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Surfactant-stabilized TiO_2 nanofluids: Experimental investigation on thermal and viscous behavior for PV module cooling

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Abstract

The potential application of nanofluids looks promising in various fields due to their enhanced thermal conductivity properties. The use of nanofluids in hybrid solar collectors looks particularly attractive. The thermal conductivity of the nanofluid, along with viscosity characteristics, has a significant impact on the efficiency of the solar collector. This article investigates the thermophysical properties, such as thermal conductivity and kinematic viscosity of TiO2-bidistilled water nanofluid in the presence of SDBS and CTAB surfactants at TiO_2-surfactant ratios of 1:0.1, 1:0.5, 1:1 in the temperature range of 20-60°C (293-333K). Thermal conductivity was determined using Thermtest THW-L2 equipment. Viscosity was measured using a glass capillary viscometer. The highest enhancement in thermal conductivity was observed with the SDBS surfactant, which corresponded to a lower viscosity index. At 60°C, the TiO_2-bidistilled water nanofluid containing SDBS exhibited a significant thermal conductivity increase, reaching 0.690 W/(m·K). In comparison, the CTAB surfactant led to a more pronounced rise in the kinematic viscosity of the nanofluid relative to SDBS. At a 1:0.1 TiO_2-to-surfactant ratio, the nanofluid stabilized with CTAB had a viscosity of 1.613 cSt at 20°C, whereas with SDBS, it measured 1.546 cSt. A regression analysis was conducted on the thermophysical data, leading to the development of descriptive models.

Keywords: Nanofluid, Surfactant, Thermal conductivity, Kinematic viscosity, PV-module cooling

1. Introduction

The transition from conventional energy sources to renewable energy sources has become increasingly prevalent. Currently, renewable energy accounts for 29% of global electricity production [1] and is expected to supply approximately 95% of the projected increase in electricity demand by 2027 [2]. Within the spectrum of renewable energy sources, solar energy utilization is experiencing significant growth. This is demonstrated by the substantial increase in installed capacity of solar modules, which rose from 179,639 MW in 2014 to 1,418,016 MW in 2023 [3]. Despite this rapid expansion, several challenges persist in the operation of solar modules, including the low efficiency of solar energy conversion to electrical energy [4, 5] and a reduction in efficiency as the surface temperature of the panels increases [6-8]. The issue of heat removal has been effectively addressed through the use of hybrid solar collectors, which integrate the production of both electrical and thermal energy [9-13]. There is considerable interest in the application of nanofluids within these hybrid solar collectors, as their enhanced thermal conductivity contributes to efficiently cooling the solar panels, thereby mitigating the problem of overheating [14-20].

A nanofluid consists of a base liquid containing nanoparticles, which are homogenized within the liquid and measure up to 100 nm in size. These nanoparticles can be composed of various metal and nonmetal oxides, metals, and carbon nanotubes. Metal and nonmetal oxides, in particular, have garnered significant attention due to their affordability and relatively high thermal conductivity [21-23]. TiO_2 nanofluid has been extensively studied as a coolant in hybrid solar collectors [24-26], owing to its mechanical and chemical stability, hydrophilicity [27-29], and superior optical properties. Currently, the two-stage method for preparing nanofluids is prevalently employed, as it proves to be more cost-effective on an industrial scale compared to the one-stage method [30]. Nonetheless, the two-stage method often results in nanofluids with low stability, attributed to intermediate processes such as storage, transportation, drying, and dispersion [31]. To enhance stability, nanofluids are stabilized both mechanically and chemically. Chemical stabilization is achieved by using various types of stabilizing substances: surfactants, pH adjustment, and the use of polymers and nonionic surfactants [31, 32]. Due to their economic feasibility, ionic surfactants have garnered significant interest for stabilization purposes [33]. The previous study conducted by our research group demonstrated that the addition of surfactants CTAB and SDBS to TiO2–bidistilled water nanofluids resulted in reduced sedimentation, as confirmed by UV–vis spectrophotometric analysis [34].

The thermal conductivity of nanofluids containing TiO_2 nanoparticles has attracted significant interest. Notably, Murshed et al. examined the thermal conductivity of TiO_2 in deionized water at a 5 vol.% concentration, comparing rod-shaped and spherical nanoparticles [35]. The study reported enhancements of 33% and 30%, respectively, which were assessed against predictions from the Hamilton–Crosser and Bruggeman models. Similarly, Duangthongsuk and Wongwises observed an increase in thermal conductivity ranging from 3% to 7% for TiO_2 nanofluids with volume concentrations between 0.2 vol.% and 2.0 vol.% [36]. Girhe et al. investigated the thermal conductivity of TiO_2, ZnO, and CuO nanoparticles dispersed in double-distilled water, within a volumetric concentration range of 0.1-0.5 vol.% and a temperature range of 30-70°C [37]. Their findings highlighted that the TiO_2-bidistilled water nanofluid exhibited a thermal conductivity increase from 0.5685 to 0.6009 W/m·K at 0.1 wt.% and from 0.5998 to 0.6611 W/m·K at 0.5 wt.%. However, the unstable state of the nanofluid, caused by van der Waals attractive forces between particles and electrostatic repulsion forces, reduces thermal conductivity. Stabilization techniques, particularly the use of surfactants, are commonly employed to address this issue [38-40]. Nevertheless, while increasing surfactant concentration can aid stabilization, it does not always improve thermal conductivity. Suganthi and Rajan observed that low surfactant concentrations could enhance thermal conductivity, whereas higher concentrations tended to diminish it [41]. Mare et al. studied the thermal conductivity of water-based nanofluids with carbon nanotubes stabilized by SDBS as a surfactant, focusing on how it varies with volume fraction [42]. The findings indicated that increasing the surfactant content results in a reduction in the thermal conductivity of the base fluids.

