

# Effects of Preparation Parameters on $\text{TiO}_2$ /water Nanofluid Stability

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## ABSTRACT

*Nanofluid is of great interest as innovative medium for heat transfer unit due to high thermal conductivity of particles suspended in base fluid. Stability of nanofluid is a critical barrier of its versatile applications. This research aims at the preparation of high stability  $\text{TiO}_2$ /water nanofluid. The variation of the amount of  $\text{TiO}_2$  particle containing in water and concentration of dispersant (CTAB; Cetyl Trimethyl Ammonium Bromide) were investigated. Moreover, the effect of temperature change during the operation was monitored. The results showed that nanofluid prepared at volumetric ratio of  $\text{TiO}_2$ /water up to 6.0% (v/v) without CTAB has the good stability. However, in order to get the higher thermal conductivity, nanofluid containing  $\text{TiO}_2$ /water 9.0% (v/v) with CTAB  $1.92 \times 10^{-4}$  mol/L at  $30^\circ\text{C}$  exhibited the highest stability. Nevertheless, the stability decreased with increasing of temperature.*

**Keywords:** Nanofluid, Stability, Titanium dioxide, Cetyl Trimethyl Ammonium Bromide (CTAB)

## 1. INTRODUCTION

Heat exchanger is the equipment that is employed to transfer heat from higher energy source to lower energy sink. The heat transfer plays a major role in various industrial processes such as power generation, chemical industries. Heat loss in America Region was found highly at 20-50% of  $10^{15}$  Btu of the energy consumption [1] or it may say that energy consumption is ineffective. Alternative way to enhance the efficiency of energy consumption is to minimize heat loss or to rise up heat transfer in the system. The most efficient heat exchanger should minimize heat loss to environment for

energy conservation. Nanofluid is prepared by suspending nanoparticles with average sizes below 100 nm in the traditional heat transfer fluid such as water, oil, and ethylene glycol. Nanofluid is one of interesting methods that can improve an efficiency of heat transfer in heat exchanger in short period. It is very practical and economical, whereas improvement of heat exchanger, such as increasing the surface area, is time consuming and expensiveness.

Nanofluid contains nanoparticles, dispersant, and based fluid. The fluid is capable of highly transferring heat because of its higher conductive and convective heat transfer assigned to nanoparticles [2]. Currently, titanium dioxide has been introduced in preparation of nanofluid because of self-cleaning surface under UV irradiation and less attrition compared to metal-nanoparticles. The thermal conductivity of titanium dioxide nanofluid rises up to 7% comparing with based fluid [3]. The surfactant assists particles to be well dispersed in based fluids by electrostatic repulsive interaction among the particles and hydrophilic head of surfactant [4]. By that reason, Cetyl Trimethyl Ammonium Bromide (CTAB) cationic surfactant was used to enhance stability and proper dispersion for all cases in our experiments. Two factors that may affect on stability of nanofluid i.e. the amount of titanium dioxide/water % (v/v) and CTAB concentration were investigated. We have found the condition that gave the highest stability with some reasonable discussions.

## 2. EXPERIMENTAL

### 2.1 Nanofluid Preparation

Nanofluid was comprised of Degussa P-25 titanium dioxide at 1%, 3%, 6% and 9% (v/v) that were suspended by Cetyl Trimethyl Ammonium Bromide (CTAB 96%, Fluka) at various concentrations based on

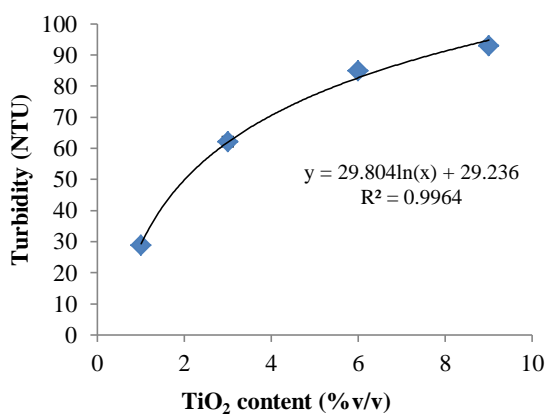
critical micelle concentration (CMC). Deionized water was employed as a based coolant. The CMC was determined at a critical point of surface tension that became constant while increasing the amount of CTAB concentrations. Surface tension of CTAB dissolved in based coolant was measured at 30 °C by Du-Nouy ring method. The result revealed that CMC of CTAB dissolved in deionized water was at  $9.0 \times 10^{-4}$  mol/L. Thus, the experiments were varied concentrations of surfactant at 0, 0.3, 0.6, 1.0, 1.3CMC. The mixture of titanium dioxide, CTAB and deionized water were prepared under ultrasonic vibration for 15 minutes. The resulting solution was named nanofluid.

