductivity measurements

Thermal conductivity measurements of Al_2O_3 nanofluids with surfactants (A10OA2, A07OA2 and A03OA1) and without surfactants (A03XX, A07XX and A10XX) at different volume concentrations (0.3%, 0.7% and 1%) and the reference base fluid (Therminol 66) were performed in order to investigate the influence of the surfactant. From results reported in Figure 12, it has been noted that the presence of oleic acid does not affect the thermal conductivity that, for a volume fraction of 0.3%, increases up to 1.2% if compared to thermal conductivity of base fluid. Enhancements of 3.0% and 4.0% have been obtained with 0.7% and 1.0% of volume concentrations of solid phase respectively. In Figure 12 the trend of the variation of the thermal conductivity is very similar to nanofluids with and without surfactants at all concentrations. The addition of more surfactants is not effective in the Al_2O_3-oil suspensions. This physical phenomenon is due to the fact that the heat transfer area is narrower, due to the amount of the surfactants on the particle surface, as explained also by Li et al. [36].

Figure 12 - Thermal conductivity measurements of Al_2O_3 -based nanofluids with surfactants (A10OA2, A07OA2 and A03OA1) and without surfactants (A03XX, A07XX and A10XX) at different volume concentrations (0.3%, 0.7% and 1% respectively) and the base fluid (Therminol 66).

Table 2 shows both upper limit and lower limit of 95% confidence interval for all investigated samples.

Table 2– Average, Standard Deviation, upper and lower limit of 95% confidence interval of thermal conductivity of investigated samples of nanofluid

3.5 Average clusters size measurements

Average aggregate size of all samples was investigated with Zetasizer Nano ZS. Table 3 shows average size for sample nanofluids with surfactant. It is possible to note that aggregate size increases by increasing the volume fraction as Diaa-Eldin A. Mansour et al. [37] have obtained for oil transformer/SiO_2 nanofluids.

Aggregate size distributions for samples without surfactant are shown in Table 4. Experimental results for samples without surfactant show a strong variability on measurements. This behavior is due to the presence of large aggregates and polydisperse samples.

Table 3 – Average aggregate size for sample nanofluid with surfactant

Table 4 – Average aggregate size for sample nanofluid without surfactant

3.6 Viscosity measurements

Rheological analysis has been performed on all samples to study the viscosity of suspensions with and without surfactants. Kole et al. [38] presented results on the effect of the surfactants on nanofluids and they demonstrated that their presence does not influence the viscosity of the base fluid (oil) and its Newtonian properties. In literature, theory on viscosity of suspensions is treated with Einstein equation [39 40] for particle volume fraction $\phi<0.02$, that is given by the following equation (2):

$$\mu_{nf} = \mu_{bf}(1 + 2.5\phi) \quad (2)$$

where μ_{bf} is the viscosity of the base fluid (diathermic oil) and μ_{nf} is the viscosity of nanofluids. From this equation with the increasing of the amount of nanoparticles (volume concentration) the nanofluid's viscosity could increase and the viscosity of the nanofluid is close to that of diathermic oil for low volume concentration of nanoparticles.

Viscosity dependency of Al_2O_3 – diathermic oil based nanofluids with surfactant on share rate, γ, is shown in Figure 13, whereas Figure 14 shows viscosity behavior of samples of nanofluid without surfactant.

Experimental measurements of the viscosity coefficient have been performed at the same temperature at which stability has been investigated with Turbiscan LabExpert, 60°C. It is possible to note that viscosity of oil is lower than that of all samples and its mean value is 12.55 mPa, close to the value (11.53 mPa) reported in bibliography [41] and that viscosity is directly proportional to volume fraction of solid phase. Besides, at same volume fraction, viscosity of samples of nanofluid with surfactant is lower than those without it. Finally a marked non-Newtonian behavior was obtained at high volume fraction (1.0%vol for samples with surfactant and 0.7%vol and 1.0%vol for sample without surfactant). These results are consistent with that reported by Mahbubul et al. [42].

Figure 13 – Viscosity versus share rate of samples of nanofluids with surfactant

Figure 14 – Viscosity versus share rate of samples of nanofluids without surfactant

Figure 15 shows that there is not agreement between viscosity, measured at a fixed share stress value, and predicted value through equation (2), because Einstein equation does not take into account various parameters as particle size, aggregation and share rate [43 44].

Figure 15 – Comparison between experimental results and predicted values through Einstein equation

Table 5 summarizes cluster size and viscosity values (at fixed shear stress) for all investigated Al_2O_3 – diathermic oil nanofluid samples. Viscosity of samples with oleic acid is lower than that without surfactant for each volume fraction of solid phase. Besides for samples without oleic acid viscosity was between 14.07 and 20.43 mPa·s, while for samples with oleic acid it was between 13.21 and 15.21 mPa·s. Therefore for diathermic oil based nanofluids without oleic acid the viscosity increase was of 45.20%. By using oleic acid as surfactant this increase was of 15.14%.

Table 5– Viscosity and average cluster size of Al_2O_3 – diathermic oil nanofluids

4 Conclusions

Thermal conductivity, viscosity measurements and a stability analysis were performed in order to establish a suitable preparation technique of Al_2O_3–diathermic oil nanofluids, which have good potential for using in high temperature solar energy systems. During the preparation, the effect of the mixing with magnetic stirrer at high temperature (120°C) is equivalent to the second sonication of ultrasonic vibrator when magnetic stirrer is used at room temperature. The best stability of alumina nanofluid in diathermic oil at 120°C or sonicated two times was explained by FIR IR measurements characterized by IR spectrophotometer.

Another important result was the effect of the surfactants on the nanofluids stability. The presence of oleic acid as surfactant in nanofluids makes them more stable than those without. It was observed that excess of surfactant determines sedimentation inside the sample, due to double chain that oleic acid forms on clusters of nanoparticles. Moreover by observing nanofluid samples after one month from preparation, clarification phenomenon on the top of the cuvettes of the samples is directly proportional to volume fraction. The effect of surfactants is evident at long term.

Through the procedure explained in this work it is possible to obtain an acceptable stable suspension, with a minimal amount of surfactant and to avoid next steps to eliminate excess amount of surfactant as proposed by other authors. Besides if nanofluid is mixed at high temperature with magnetic stirrer, time of sonication can be reduced.

The presence of surfactants in nanofluids is negligible for thermal conductivity enhancement. At every volume fraction and temperature measurement, thermal conductivity differences between the sample with surfactant and the one without are comparable to the error of the measuring instrument. Average cluster size of nanofluids with and without surfactants was analyzed by means of DLS technique. Experimental data show that by increasing volume concentration, the average cluster size increases.

Finally, rheological analysis was studied on all samples.

Highlighted data can be summarized as follows:

- viscosity increases by increasing the volume fraction;
- a marked non-Newtonian behavior at high volume fraction (1.0%vol for samples with surfactant and 0.7%vol and 1.0%vol for sample without surfactant);
- viscosity increase is less pronounced for samples with oleic acid.

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Figure captions

Figure 1 - Flowchart of the procedure of sample preparation and properties analysis

Figure 2 - SEM images at 25000X and 100000X magnification of Al_2O_3 nanoparticles (1% vol.)

Figure 3 - Orientation of surfactant molecules inside polar and apolar solvent

Figure 4 - Turbican LabExpert (a), Zetasizer Nano ZS (b), Bohlin rheometer (c) PerkinElmer Spectrum Two FT-IR spectrometer (d).

Figure 5 - Hot wire apparatus

Figure 6 - Delta backscattering of a) A10OA1 after the first sonication, b) A10OA1 after the second sonication

Figure 7 - Delta backscattering of A10OA after a mixing at room temperature, 40 °C, 80 °C and 120 °C.

Figure 8 - FT-IR spectra of: a) A10OA1 after the second sonication, A10OA1 after the first sonication, b) A10OA1 at 120°C, nanoparticles of alumina, and diathermic oil plus oleic acid

Figure 9 - a) A03OA1 and A03OA7 after nine days from sample preparation, b) double chain due to excess of surfactant, c) A10OA2 and A10OA3 after five days of sample preparation

Figure 10 - TSI for Al_2O_3 – diathermic oil based nanofluids at 60 °C for 2 hours

Figure 11 - Sedimentation of solid phase inside samples of Al_2O_3 – diathermic oil based nanofluids after a) eight days and b) one month from preparation

Figure 12 - Thermal conductivity measurements of Al_2O_3 -based nanofluids with surfactants (A10OA2, A07OA2 and A03OA1) and without surfactants (A03XX, A07XX and A10XX) at different volume concentrations (0.3%, 0.7% and 1% respectively) and the base fluid (Therminol 66).

Figure 13 - Viscosity versus share rate of samples of nanofluids with surfactant

Figure 14 - Viscosity versus share rate of samples of nanofluids without surfactant

Figure 15 - Comparison between experimental results and predicted value through Einstein equation

Table captions

Table 1– Nanofluid samples used in this investigation

Table 2– Average, Standard Deviation, upper and lower limit of 95% confidence interval of thermal conductivity of investigated samples of nanofluid

Table 3 – Average aggregate size for sample nanofluid with surfactant

Table 4 – Average aggregate size for sample nanofluid without surfactant

Table 5– Viscosity and average cluster size of Al_2O_3 – diathermic oil nanofluids