The addition of nanoparticles to a liquid impacts both its thermal conductivity and viscosity. The viscosity of a nanofluid, as well as thermal conductivity, depends on various conditions: concentration of nanoparticles, size and shape of nanoparticles, temperature, shear rate [43]. According to Prasher et al., the concentration of particles has a more significant impact on viscosity than other parameters [44]. Studies conducted by other researchers on TiO_2 nanofluids at various nanoparticle concentrations have demonstrated an increase in viscosity and have led to the development of viscosity models [45, 46]. Jararhead et al. also measured the viscosity of nanofluids containing TiO_2 and Al_2O_3 using capillary and Hoppler viscometers for weight concentrations of 3%, 6%, and 9% [46]. Also in this study, an increase in the viscosity of the TiO_2 nanofluid was observed in the presence of the polymer Polycarboxylate, Trioxadecane acid. Borode et al. examined the impact of surfactants GA, SDBS, SDS, and TWEEN 80 on the thermophysical properties of GNP in various ratios, noting that all four surfactants resulted in a maximum viscosity increase at 55°C [47]. Das et al. reported an enhancement in the viscosity characteristics of TiO_2 nanofluid when stabilized with CTAB and AA [48].

This article aims to determine the thermophysical properties, such as thermal conductivity and kinematic viscosity, of a bidistilled water-based TiO_2 nanofluid stabilized with the surfactants SDBS and CTAB, and to examine the effect of these surfactants on the nanofluid's thermal conductivity and viscosity. Considered proportions of TiO_2:SDBS and TiO_2:CTAB 1:0.1, 1:0.5, 1:1.

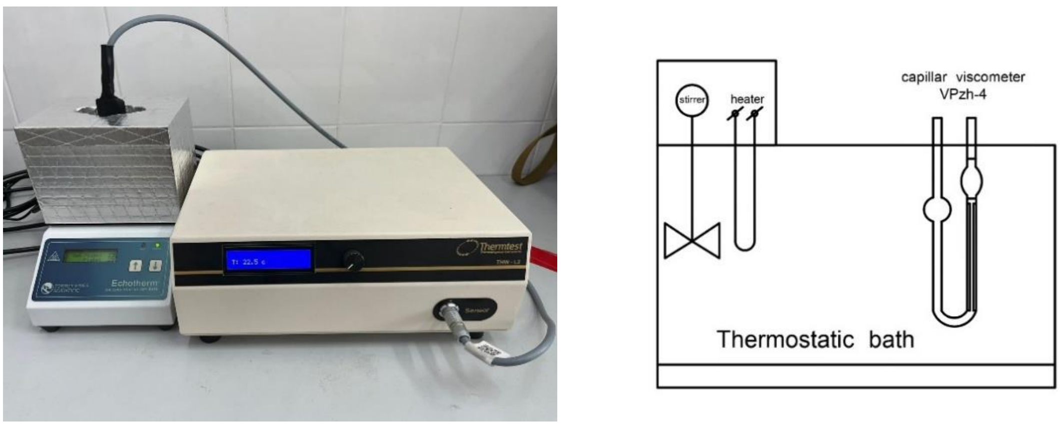
2. Research method

TiO_2 nanoparticles, along with the surfactants CTAB and SDBS, were supplied by Sigma-Aldrich. According to the provided specifications, the TiO_2 nanoparticles have a maximum size of 50 nm. The quantitative analysis of the TiO_2 nanoparticles was performed using an INCA Energy 250 energy dispersive spectrometer of a Jeol JSM-6390LV scanning electron microscope.

The nanofluid homogenization was achieved using a Scientz ultrasonic dispersant model “JY92-IIDN,” with a power output of 900 W and an ultrasonic frequency of 20 kHz. Weighing of nanoparticles and surfactants was carried out using an analytical balance. The INTLLAB magnetic stirrer is manufactured by Shenzhen Jiashi Technology Co., Ltd.

The nanofluid was synthesized using a two-step method, with bidistilled water (DDW) serving as the base fluid. Volume concentration of nanoparticles was maintained at 3%. The ratios of TiO_2 to CTAB and TiO_2 to SDBS were set at 1:0.1, 1:0.5, and 1:1. The preparation of the nanofluid involved three main steps. First, dispersing TiO_2 nanoparticles in bidistilled water for 30 minutes at 50% power; second, dissolving the surfactant in bidistilled water to prepare the surfactant solution; and finally, combining the TiO_2 dispersion with the surfactant solution and stirring the mixture using a magnetic stirrer for 30 minutes.

Thermal conductivity was measured by THW-2, utilizing the transient hot wire method. The Transient Hot Wire (THW-L2) Liquid Thermal Conductivity Meter is an advanced system designed for the direct measurement of the thermal conductivity of liquids and pastes, compliant with ASTM D7896-19 standards (Figure 1a). The THW-L2 employs a non-stationary measurement technique and quick testing times to minimize convective effects in samples with diverse viscosities, achieving accuracy within 1%. A series of measurements was taken, each consisting of five readings for every temperature. The nanofluid's temperature was controlled using the EchoTherm Digital Electronic Chilling/Heating Dry Bath Series IC35, manufactured by Torrey Pines Scientific (USA).



(a) (b)

Figure 1. Equipment for measuring thermophysical properties. a) THW-L2 for thermal conductivity measurement; b) Viscosity measurement setup

The relative change in thermal conductivity k_r was determined by comparing the nanofluid with surfactant to the base fluid (DDW). This comparison was calculated using the following formula:

$$k_r = \frac{k_{nf+surf} - k_{bf}}{k_{bf}} \cdot 100\% \quad (1)$$

Kinematic viscosity was measured using a capillary viscometer VPZh-4 with a capillary diameter of 0.37 mm. Viscosity measurements were performed over a temperature range of 293-333 K, with intervals of 10 degrees, regulated by a LOIP-LT thermostat (Figure 1b). Temperature equilibrium between the heated medium and the nanofluid within the viscometer was achieved within 1 minute, as indicated by the repeatability of the results. Additional environmental monitoring was ensured through the use of a temperature sensor.

The kinematic viscosity was calculated using the following formula:

$$\nu = \frac{g}{9.807} \cdot t \cdot K \quad (2)$$

Where ν is the kinematic viscosity of the liquid (cSt), g is the acceleration of gravity, t is the time during which the liquid passes the two extreme marks of the viscometer (sec.). K – viscometer constant (according to the device data sheet, $K = 0.003187$).

The relative change in kinematic viscosity ν_r was determined by comparing the nanofluid with surfactant to the base fluid (DDW). This comparison was calculated using the following formula:

$$\nu_r = \frac{\nu_{nf+surf} - \nu_{bf}}{\nu_{bf}} \cdot 100\% \quad (3)$$

For each measurement temperature, the standard deviation remains below 0.005 for viscosity measurements and below 0.003 for thermal conductivity assessments, as calculated using the following expression:

$$\sigma = \sqrt{\frac{(x-\overline{x})}{(n-1)}} \quad (4)$$

Where x is the measured value, $\bar{x}$ is the average value, and n is the number of measurements.

3. Results and discussion

The results regarding the measurement of thermal conductivity and viscosity at different temperatures for various nanoparticle ratios are presented and discussed in this section. The thermal conductivity for both surfactant variants exhibits a comparable trend. Specifically, the thermal conductivity of TiO_2/SDBS in a ratio of 1:0.1 (Figures 2 and 3) nanofluid within the temperature range of 20–60 °C increases from 0.635 W/(m·K) to 0.689 W/(m·K). In contrast, TiO_2-DDW nanofluid without any surfactants demonstrates higher thermal conductivity values, ranging from 0.645 W/(m·K) to 0.703 W/(m·K). The TiO_2/SDBS (1:0.5) proportion displays an average increase of 6% across temperature range compared to 6.6% of TiO_2/SDBS (1:0.1). The smallest increase in thermal conductivity, nearly 5.4% at each temperature interval, is observed in the TiO_2/SDBS (1:1) formulation, with the maximum reduction occurring at 60°C where the thermal conductivity reaches 0.682 W/(m·K).

In comparison, the CTAB surfactant (Figures 4 and 5) results in lower thermal conductivity values across all concentrations. At 20°C, the thermal conductivity of the TiO_2/CTAB nanofluid registered at 0.630 W/(m·K), which is lower than the of TiO_2/SDBS in ratio 1:0.1. For TiO_2/CTAB (1:0.5) and TiO_2/CTAB (1:1), an average increasing of 5.2% and 4.4% is observed, with the thermal conductivity beginning from 0.627 W/(m·K) for ratio 1:0.5 to 0.622 W/(m·K) for ratio 1:1 at 20°C. A similar increase trend in thermal conductivity is also noted for TiO_2/CTAB (1:0.5) and TiO_2/SDBS (1:1), spanning from 0.627 W/(m·K) to 0.682 W/(m·K) over the 20–60°C temperature range.

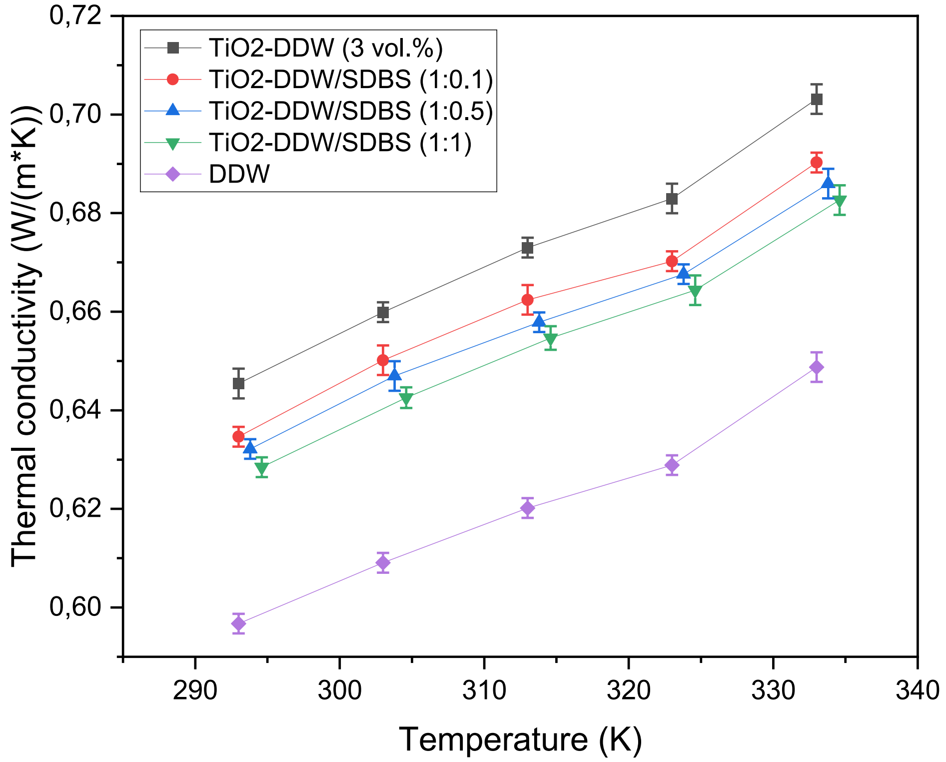


Figure 2. Bidistilled water-based TiO_2 nanofluid stabilized by SDBS. Thermal conductivity

Horizontal offset of ±0.8 K was applied only to TiO_2-DDW/SDBS (1:0.5) and (1:1) samples to distinguish overlapping data points.

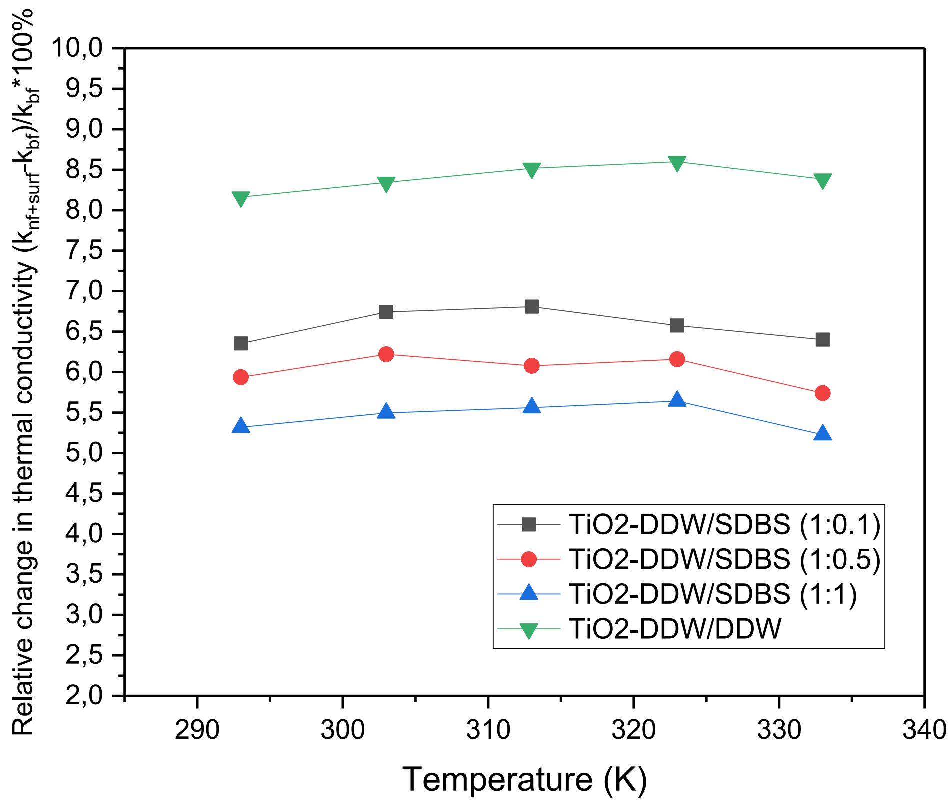


Figure 3. Bidistilled water-based TiO_2 nanofluid stabilized by SDBS. Relative change in thermal conductivity of the nanofluid with respect to bidistilled water

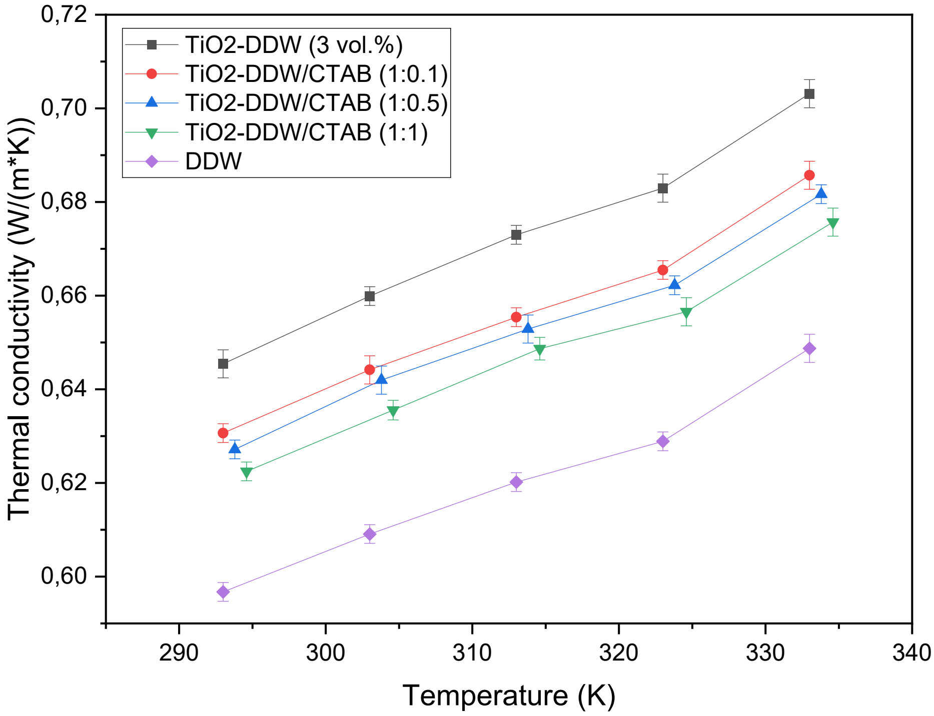


Figure 4. Bidistilled water-based TiO_2 nanofluid stabilized by CTAB. Thermal conductivity

Horizontal offset of ±0.8 K was applied only to TiO_2-DDW/CTAB (1:0.5) and (1:1) samples to distinguish overlapping data points.

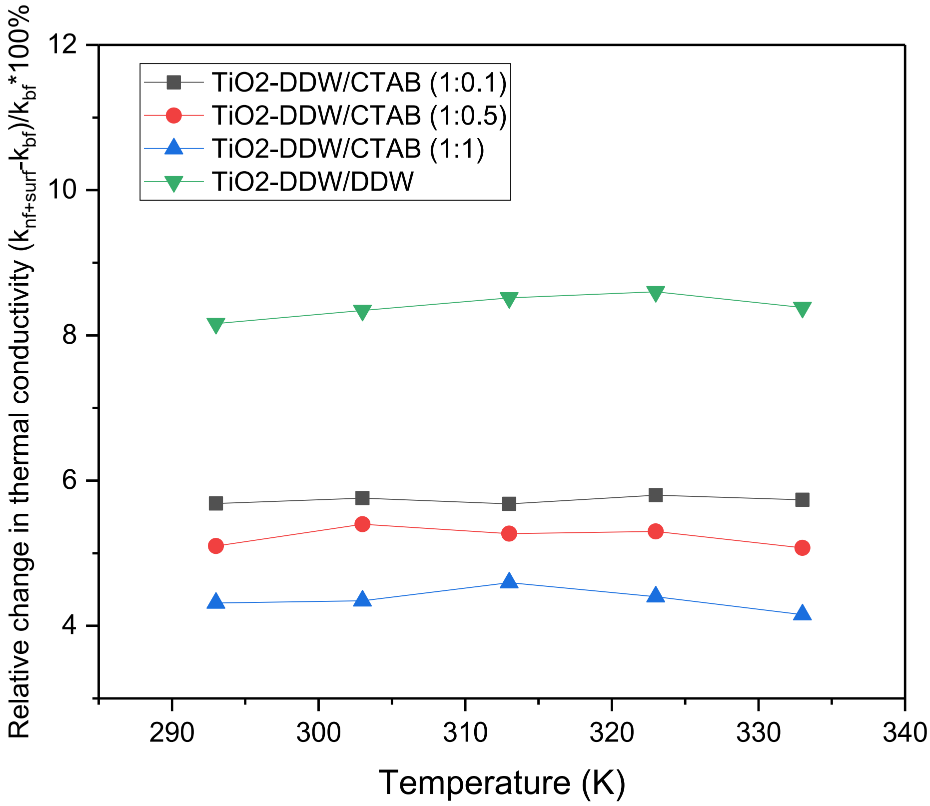


Figure 5. Bidistilled water-based TiO_2 nanofluid stabilized by CTAB. Relative change in thermal conductivity of the nanofluid with respect to bidistilled water

Figures 6, 7, 8, and 9 illustrate the viscosity behavior of TiO2–bidistilled water nanofluids, influenced by SDBS and CTAB surfactants. The kinematic viscosity of TiO_2-based nanofluids varies significantly depending on the type and concentration of surfactants used. At a TiO_2:surfactant ratio of 1:0.1 and a temperature of 20°C, the presence of CTAB surfactant results in a 64.4% increase in viscosity, whereas the use of SDBS surfactant leads to a 57.6% increase. Over the temperature range of 20–60°C, the average viscosity increase is 49% for CTAB and 43.7% for SDBS. At a TiO_2:CTAB ratio of 1:0.5, the viscosity decreases from 70% at 20°C to 38.1% at 60°C. Similarly, for SDBS, the corresponding increase is smaller, with values of 63.1% and 34.4%, respectively. The maximum viscosity increase occurs at a TiO_2:surfactant ratio of 1:1 at 20°C, where the nanofluid with CTAB achieves a kinematic viscosity of 1.708 cSt, which is 3% higher than the 1.667 cSt recorded for SDBS. At 60°C, the kinematic viscosity decreases to 0.677 cSt for CTAB and 0.660 cSt for SDBS.

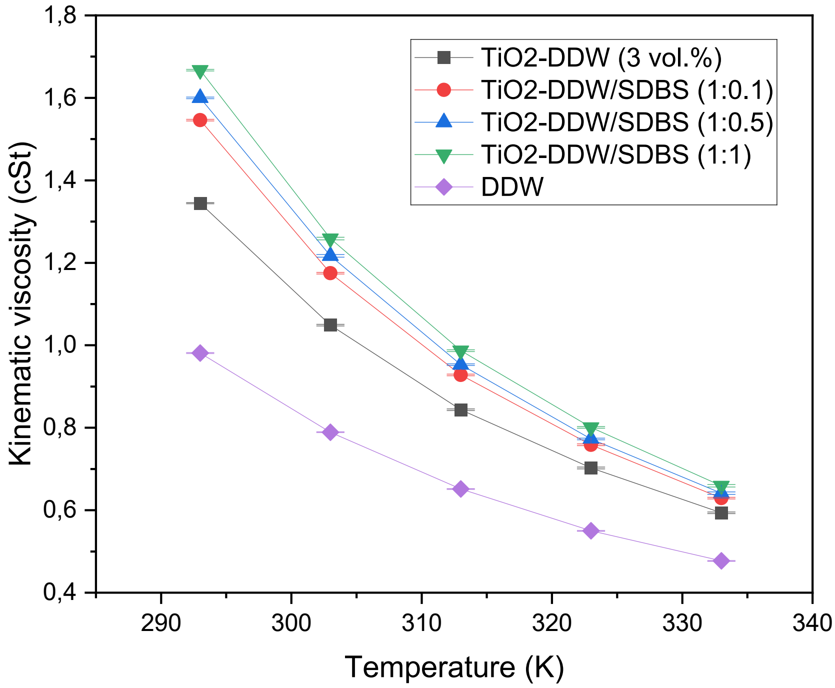


Figure 6. Bidistilled water-based TiO_2 nanofluid stabilized by SDBS. Kinematic viscosity

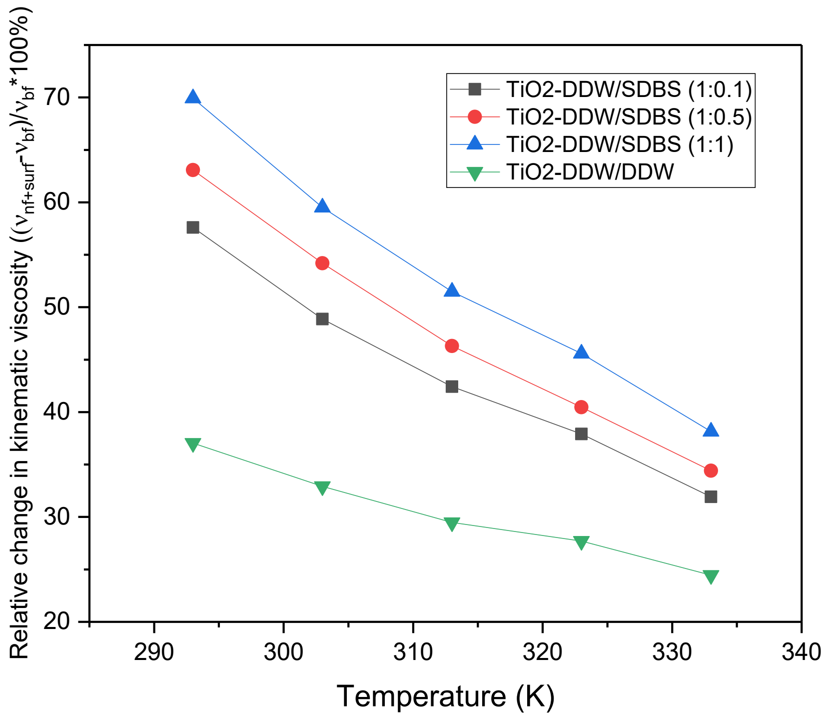


Figure 7. Bidistilled water-based TiO_2 nanofluid stabilized by SDBS. Relative change in kinematic viscosity of the nanofluid with respect to bidistilled water

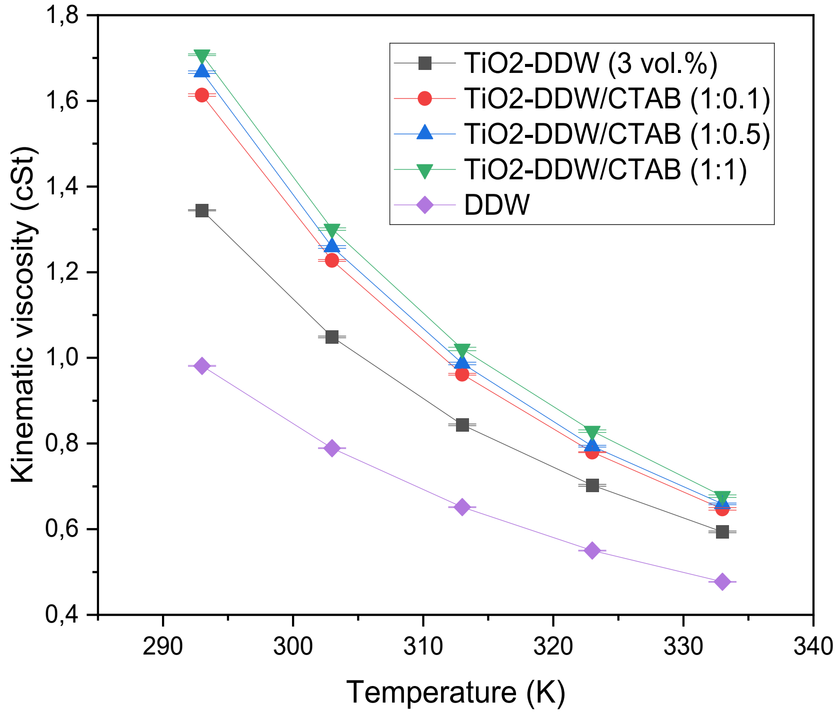


Figure 8. Bidistilled water-based TiO_2 nanofluid stabilized by CTAB. Kinematic viscosity

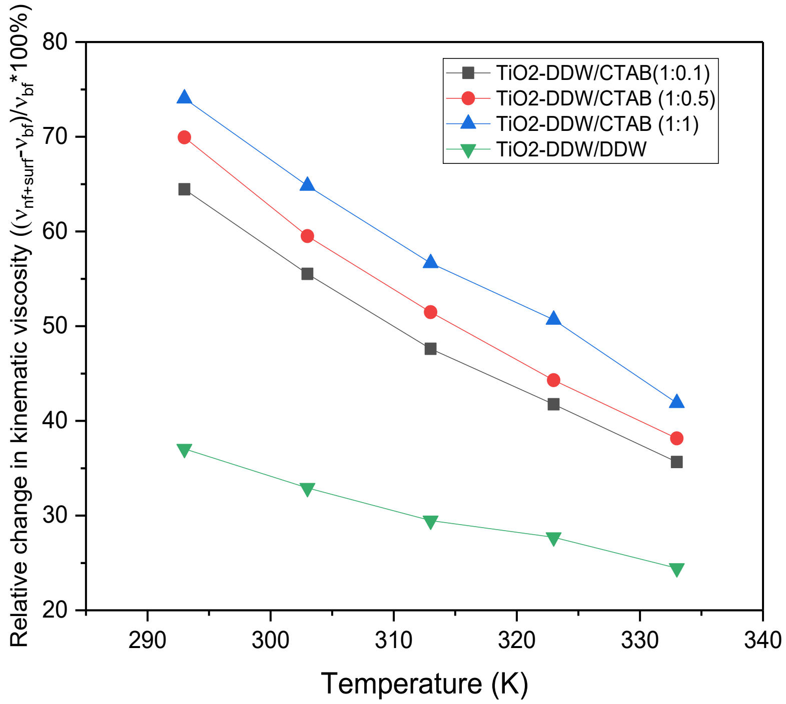


Figure 9. Bidistilled water-based TiO_2 nanofluid stabilized by CTAB. Relative change in kinematic viscosity of the nanofluid with respect to bidistilled water

Figures 10 and 11 illustrate the dependence of the thermal conductivity of the nanofluid on the concentrations of surfactants SDBS and CTAB. Thermal conductivity decreases as surfactant concentration increases for both SDBS and CTAB stabilized nanofluids. For the TiO_2-distilled water nanofluid in the presence of the surfactant SDBS, the reduction in thermal conductivity is less pronounced compared to that observed with CTAB. At lower temperatures (293K), the rate of decrease is lower (0.005 W/(m·K)/%) for SDBS surfactant. TiO_2-CTAB nanofluid has a slightly higher decline rate (0.007 W/(m·K)/%) at the same temperature.

The data follow a nonlinear decreasing trend, indicating that excess surfactant leads to lower thermal conductivity. The curve fitting suggests an asymptotic behavior, where increasing the surfactant concentration beyond ~1 vol.% has a diminishing effect on reducing thermal conductivity.

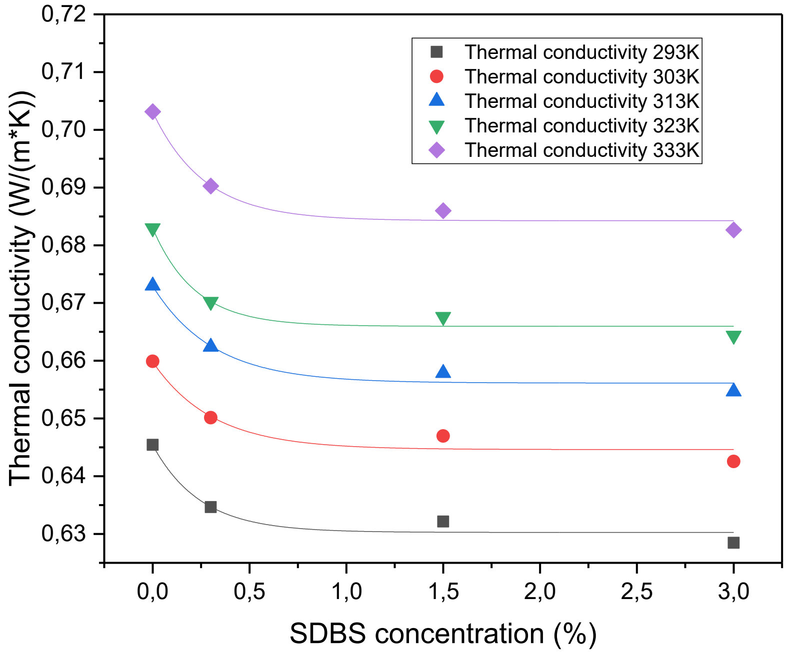


Figure 10. Thermal conductivity as a function of surfactant volume concentration. Bidistilled water-based TiO_2 nanofluid stabilized by SDBS surfactant.

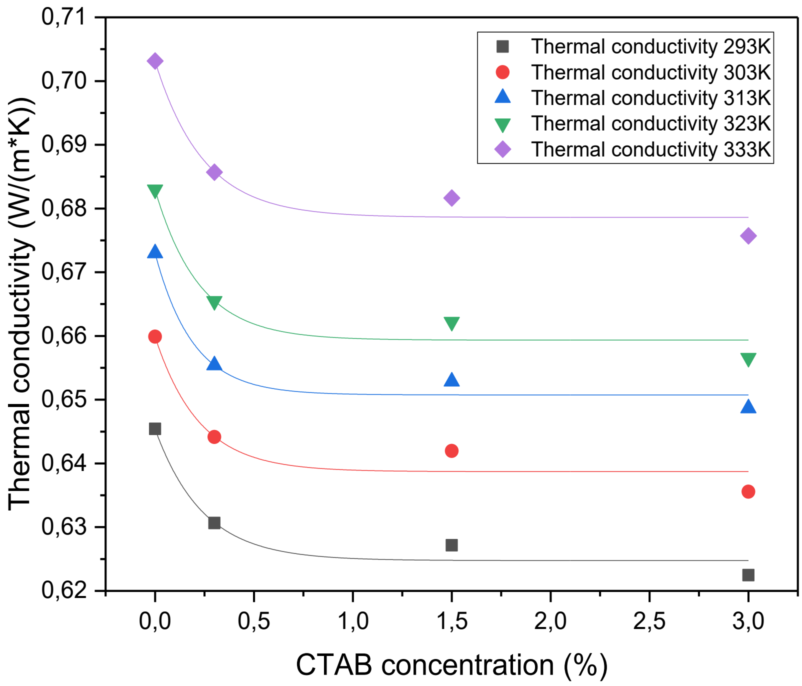


Figure 11. Thermal conductivity as a function of surfactant volume concentration. Bidistilled water-based TiO_2 nanofluid stabilized by CTAB surfactant.

Figures 12 and 13 illustrate the viscosity of TiO2–bidistilled water nanofluids as a function of surfactant volume concentrations. It shows a significant increase in viscosity with increasing surfactant content, particularly pronounced at 3 vol.%. Notably, the presence of CTAB results in a sharper viscosity increase compared to SDBS.

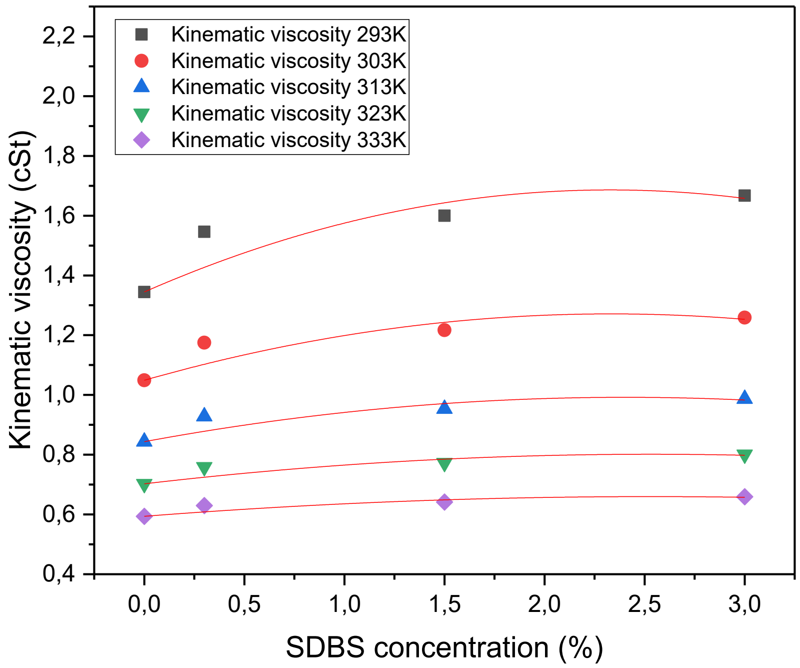


Figure 12. Kinematic viscosity as a function of surfactant volume concentration. Bidistilled water-based TiO_2 nanofluid stabilized by SDBS surfactant.

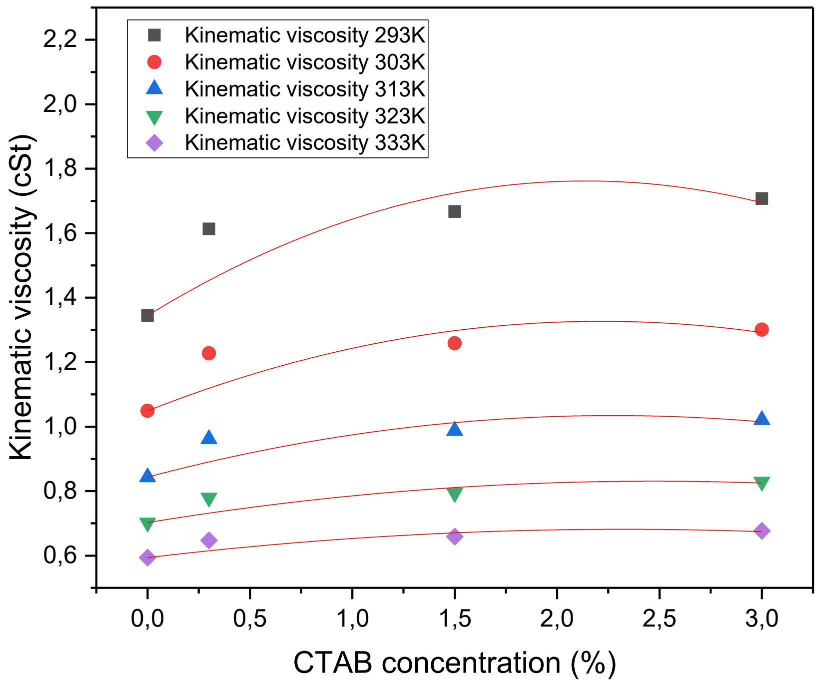


Figure 13. Kinematic viscosity as a function of surfactant volume concentration. Bidistilled water-based TiO_2 nanofluid stabilized by CTAB surfactant.

Based on the collected data, a relationship describing the thermophysical characteristics of nanofluids with the addition of surfactants SDBS and CTAB was proposed (Tables 1 and 2). The graphs were fitted using an asymptotic curve fit for thermal conductivity and a polynomial curve fit for kinematic viscosity.