## 2.2 Stability of Nanofluid

The stability of nanofluid was examined after 7 hours particle settlement. The supernatant after particle settlement (5 mL) was taken to be measured its turbidity by UV-Vis spectrophotometer for color. The measured turbidity was independent on CTAB concentrations, but it was only governed by amount of titanium dioxide particles in our experiment. The turbidity measurement was carried out at 1, 4 and 7 hours. In order to monitor the stability change with temperature during heat transfer operation, nanofluids were settled in the water bath for controlling operation temperature at 30 and 90 °C.

## 3. RESULTS AND DISCUSSION

### 3.1 Relationship between turbidity and TiO<sub>2</sub> suspended in nanofluid

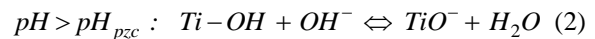
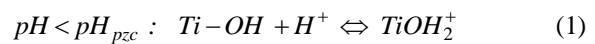


**Fig.1.** The turbidity results from spectrometer corresponding to TiO<sub>2</sub> content (%v/v)

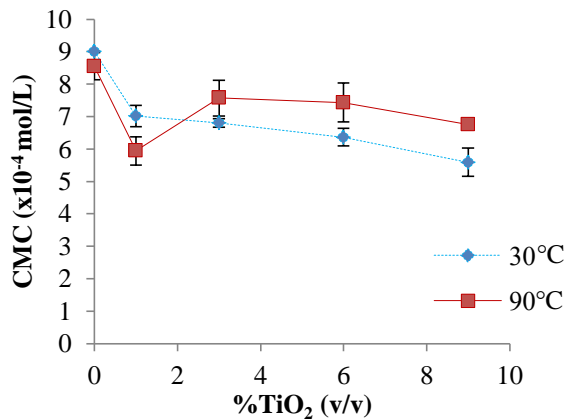
The stability of nanofluid was determined by the ratio of the amount of titanium dioxide particles that were suspended in deionized water after 1, 4 and 7-hours settlement and the amount of titanium dioxide particles initially dispersed in deionized water. The amount of dispersed titanium dioxide particles was indirectly determined by turbidity that was related to titanium dioxide content (% v/v) without CTAB as shown in Fig. 1.

### 3.2 Effect of suspended nanoparticles on CMC

Generally, critical micelle concentration of surfactant is a concentration that surfactant molecules fully occupy interfacial area and the rest free surfactant molecules can form a group of micelle dispersed in based liquid. Addition of surfactant in nanofluid can stabilize titanium dioxide particles suspended in nanofluid that can cause a change of critical micelle concentration. The titanium dioxide particles suspended in nanofluid with CTAB concentrations in the range of  $0-12 \times 10^{-4}$  mol/L gave the pH at 5.5, whereas  $pH_{pzc}$  of Degussa-P25 titanium dioxide was reported at 6.25[5] leading to positive surface charge of suspended TiO<sub>2</sub> particles as shown in equation 1.



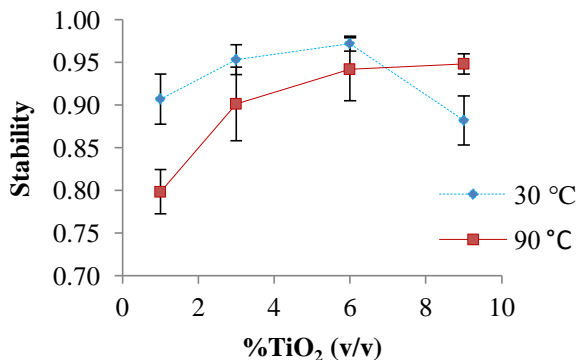
Owing to  $pH_{\text{solution}} < pH_{pzc}$ , surface of TiO<sub>2</sub> discharge to solution was positive since hydronium ions in solution were dominating to protonate Ti-OH to TiOH<sub>2</sub><sup>+</sup>. At 1%(v/v) titanium dioxide nanofluid, increasing CTAB concentrations affected on decrease of surface tension of nanofluid which became constant while reaching CTAB concentration  $7.02 \times 10^{-4}$  mol/L at temperature of 30 °C. The CMC points seemed to be lower while increasing titanium dioxide concentration at as reported in Fig. 2. The electrostatic repulsive force of CTAB and TiO<sub>2</sub> particles that both obtained positive surface charge while suspended in nanofluid may speed up agglomeration rate of CTAB to form micelle, therefore critical micelle concentrations became lower. The same tendency was observed at the operation temperature at 90 °C.



