

THERMAL CONDUCTIVITY CHARACTERISTIC OF TITANIUM DIOXIDE WATER BASED NANOFLUIDS SUBJECTED TO VARIOUS TYPES OF SURFACTANT

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Abstract

In nanofluid preparation, surfactants such as gum Arabic, sodium dodecylbenzenesulfonate, and polyvinylpyrrolidone are often added to minimize the nanoparticles sedimentation problems and eventually improve nanofluids stability. However, the inclusion of surfactant will affect the thermal conductivity of nanofluids. Proper amount of surfactant is required not only to improve nanofluids stability but also to optimize its thermal conductivity enhancement. Thus, the present study investigated the effect of gum Arabic, sodium dodecylbenzenesulfonate and polyvinylpyrrolidone with two different surfactant to nanoparticles ratio (1:1 and 2:1) on thermal conductivity of titanium dioxide water based nanofluids. The nanofluid samples were prepared via two-step method while KD2-Pro thermal analyser was used to measure the thermal conductivity. Study concluded that the thermal conductivity of non-surfactant titanium dioxide based nanofluids is higher than surfactant based titanium dioxide nanofluids. This study concludes that in comparison with types of surfactant, nanofluids (1:1 ratio) at 0.8 volume percentage of titanium dioxide added with sodium dodecylbenzenesulfonate exhibit highest thermal conductivity value followed by gum Arabic and polyvinylpyrrolidone.

Keywords: Nanofluids; Titanium dioxide; Thermal conductivity, Surfactant.

1. Introduction

Thermal systems such as radiator, heat exchangers, and heat pipes are widely used in industry for cooling or heating purposes. These systems utilize conventional heat transfer fluids such as water, ethylene glycol and oil. However, their efficiency is limited by the low thermal conductivity of these conventional heat transfer fluids.

Nomenclatures

vol. % Volume percentage

Abbreviations

AA	Acetic Acid
CNT	Carbon Nanotube
CTAB	Cetyl Trimethyl Ammonium Bromide
GA	Gum Arabic
OA	Oleic Acid
PVP	Polyvinylpyrrolidone
SDBS	Sodium Dodecylbenzenesulfonate
SDS	Sodium Dodecylsulfate
TiO ₂	Titanium Dioxide

Effort to improve thermal conductivity by adding solid particles into base fluid has been started since introduction of mixture theory developed by Maxwell [1]. Murshed et al. [2] stated that initially, most of the studies focused on the addition of millimetre and micrometre-sized particles. However, additional problems occurred due to rapid settling of particles, clogging of fluid channels, wear, and damage of wall channel or pipe. In addition, higher-pressure drop is also observed from these “big” particles.

Therefore, a group of scientist from Argonne National Laboratory has developed a new generation of heat transfer fluid known as nanofluids. Nanofluid is defined by suspension of nanoparticles in the conventional base fluid. Nanofluids have the potential to be applied in various thermal systems such as shell and tube heat exchanger [3], compact heat exchanger [4], as well as refrigeration system [5]. Nanoparticles have high surface to volume ratio which enable them to remain stable in the suspension and also capable of minimizing erosion and clogging problems [2]. This novel heat transfer fluid has attracted interest among the researchers where numerous studies related to nanofluids have been carried out extensively [3-13].

According to Yang and Du [14], there are three categories of nanoparticles that often used in development of nanofluids, namely a) advanced materials with very high thermal conductivity (graphene, carbon nanotube); b) metallic materials (copper, iron, silver, gold); c) metal or non-metallic compounds (titanium dioxide, zinc oxide, aluminium oxide). Each of these particles have their own advantages and disadvantages. For instance, carbon nanotube has high thermal conductivity but it is very difficult to be dispersed into base fluid due to hydrophobic characteristics of carbon nanotube (CNT) surface [15]. It is noteworthy that copper, diamond, and silver exhibit high thermal conductivity but it is always associated with higher cost. In addition, titanium dioxide nanoparticles offer several advantages such as non-toxic, can be produced in large scale, resistance to caustic corrosions and high temperature, excellent chemical stability and good dispersion in polar and non-polar base fluid [14].

The shelf-life (stability) of nanofluids is one of the main concerns among researchers. Nanoparticles, regardless of its types, tend to agglomerate or aggregate due to the van der Waals forces, which can bind several particles together into a lump of particles. Due to gravitational effects, these “heavier” particles tend to settle at the bottom. Nanofluid’s thermo-physical properties especially the thermal

conductivity is affected by this problem [15]. One of the possible approaches to solve this problem is by introducing surfactant to the nanofluid [16]. Minzheng et al. [17] defined surfactant as long organic molecules that consist of hydrophilic and lipophilic groups. Surfactants can be classified into few types, namely anionic (SDS, SDBS), cationic (CTAB), non-ionic (GA, PVP) and amphoteric (lecithin) [18]. Ghadimi et al. [16] explained that the function of surfactant is to convert the hydrophobic surface of nanoparticles to hydrophilic or vice versa for non-aqueous liquids. Addition of surfactant will increase the repulsive force between the nanoparticles. It is noted that when the repulsive force is higher than van der Waals force (attraction forces), the possibility of particles agglomeration can be minimized. This theory has been presented by Leong et al. [15], Ghadimi et al. [16], and Minzheng et al. [17] that states that addition of surfactant is capable of improving nanofluids' stability.

Nanofluids stability and thermo-physical properties are co-related to each another. In nanofluids related studies, the researchers utilized surfactant in their preparation of nanofluids. For instance, Fedele et al. [19] evaluated thermal conductivity of titanium dioxide water based nanofluids added with acetic acid as surfactant. Study implied that the thermal conductivity augmentation is substantial at higher operating temperature. Jin et al. [20] compared two types of nanofluids namely titanium dioxide and fullerene nanofluids. Mineral oil and Span 80 were used as the base fluid and surfactant, respectively. They found that at low concentration of nanoparticles (0.1%), addition of both nanoparticles have negligible effect on the thermal conductivity of mineral oil. Reddy and Rao [21] investigated the effect of titanium dioxide nanoparticles to the thermal conductivity of water and water/ethylene glycol mixtures. Oleic acid and CTAB (Cetyl Trimethyl Ammonium Bromide) were used as surfactant to ensure stability of the prepared samples. The study observed that temperature and amount of nanoparticles added into nanofluids have significant effect to the thermal conductivity of nanofluids. This finding was proven further by Azmi et al. [22] which found that thermal conductivity enhancement is almost linear with temperature, especially at low particles concentration. Authors added that more kinetic energy is produced at higher temperature due to collision among the nanoparticles. Khedkar et al. [23] found that thermal conductivity ratio of titanium dioxide ethylene glycol based nanofluids increases linearly with the increase of nanoparticles concentration. 19.52% thermal conductivity enhancement is observed at 7 vol.% of titanium dioxide. Authors revealed that this is attributed to large particle to particle interaction.

Abdolbaqi et al. [24] used BioGlycol/water mixtures as base fluid in their preparation of titanium dioxide nanofluids. The maximum thermal conductivity augmentation (12.6%) is recorded at 2 vol.% of titanium dioxide added into BioGlycol/water (20:80 mixture ratio). Das et al. [25] used four different types of surfactants cetyl trimethyl ammoniumbromide (CTAB), acetic acid (AA), oleic acid (OA) and sodium dodecyl sulfate (SDS) to prepare titanium dioxide nanofluids. The thermal conductivity of CTAB and AA-stabilized nanofluids is found to increase monotonically with concentration of nanoparticles and also the operating temperature. Polyvinylpyrrolidone (PVP) and Tween 20 were applied as surfactants by Chakraborty et al. [26]. PVP was found to improve the nanofluids stability of titanium water based nanofluids, while Tween 20 has little effect on the nanoparticles dispersion in the base fluid. Study found that the addition of PVP

only slightly improves the thermal conductivity of titanium nanofluids while Tween 20 has no positive impact.

Based on previous literatures, it is found that there are substantial studies focused on thermal conductivity of titanium dioxide nanofluids. However, as far as the authors are concerned, there are limited studies which investigate the effect of various types of surfactants together with the effect of surfactant to nanoparticles ratio on thermal conductivity of titanium dioxide water based nanofluids. For instance, Saleh *et al.* [27] did not vary the amount of surfactant added in the titanium dioxide water based nanofluids, although the effects of SDS, CTAB and Span-80 on nanofluids thermal conductivity were examined by them. Thus, the present study intends to fill the gap in this area. This study tried to expand the thermal conductivity data of titanium dioxide water based nanofluids for different types of surfactants (GA, SDBS and PVP) and also examine the effect of different surfactant to nanoparticles ratio (1:1; 2:1) to nanofluids thermal conductivity.

2. Methods

Preparation of nanofluids and thermal conductivity measurement

Commercial nanoparticles and surfactants were used in this study. The primary size of titanium dioxide declared by the manufacturer is 21nm. Three types of surfactants were used namely; GA, SDBS and PVP. Initially, magnetic stirrer as shown in Fig. 1 was used to mix the distilled water and surfactant for about 5 minutes at 500 rpm. This is to ensure the surfactant is completely dissolved in the distilled water.



Fig. 1. Magnetic stirrer.

The amount of surfactant added into the base fluid is based on surfactant to nanoparticle weight ratio. Ratio of 1:1 and 2:1 were chosen in the present study.

Then, titanium dioxide nanoparticles were added into the solution where it was dispersed using ultrasonic (QSonica 700 - Fig. 2) for 30 minutes.



Fig. 2. QSonica 700 - Sonicator.

In order to prevent overheating of the samples, pulse sonication method was used where the sonication is alternately switched on and off for 5 and 2 seconds respectively. Overall, the nanofluid samples were prepared based on Table 1.

Table 1. Preparation of samples.

Num.	Samples without surfactant	Samples with surfactant	
		Ratio 1:1 (Surfactant: Nanoparticle)	Ratio 2:1 (Surfactant : Nanoparticle)
1	Distilled water + 0.2 vol.% TiO ₂	Distilled water + 0.2 vol.% TiO ₂ + Surfactant	Distilled water + 0.2 vol.% TiO ₂ + Surfactant
2	Distilled water + 0.4 vol.% TiO ₂	Distilled water + 0.4 vol.% TiO ₂ + Surfactant	Distilled water + 0.4 vol.% TiO ₂ + Surfactant
3	Distilled water + 0.6 vol.% TiO ₂	Distilled water + 0.6 vol.% TiO ₂ + Surfactant	Distilled water + 0.6 vol.% TiO ₂ + Surfactant
4	Distilled water + 0.8 vol.% TiO ₂	Distilled water + 0.8 vol.% TiO ₂ + Surfactant	Distilled water + 0.8 vol.% TiO ₂ + Surfactant

This study focused on investigating the effect of surfactant on thermal conductivity of nanofluids. The stability aspect was not examined since there are substantial amount of studies that presented the ability of surfactants in improving nanofluids stability. Thermal conductivity analyser (KD2 Pro thermal analyser-Fig. 3) was used to measure the thermal conductivity of the samples. This instrument uses the concept of transient line heat source to determine the sample's thermal conductivity. During the measurement, the current flows to the sensor. The changes of sensor temperature with respect to time is monitored by the controller and with these, the thermal conductivity can be determined. Sensor needle KS-1 is chosen since this is the best sensor for fluid thermal conductivity measurement as recommended by the manufacturer. Free convection is prevented during measurements since sensor KS-1 only applies small amount of heat. The accuracy of this sensor is $\pm 5\%$ [28].



Fig. 3. KD2 Pro thermal analyzer.

Measurements were done at room temperature (about 24°C). In order to ensure experimental accuracy and minimizing measurement errors, several precaution procedures were carried out as follows:

- (a) Measurement started 15 minutes after the sensor is immersed in the sample. With this method, the sample and sensor can reach thermal equilibrium.
- (b) Any source of vibration was eliminated as much as possible to ensure that there is no vibration during the measurement. This is to minimize micro-convection within the fluid.

In addition, the set of thermal conductivity data for each sample is ensured to have standard deviation of less than 0.02. If the set of data has higher standard deviation, the measurement will be repeated.

3. Results and Discussion

3.1. Thermal conductivity of titanium dioxide water based nanofluids

In order to verify the instrument accuracy, the thermal conductivity value of distilled water obtained from experiment is compared against the values from reference [29]. The deviation between these values are relatively small, which can be concluded as acceptable range of error. This proves that the instrument and procedures used in the present study are accurate and reliable.

Thermal conductivity characteristic of titanium dioxide water based nanofluids without surfactant is illustrated in Fig. 4. The experimental data is compared against data obtained from Maxwell model [1] and experimental data from previous study [30].

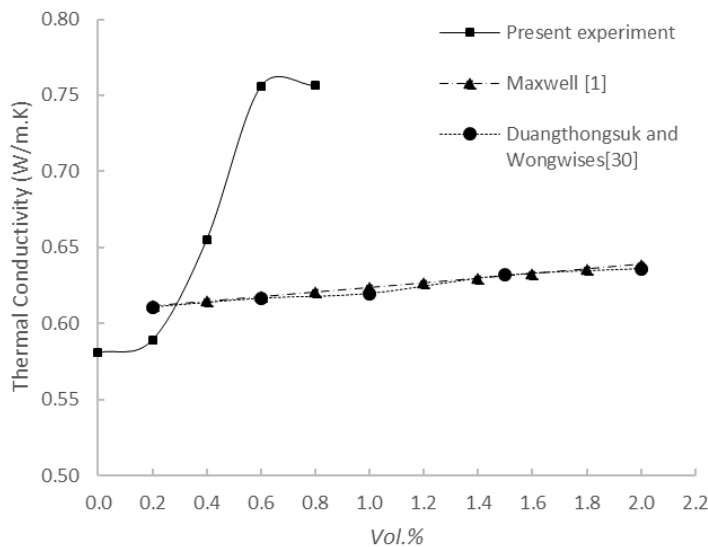


Fig. 4. Thermal conductivity of titanium dioxide water based nanofluids.

Based on Fig. 4, it was shown that thermal conductivity of titanium dioxide water based nanofluids obtained from present study is higher than results from [1] and [30]. Comparison was only carried out for cases with *vol. %* less than 0.8, since sedimentation are most likely to happen with nanofluids with higher particles concentration. In all applications, higher particles concentration will also lead to substantial increase of viscosity which will demand higher pumping power in the thermal system. The study implied that thermal conductivity of titanium dioxide nanofluids increases with the increase of particle volume concentration. The experimental data also showed that there is a sharp thermal conductivity increase starting from 0.2 *vol. %*. Thermal conductivity at 0.6 *vol. %* and 0.8 *vol. %* were almost similar. Particles clusters may have formed at these concentrations which limit the increment of thermal conductivity value. At 0.8 *vol. %* of nanoparticles, the nanofluid exhibited 30.3% thermal conductivity augmentation compared to that of base fluid. The maximum thermal conductivity enhancements at 2.0 *vol. %* for Maxwell [1] and Duangthongsuk and Wongwises [30] are 10.0% and 9.5%,

respectively. The augmentation of nanofluids thermal conductivity is attributed to the nature of nanoparticles itself, which has higher thermal conductivity compared to that of base fluid and Brownian motion of the nanoparticles. In this case, titanium dioxide definitely has higher thermal conductivity compared to water. Furthermore, the interfacial layer of water molecules surrounding the nanoparticles are also believed to have contributed to the thermal conductivity enhancements. The water molecules covering the nanoparticles are more ordered and uniformly distributed which lead to higher thermal conductivity compared to that of other water molecules. This facilitates heat transfer process in the nanofluids.

It is worth noting that Maxwell [1] model only considers particle *vol. %*, thermal conductivity of nanoparticles and base fluid without considering these important factors. This explains the deviation between present experiment data and Maxwell [1]. Regarding the deviations against data by Duangthongsuk and Wongwises [30], it can be attributed to the duration of sonication time. The nanofluids prepared in the present study underwent 30 minutes of sonication process, while Duangthongsuk applied 2 hours. When longer sonication period is applied to the nanofluids, intermolecular between the nanoparticles and water increases and nanoparticles clusters starts to form. The effective surface area to volume ratio also decreases and as the result, the thermal conductivity of the sample decreases [31]. It can be said that 30 minutes used in the present study dispersed the nanoparticles efficiently and able to prevent formation of nanoparticles clusters. Longer sonication period will encourage the formation of nanoparticles clusters.

3.2. Thermal conductivity of Titanium dioxide water based nanofluids added with surfactants

Figures 5 to 7 show the thermal conductivity characteristics of titanium dioxide water based nanofluid samples added with GA (non-ionic), SDBS (anionic) and PVP (non-ionic), respectively. Thermal conductivity of nanofluids without inclusion of surfactant also included in these figures. For samples with surfactant, two different ratio of surfactant to nanoparticles were compared, namely 1:1 and 2:1, from 0.2 - 0.8 *vol. %* of TiO₂. In general, the results reveal that titanium dioxide water based nanofluids without surfactant experienced higher thermal conductivity compared to surfactant based nanofluids. The inclusion of surfactant is an effective way to improve nanoparticles stability in base fluid [16, 18].

Based on Derjaguin-Landau Verwey-Overbeek (DLVO) theory, the interaction between particles depends on van der Waals and repulsive forces between the nanoparticles. Adding surfactants in the present nanofluids will enhance the repulsive force and eventually minimize the particles clustering or agglomeration. However, the inclusion of surfactant increases the thermal resistance between nanoparticles and base fluid, and as the results, decreasing the thermal conductivity of nanofluids [18]. This scenario depends on the types of nanoparticles and base fluids used to prepare the nanofluids. Thermal resistance that exists between the nanoparticles and base fluid will limit the heat transfer properties in the nanofluids. Apart from that, the amount of surfactant plays a vital role in determining the thermal conductivity of nanofluids. This explains the difference in characteristics between nanofluids with different surfactant ratios in the present study.

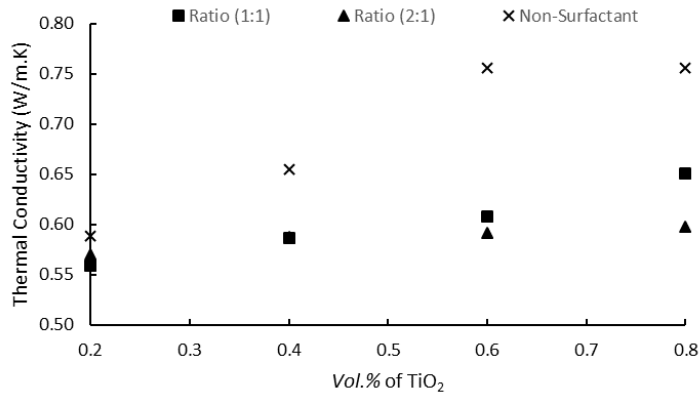


Fig. 5. Thermal conductivity characteristic of titanium dioxide water based nanofluids added with gum Arabic.

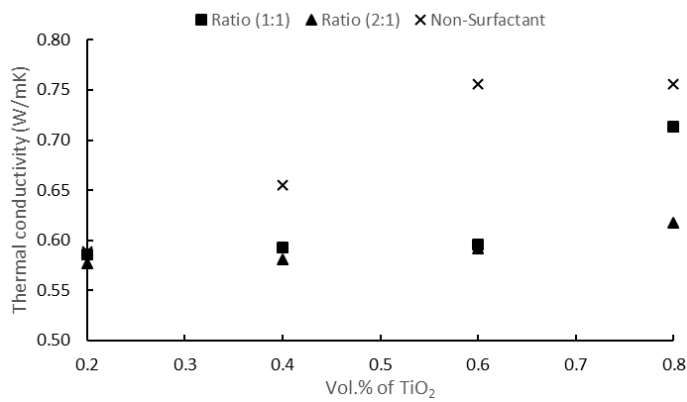


Fig. 6. Thermal conductivity characteristic of titanium dioxide water based nanofluids added with SDBS.

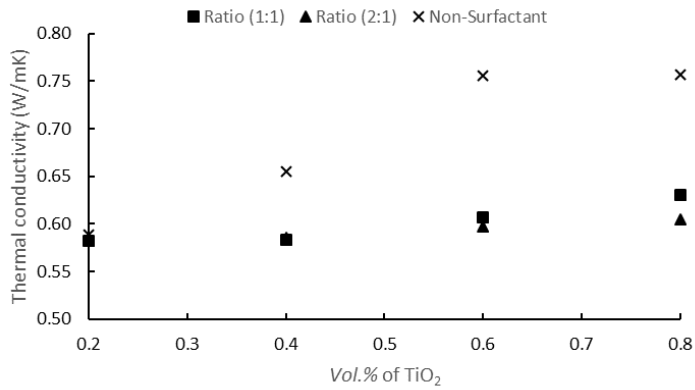


Fig. 7. Thermal conductivity characteristic of titanium dioxide water based nanofluids added with PVP.

Based on these figures, it can be observed that the amount of surfactant added into nanofluids affect its thermal conductivity. Study implies that thermal conductivity of nanofluids with 2:1 ratio is lower than 1:1 ratio especially at higher particle concentration (0.8 vol.%), which proves that the addition of excessive surfactant on nanofluids will reduce its thermal conductivity. Mingzheng et al. [17] agreed that addition of surfactant such as PVP will decrease the thermal conductivity ratio. Furthermore, Xia et al. [32] also revealed that maximum thermal conductivity enhancement is associated with optimum concentration ratio between surfactant and particles. In addition, the nanoparticles size is also influenced by this ratio. Therefore, proper and optimum selection of the amount of surfactant is very important in order to have stable sample and a maximum thermal conductivity properties. These three figures also illustrate that the highest thermal conductivity is achieved at 0.8 vol.% of titanium dioxide and 1:1 surfactant to nanoparticles ratio in comparison with nanofluids with surfactant. The same observations can be seen for all types of nanofluids studied in this research with the nanofluid added with SDBS exhibits highest thermal conductivity, followed by GA and PVP. SDBS is an anionic surfactant in nature which has higher thermal conductivity compared to non-ionic surfactant (GA and PVP). This is also agreed by Minzheng et al. [22].

4. Conclusions

The present study investigated the effect of surfactant addition in titanium dioxide water based nanofluids to its thermal conductivity characteristic. The conclusions that can be derived from present study are as follows:

- Thermal conductivity of titanium dioxide water based nanofluids added with GA, SDBS or PVP is lower than non-surfactant nanofluids. This might due to increase of thermal resistance between the nanoparticles and water.
- Thermal conductivity of titanium dioxide water based nanofluid increases with the increase of nanoparticles concentration. At 0.8 vol.%, nanofluids without surfactant exhibited 30.3% thermal conductivity augmentation compared to that of base fluid.
- Nanofluids added with surfactant (1:1) exhibit higher thermal conductivity compared to samples with 2:1 ratio at higher particle volume concentration (0.8 vol.%).
- The type of surfactant also plays major effect. At 0.8 vol.%, nanofluids added with SDBS (1:1 surfactant to nanoparticles ratio) exhibit highest thermal conductivity followed by GA and PVP. This is due to the fact that SDBS is an anionic type of surfactant, while GA and PVP are non-ionic surfactant.

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