Table 1 presents the coefficients of a regression analysis for modeling the thermal conductivity of TiO_2-bidistilled water nanofluids. The analysis considers the impact of two surfactants, SDBS and CTAB, across a concentration range of 0–3 vol.% and temperatures between 20°C and 60°C. The regression model used is $k_{nf+surf} = A - B \cdot C^{\varphi}$, where A, B, and C are the coefficients determined for each surfactant and temperature.

These coefficients provide a quantitative relationship between thermal conductivity and surfactant concentration, highlighting the influence of surfactant type and temperature. The fitting yielded a coefficient of determination (R^2) greater than 0.99, indicating a robust description of the data dependency and high predictive accuracy.

Table 1. Coefficients of regression analysis of the kinematic viscosity of TiO_2-bidistilled nanofluid depending on the volume concentration of CTAB and SDBS

Name of surfactant	Concentration range (vol.%)	Temperature (°C)	Regression curve fit	A	B	C
SDBS	0-3	20	$k_{nf+surf} = A - B \cdot C^{\varphi}$	0.63027	-0.01515	0.01677
		30		0.64462	-0.01521	0.03906
		40		0.65614	-0.01681	0.04058
		50		0.66597	-0.01699	0.01025
		60		0.68426	-0.01886	0.0233
CTAB	0-3	20		0.62476	-0.02066	0.01594
		30		0.63872	-0.02117	0.01126
		40		0.65075	-0.02224	0.00548
		50		0.65935	-0.02361	0.01155
		60		0.67861	-0.0245	0.01692

Table 2 provides the coefficients for the regression analysis describing the kinematic viscosity of TiO_2-bidistilled water nanofluids with CTAB and SDBS surfactants. The concentration range of the surfactants varies from 0 to 3 vol.% across temperatures between 20°C and 60°C.

The regression model applied is $\nu_{nf+surf} = A + B_1 \cdot \varphi + B_2 \cdot \varphi^2$, where A, B_1, and B_2 are determined as fitting coefficients for each temperature and surfactant. Importantly, the initial coefficient A reflects the kinematic viscosity of the nanofluid without any added surfactant. The regression fit achieved a high coefficient of determination (R^2>0.97), indicating strong agreement between the experimental data and the model. Additionally, the Residual Sum of Squares (RSS) ranges from 0.0001 to 0.01, demonstrating a precise fit and a reliable representation of the data.

Table 2. Coefficients of regression analysis of the kinematic viscosity of TiO_2-bidistilled nanofluid depending on the concentration of CTAB and SDBS

Name of surfactant	Concentration range (vol.%)	Temperature (°C)	Regression curve fit	A	B_1	B_2
SDBS	0-3	20	$\nu_{nf+surf} = A + B_1 \cdot \varphi + B_2 \cdot \varphi^2$	1.34456	0.29351	-0.06304
		30		1.04904	0.19053	-0.04084
		40		0.84354	0.12354	-0.02569
		50		0.703	0.07818	-0.01544
		60		0.59381	0.05216	-0.01031
CTAB	0-3	20		1.34456	0.39033	-0.09119
		30		1.04904	0.25065	-0.05654
		40		0.84354	0.16812	-0.03699
		50		0.703	0.10393	-0.02102
		60		0.59381	0.07569	-0.01628

The adsorption of surfactants on the surface of TiO_2 nanoparticles increases with rising surfactant concentration, aligning with the monomolecular Langmuir adsorption theory.

Changes in the thermophysical properties of the TiO_2-bidistilled water nanofluid are associated with the structure of surfactants. The surfactant's structure plays a crucial role in affecting the nanofluid's viscosity. For instance, CTAB has a hydrocarbon tail comprising 16 carbon atoms, while SDBS has 12. CTAB's head group is a positively charged quaternary ammonium group, whereas SDBS has a sulfonate group attached to a benzene ring. The micelles formed by the CTAB surfactant are larger in size compared to those formed by SDBS, leading to increased steric hindrance in the presence of CTAB. This results in an average 5% higher kinematic viscosity for the TiO_2/CTAB-bidistilled water nanofluid compared to the TiO_2/SDBS-bidistilled water nanofluid. Viscosity influences the flow behavior and convective heat transfer in the fluid, which indirectly affects the overall energy transfer efficiency between liquid layers. The increased viscosity, in turn, contributes to a slight reduction in thermal conductivity at lower surfactant concentrations.

Furthermore, the specific structural characteristics of the surfactants significantly influence thermal conductivity variations. The most pronounced enhancement in thermal conductivity is observed at a TiO_2-to-surfactant ratio of 1:0.1, which also shows the minimum viscosity, whereas the 1:1 ratio results in the lowest thermal conductivity enhancement and the highest viscosity increase. While the presence of surfactants slightly reduces the thermal conductivity of the nanofluid compared to that without surfactants, a significant overall increase in thermal conductivity is still observed.

4. Conclusions

This study examines the impact of CTAB and SDBS surfactants on the thermophysical properties of TiO_2-bidistilled water nanofluid at surfactant ratios of 1:0.1, 1:0.5, and 1:1. The results indicate that increasing the surfactant concentration leads to a rise in the nanofluid's kinematic viscosity. Concurrently, a decrease in thermal conductivity is observed with higher surfactant proportions. The optimal balance of maximum thermal conductivity and minimum viscosity is achieved at a TiO_2-to-surfactant ratio of 1:0.1. Particularly, at 20 °C to 60 °C for TiO_2:SDBS (1:0.1), there is an increase of thermal conductivity from 0.635 to 0.690 W/(m·K). TiO_2:CTAB shows less increase, 0.630-686 W/(m·K). In contrast, the highest kinematic viscosity and the largest reduction in thermal conductivity are observed at a ratio of 1:1 at 20 °C, which are 1.667 cSt and 0.628 W/(m·K) for TiO_2:SDBS nanofluid and 1.706 cSt and 0.622 W/(m·K) for TiO_2:CTAB nanofluid.

Regression analysis reveals that the thermal conductivity of the nanofluid, influenced by the presence of SDBS and CTAB surfactants, follows an asymptotic trend, while the kinematic viscosity is best described by a second-degree polynomial.

Declaration of competing interest

The authors declare that they have no known financial or non-financial competing interests in any material discussed in this paper.

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Author contribution

A. Kassymov, M. Arıcı: study conception and design; A. Adylkanova, T. Umyrzhan: data collection; Zh. Akishov, A. Bektemissov: analysis and interpretation of results. All authors approved the final version of the manuscript.

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