**Fig2.** The CTAB Critical micelle concentration of %TiO<sub>2</sub> suspended in nanofluid.

### 3.3 Effect of suspended TiO<sub>2</sub> in nanofluid on stability without CTAB

The nanofluid containing titanium dioxide particles in the range of 1-6% (v/v) was likely to stabilize at 7 hours without CTAB. The higher amount of titanium dioxide particles may cause a narrow distance between particles resulting in stronger electrostatic repulsive force that may overcome gravitational force to stabilize nanoparticles in the fluid; however high collision rates arising from highly dense particles at 9% (v/v) may contribute agglomeration of particles and loss of nanofluid stability as shown in Fig. 3. Nevertheless, the stability of nanofluid at 90 °C was lower than those at 30 °C at the same amount of TiO<sub>2</sub>. This might pronounce the higher collision rate of TiO<sub>2</sub> particles at higher temperature owing to the increasing in kinetics energy of particles.

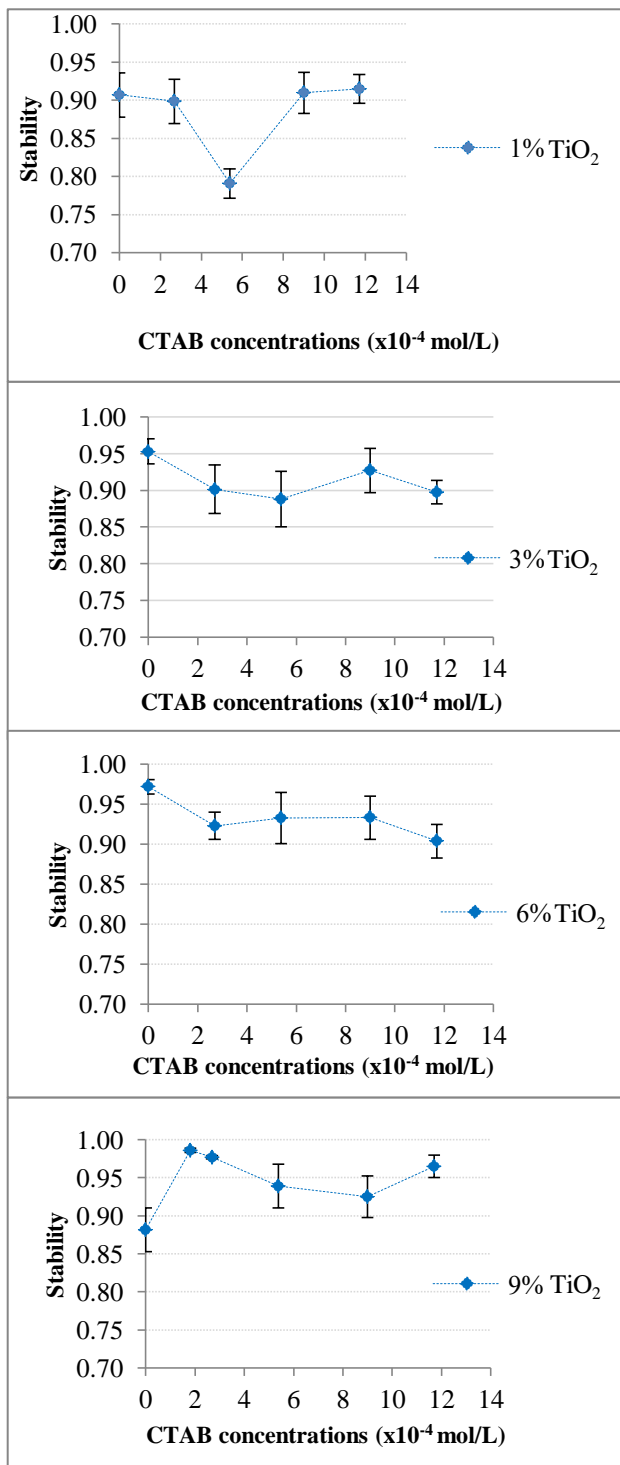


**Fig.3.** Stability of nanofluid without CTAB at various TiO<sub>2</sub> concentrations.

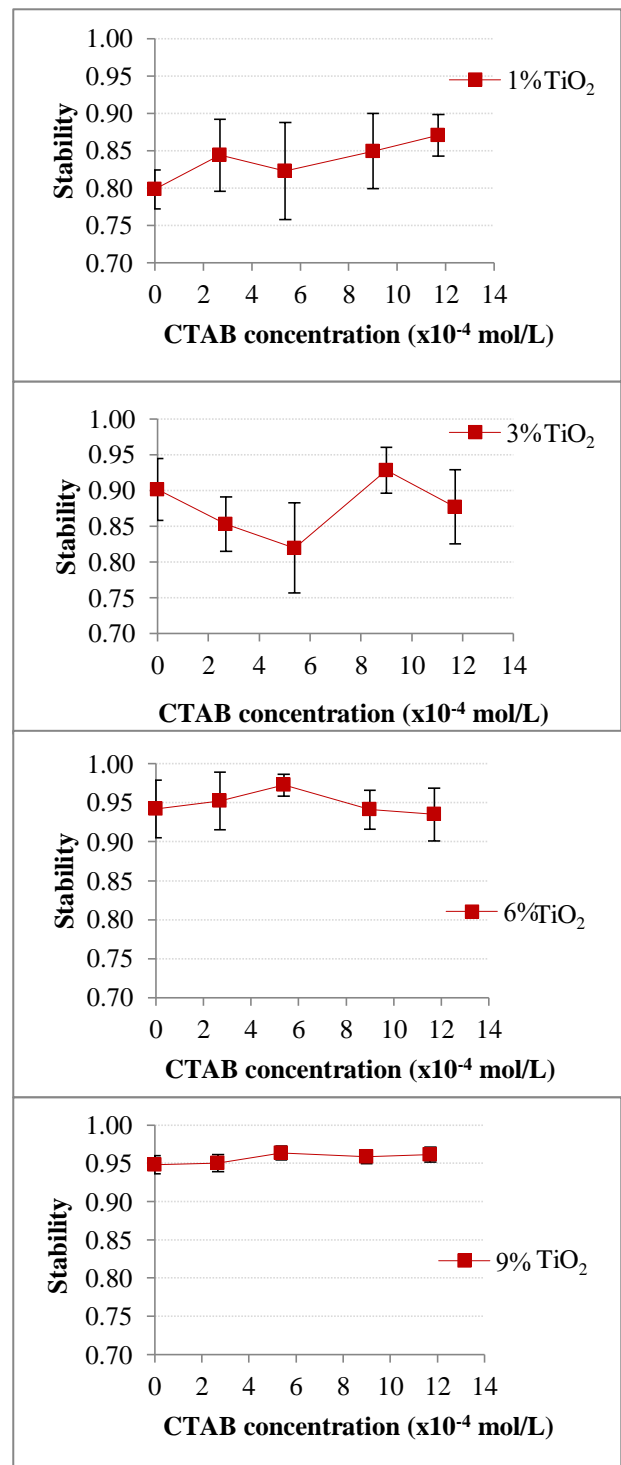
### 3.4 Effect of CTAB concentration on nanofluid stability

There were two reasons that may render nanofluid stabilization i.e. steric structure of CTAB and electrostatic repulsive force. The critical micelle concentration (CMC) of CTAB was  $9.6 \times 10^{-4}$  mol/L. The CMCs of nanofluids containing TiO<sub>2</sub> shifted lower to  $7.02 \times 10^{-4}$ ,  $6.80 \times 10^{-4}$ ,  $6.36 \times 10^{-4}$  and  $5.59 \times 10^{-4}$  mol/L for 1%, 3%, 6% and 9% (v/v) titanium dioxide particles, respectively in Fig. 2.

Fig. 4 illustrated the effect of CTAB concentration on nanofluid stability containing various amounts of TiO<sub>2</sub> at 30 °C. At 1% (v/v) TiO<sub>2</sub> particles, the addition of CTAB less than the CMC may cause decreasing nanofluid stability. It might be that the hydrophobic tails of these CTAB molecules probably gave steric affect on titanium dioxide particles which may neutralize electrostatic surface charge resulting in weakness of electrostatic repulsive force so as to the lowest stability [6] – [7]. However, the stability increased when the concentration of CTAB reach at CMC. This may be explained that the CTAB molecule partially desorped from TiO<sub>2</sub> surface to form micelle, consequently the hinder electrostatic repulsive force between TiO<sub>2</sub> particle was appeared. