Effect of surfactants on the stability and solar thermal absorption characteristics of water-based nanofluids with multi-walled carbon nanotubes

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A B S T R A C T

This paper reports the effect of various surfactants on the suspension stability and the solar thermal absorption characteristics of water-based nanofluids containing multi-walled carbon nanotubes (MWCNTs) that can be used as working fluids for volumetric solar thermal receivers. The water-based MWCNT nanofluids were prepared using a two-step method with four commonly used surfactants: sodium dodecylbenzenesulfonate (SDBS), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and Triton X-100 (TX-100). The stability of the four surfactant-treated nanofluids was analyzed for over a month with an in-house developed laser transmission system. The effect of temperature on the stability of the nanofluid/surfactant mixtures was also examined. In addition, to identify the absorption characteristics of the four nanofluids, the spectral extinction coefficients were measured using an UV–Vis–NIR spectrophotometer. The absorbed sunlight fraction was calculated using the measured spectral extinction coefficient, which enabled an evaluation of the absorption characteristics of the nanofluids. The MWCNT nanofluids were clearly shown to enhance the absorption rate of solar thermal energy. The suspension stability and the absorption characteristics were also strongly affected by the type of surfactant. Moreover, using the absorbed sunlight fraction and suspension-stability factor, we experimentally show the relation between the absorption characteristics and suspension stability in nanofluids.

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1. Introduction

Traditional thermal receivers, including flat-plate and parabolic trough receivers, have been widely used to capture solar thermal energy. These receivers, also called surface-based solar thermal receivers, capture solar thermal energy using metal plates or tubes with selective coatings. The thermal energy captured by the receiver is then transferred to a working fluid [1]. However, surface-based solar thermal receivers have inherent limitations in efficiency due to the irreversibility associated with the heat exchange between the solar plates and the working fluid [1–4]. To overcome these challenges, the direct-absorption solar collector (DASC), which uses the concept of volumetric absorption, has been introduced to the field of solar thermal applications [3–18].

Instead of using metal plates or tubes with selective coatings, the DASC captures solar thermal energy directly in a working fluid volume that has a high extinction coefficient. Conventional working fluids such as water, ethylene glycol, and thermal oil cannot be efficiently used for direct absorption of solar thermal energy due to their low extinction coefficients. However, working fluids containing multi-walled carbon nanotubes (MWCNTs) are a viable alternative for the direct absorption of solar thermal energy [3,4,11,17] because the MWCNT nanofluids have not only high thermal absorption characteristics, but also high thermal conductivity [19–23].

Typically, investigators use surfactants to prepare MWCNT nanofluids in order to ensure that the light absorbing nanoparticles remain well-dispersed in the liquid. For instance, Bandyopadhyaya et al. [24] manufactured water-based MWCNT nanofluids using surfactants including sodium dodecyl sulfate (SDS), cetyltrimethylammonium chloride (CTAC), and gum arabic. They also reported on the suspension stability of nanofluids with various surfactants, using X-ray scattering with dry nanoparticles and cryogenic
transmission electron microscopy (Cryo-TEM) at or below -170 °C. Unfortunately, these methods cannot be used to measure the suspension stability of nanofluids at operating temperature conditions.

Wen et al. [25] employed sodium dodecylbenzene sulfonate (SDBS) in preparing water-based nanofluids with MWCNTs. They reported the aggregation of MWCNT nanofluids with SDBS when heated to temperatures between 60 °C and 70 °C. A satisfactory criterion for quantifying MWCNT nanofluids suspension stability does not exist in the current literature. Assael et al. [26] used three types of surfactants (hexadecyltrimethyl ammonium bromide [CTAB], NanoSperse AQ,1 and SDS) to obtain MWCNT nanofluids with high suspension stability. They characterized the suspension stability of the nanofluids using scanning electron microscopy (SEM) and micro-Raman spectroscopy. However, SEM and micro-Raman were used to measure the size and morphology of nanoparticles by measuring dry nanoparticles, rather than nanofluids. Rastogi et al. [27] manufactured water-based MWCNT nanofluids with surfactants such as Triton X-100 (TX-100), Tween 20, Tween 80, and SDS. However, they reported absorption characteristics using UltraViolet–Visible (UV–Vis) spectroscopy results for only the initial condition (soon after preparation), rather than the absorption characteristics over time.

Although much of the past research with MWCNT nanofluids has been done with surfactants resulting in good suspension stability, there is no systematic research that examines both suspension stability over time and the extinction coefficient. Therefore, this paper systematically reports the effect of surfactants on both suspension stability and the extinction coefficient of water-based MWCNT nanofluids over time. In addition, the effect of temperature on the stability of the nanofluids is examined. The results clearly show that suspension stability and absorption characteristics are strongly affected by the type of surfactant used with the base fluid. The present study shows that water-based MWCNT nanofluids produced with SDBS have a high extinction coefficient as well as high suspension stability between 10 °C and 85 °C, suggesting that SDBS is a superior surfactant for use in DASC.

2. Experimental study

2.1. Manufacturing processes of MWCNT nanofluids

Four commercial surfactants (SDBS, CTAB, SDS, TX-100) were used along with commercial MWCNT nanoparticles (\(D = 20\) nm, \(l = 1–25\) μm) to manufacture the water-based MWCNT nanofluids of this study. The water-based MWCNT nanofluids were produced using the two-step method with a wet-milling process. In the first step, the amount of each surfactant needed to produce a 0.2% surfactant mass fraction with de-ionized (DI) water was determined. All of the nanofluids had a surfactant mass fraction of 0.2%. Limiting the mass of surfactant in the nanofluid helped to limit the degradation of the thermal conductivity of the nanofluid as caused by the addition of the surfactant. In the second step, the MWCNT powder was milled with DI water using a planetary mill with a 1 mm zirconia ball for 60 min at 600 rpm (rpm). The MWCNT and the mixture of DI water and surfactant at 0.2% mass fraction were homogenized with a bath-type sonicator and mechanical stirrer at 200 rpm for approximately 1 h. Fig. 1 shows the appearance of the water-based nanofluids with MWCNT volume fraction \(\phi = 0.0005\%\), \(\phi = 0.002\%\), manufactured with different surfactants. As shown in Fig. 1, it is difficult for the naked eye, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and so on, to determine whether or not the nanofluids have high suspension stability. Consequently, in this study, a laser-scattering method is used to evaluate quantitatively the long-term suspension stability [28].

2.2. Suspension characterization of nanofluids

In this study, the intensity of light transmission (\(I\)) through each nanofluid was measured using an in-house developed laser transmission apparatus, as shown in Fig. 2 [28]. This was done to quantitatively evaluate the suspension stability of the nanofluids over the period of approximately one month. The suspension-stability factor, \(\varepsilon(t)\), quantitatively indicates the degree of suspension stability, as given by [28]:

\[
\varepsilon(t) = \frac{I_0 - I(t)}{I_0 - I_{\text{initial}}} = \frac{\Delta I(t)}{\Delta I_{\text{initial}}} 
\]

(1)

where \(I(t)\), \(I_0\), and \(I_{\text{initial}}\) are the intensity of the light transmission through the cuvette and the nanofluid as a function of time, the intensity of the light incident to the cuvette, and the initial intensity of light transmission through the nanofluid and cuvette, respectively. The \(I_{\text{initial}}\) is assumed to represent the best dispersion immediately after sonication of the nanofluid. Values of the suspension stability factor can be from zero to 1. Smaller values of \(\varepsilon(t)\) represent a larger degradation in the stability of the nanofluid suspension. The uncertainty of the \(\varepsilon(t)\) measurement was ±5% of the measurement for a 95% confidence level. All measurement uncertainties are reported at the 95% confidence level.

2.3. Extinction coefficient and absorbed sunlight fraction

Typically, the extinction coefficient is obtained from either an absolute single-beam measurement technique or a differential
The dual-beam technique. The absolute single-beam technique [7,13,14,29] directly measures the optical properties of a sample, but this technique requires knowledge of many factors, including the refractive indices, the path length, and the thickness of the cuvette. However, the differential dual-beam technique [4,5,9,30] can be used to measure the extinction coefficient of a sample without any prior information. Considering this, a UltraViolet–Visible–Near-Infrared (UV–Vis–NIR) spectrophotometer with a differential dual-beam (one beam in air and the other through the cuvette with the sample) was used in this study to determine the extinction coefficients ($\sigma_{NF}$) of the nanofluids. The relative transmittance ($T$), which is the ratio of the transmittance intensity of the nanofluid ($I_{NF}$) to that of the transmittance intensity in air ($I_{air}$), can be described by the Beer-Lambert law [31] as:

$$T = \frac{I_{NF}}{I_{air}} = \exp(-\sigma_{NF}l),$$

where $l$ and $\sigma_{NF}$ are the path length of the cuvette and the extinction coefficient of the nanofluid, respectively. Eq. (2) was solved for extinction coefficient of the nanofluid ($\sigma_{NF}$) making it equal to $-\ln T/l$. In this way, the measured values of $l$, $I_{NF}$, and $I_{air}$ were used to calculate the extinction coefficient of the nanofluid ($\sigma_{NF}$) as a function of wavelength. The uncertainty in the extinction coefficient is estimated to be less than $\pm3\%$ of the value.

The absorptivity of most substances, including nanofluids, is wavelength dependent. As a result, the extinction coefficient of the nanofluid is a function of the wavelength. Consequently, the absorptivity of solar thermal energy varies with wavelength for nanofluids, and is obtained from the absorbed sunlight fraction ($F$) and on the measured extinction coefficient [7,17,32]:

$$F = 1 - \frac{\int_{1800nm}^{2000nm} I_{NF}e^{-\sigma_{NF}l}dl}{\int_{1800nm}^{2000nm} I_{air}dl},$$

Fig. 1. Nanofluids with (a) volume fraction $\phi = 0.0005\%$, (b) $\phi = 0.002\%$ manufactured with various surfactants by the two-step method with wet-milling process.
where $F$ and $I_k$ are absorbed sunlight fraction at the path length of $l$ and intensity of sunlight. Eq. (3) represents the fraction of solar thermal energy with multi-wavelengths between 200 nm and 1800 nm that is absorbed by the nanofluids in a path length. The uncertainty in the measured $F$ was estimated to be ±3%. The uncertainty in the measured wavelength was ±0.4 nm for NIV and ±0.2 nm for UV–Vis.

3. Results and discussion

3.1. Suspension characterization of nanofluids

3.1.1. Short-term suspension-stability test

Fig. 3a is a plot of the measured suspension stability factor $\varepsilon$ for the four MWCNT nanofluids of this study for the first 3 h after manufacture at room temperature (approximately 25 °C). Fig. 3a shows that the $\varepsilon$ for all of the suspensions remain within 0.2% of the initial $\varepsilon$ for the first three hours. The stabilities of the nanofluids manufactured with SDBS, CTAB, and TX-100 are better than that manufactured with the SDS, decreasing less than 0.1% as compared to the initial $\varepsilon$.

3.1.2. Long-term suspension-stability test

Fig. 3b shows the results of a month-long observation of the suspension stability of the four nanofluids prepared with each surfactant at room temperature (25 °C). The SDBS and the TX-100 nanofluids exhibit the best stability of the four test fluids, with the $\varepsilon$ decreasing by less than 1% over a month. The CTAB nanofluid was the next best suspension, having a $\varepsilon$ that decreased by approximately 2% after one month. By comparison, the suspension stability of the SDS nanofluid decreased significantly more than the other test fluids, i.e., by nearly 6% at the end of a month-long period. Based on these results, at 25 °C, the SDBS and TX-100 nanofluids have the highest suspension stability of the four evaluated.

3.1.3. High-temperature suspension test

Wen et al. [25] reported that significant sedimentation of SDBS nanofluids occurs between 60 °C and 70 °C. In order to test for a precipitation reaction, the four nanofluid samples were heated to 85 °C in a water bath for 5 h. As Fig. 4 shows, the TX-100 nanofluids did not maintain suspension stability at this temperature; the particles aggregated and settled out. However, the precipitation was not visible to the unaided eye for the other nanofluids. As shown in Fig. 5, the measured suspension stability factors of the TX-100 nanofluids decreased rapidly with elapsed time at 85 °C. In contrast, the temperature of 85 °C had no effect on the suspension stability of the SDBS, CTAB, and SDS nanofluids. Thus, the present results do not entirely concur with the results presented by Wen et al. [25] in that better stability was observed here.

A difference between the nanofluid manufacturing process of the Wen et al. [25] study and the present study may have resulted
in a difference in the measurement results for the two studies. Wen et al. [25] used raw MWCNTs with a length of several tens of micrometers, while a wet-milling process was used in the present study, which shortens the MWCNTs. Fig. 6 shows a TEM image of the particles in the current paper after they were processed with the planetary ball mill. The image shows that the length of the particles is less than 1 μm. It is well known that the suspension stability of nanofluids is affected by the length of the MWCNTs, more so than by the type of surfactant used [3,33].

3.1.4. Low-temperature suspension-stability test

The suspension stability was also measured at a lower temperature by using a thermostat chamber to cool the nanofluids to 10 °C for over 2 days. An unexpected result of the lower temperature tests, shown in Fig. 7, was that both the CTAB and the SDS surfactants formed precipitates in the bottom of the bottle at 10 °C.

In summary, it was determined that TX-100, CTAB, and SDS are not suitable surfactants for nanofluids operating from 10 °C to 85 °C based on the results of our short and long timeframe, high and low temperature suspension stability.

3.2. Extinction coefficient of nanofluids

Fig. 8 illustrates that the four nanofluids, at room temperature (25 °C), have significantly improved extinction coefficients as compared to the base fluid (DI water). In particular, the extinction coefficient of nanofluids is much larger than that of the base fluid (DI water) at the shorter wavelengths (visible and IR ranges), regardless of surfactants, within 3 h after manufacture. These results agree with previous results [4,5,22] and clearly show that MWCNTs in nanofluids not only enhance the absorption rate of solar thermal energy with wavelengths from 200 nm to 1800 nm, but also increase the thermal conductivity of the nanofluids [19–21]. In addition, it was observed that the enhancement of the extinction coefficient strongly depends on the surfactant as shown in Fig. 8. These results clearly indicate that well suspended MWCNTs play an important role in enhancing the extinction coefficient.

Fig. 9 shows that the extinction coefficient of each nanofluid gradually increased with respect to the concentrations of MWCNTs. For the same volume fraction of MWCNT in the nanofluids, Fig. 9 shows the solid lines represent the extinction coefficient of the nanofluids measured at the initial time and the dotted lines
show the results after one month. The greater the difference between the solid lines and the dotted lines, the larger the reduction rate of the extinction coefficient of the nanofluid during the month. The TX-100 and the SDBS nanofluids both exhibit overall difference less than 2%, while the SDS nanofluids show the largest difference, on the order of 20%. Also, it is clearly shown that the extinction coefficient increases with the increase in the volume fraction of MWCNTs suspended in the nanofluid regardless of the surfactant. However, when the volume fraction is larger than 0.002%, the difference in the value between the solid lines and the dotted line depends on the surfactant. These results indicate that the suspension stability is more effective at improving the extinction coefficient using nanofluids with high nanoparticle volume fraction such as MWCNT.

3.3. Absorbed sunlight fraction of nanofluids

It is difficult to evaluate the absorption performance of nanofluids in a specific wavelength range (200–1800 nm) for solar thermal energy using the extinction coefficient measured at 632.8 nm because the extinction coefficient varies with the wavelength. A single overall value would be convenient to calculate the absorption characteristics of the nanofluids. Therefore, the absorbed sunlight fraction was calculated using the measured extinction coefficient according to the wavelength range using Eq. (3) with the path length of $l = 1$ cm. Table 1 shows the results of absorbed sunlight fraction by the MWCNT nanofluids (volume fraction $\phi = 0.002\%$). Within 3 h after manufacture (initial time) and at room temperature, the surfactant with the highest to lowest absorbed sunlight fraction: TX-100, SDBS, CTAB, and SDS. The MWCNT nanofluids with TX-100 had the highest value of absorbed sunlight fraction (approximately 98.84%). One month later, the order of surfactants based on absorbed sunlight fraction remained unchanged. The values of absorbed sunlight fraction for TX-100 nanofluids showed the smallest reduction, while the values for SDS nanofluids showed the greatest decrease at room temperature. The reduction rate in the absorbed sunlight fraction was very similar to the results of the suspension stability observations. To quantitatively analyze the relationship between suspension stability and absorbed sunlight fraction at room temperature, the absorbed sunlight fraction and suspension-stability factor were plotted in Fig. 10, which shows that the absorbed sunlight fraction increases with the suspension-stability factor. Fig. 10 indicates absorbed sunlight fraction can be enhanced by MWCNTs that are well suspended in nanofluids.

4. Conclusions

This study experimentally presents the effect of surfactants on suspension stability and the absorption characteristics of aqueous nanofluids containing MWCNTs that have been used as working fluids for volumetric solar thermal receivers. The water-based MWCNT nanofluids were prepared with four surfactants (SDBS, CTAB, SDS, and TX-100), using the two-step method with a wet-milling process. To evaluate the suspension stability of the nanofluids prepared with each of the four surfactants, a laser transmission apparatus was developed and used in house. The effect of surfactants on the suspension stability at low and high temperature (10°C and 85°C) as well as at short and long timeframes (3 h and one month) were presented. Also, the extinction coefficients of the nanofluids were measured using the UV–Vis–NIR spectrophotometer in a wavelength range specific to solar thermal energy (200–1800 nm), at initial time (within 3 h of manufacture), as well as at one month later. The resulting extinction coefficients of the nanofluids were measured using the UV–Vis–NIR spectrophotometer in a wavelength range specific to solar thermal energy (200–1800 nm), at initial time (within 3 h of manufacture), as well as at one month later. The resulting extinction coefficients of the nanofluids were measured using the UV–Vis–NIR spectrophotometer in a wavelength range specific to solar thermal energy (200–1800 nm), at initial time (within 3 h of manufacture), as well as at one month later. The resulting extinction coefficients of the nanofluids were much larger than those of the base fluid. It was clearly shown that MWCNTs in nanofluids not only enhance the absorption rate of the solar thermal energy, but also increase the thermal conductivity of the nanofluids with highly conductive
nanoparticles. The extinction coefficient is enhanced with larger volume fraction of well-suspended MWCNTs in the nanofluids.

To characterize the absorption performance of solar thermal energy, the absorbed sunlight fraction of each nanofluid was calculated with the measured extinction coefficient for wavelengths from 200 nm to 1800 nm. The values of absorbed sunlight fraction, from high to low are nanofluids with TX-100, SDBS, CTAB, and SDS, respectively. Finally, it was observed that the reduction rate in the absorbed sunlight fraction is very similar to the results of the suspension stability. These results also show that the absorbed sunlight fraction can be enhanced by well-suspended MWCNTs in nanofluids. In summary, the suspension stability and absorption characteristics are strongly affected by the type of surfactants used to create the nanofluids. In this study, SDBS is the most appropriate of the four surfactants used to create water-based MWCNT nanofluids because it has good suspension stability and high absorption characteristics in the temperature range of 10–85 °C. These results contribute to the design of water-based MWCNT nanofluids that can be used as working fluids at the direct-absorption solar collector (DASC) and other solar thermal receivers.

**Table 1**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Initial time</th>
<th>One month</th>
<th>Reduction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX-100</td>
<td>0.9884</td>
<td>0.9873</td>
<td>0.111%</td>
</tr>
<tr>
<td>SDBS</td>
<td>0.9864</td>
<td>0.9836</td>
<td>0.283%</td>
</tr>
<tr>
<td>CTAB</td>
<td>0.9769</td>
<td>0.9682</td>
<td>0.890%</td>
</tr>
<tr>
<td>SDS</td>
<td>0.9733</td>
<td>0.9426</td>
<td>3.154%</td>
</tr>
</tbody>
</table>

Abbreviations: SDBS, sodium dodecylbenzenesulfonate; CTAB, cetyltrimethylammonium bromide; SDS, sodium dodecyl sulfate; TX-100, Triton X-100.
Conflict of interest

The authors declare that there is no conflict of interest.

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References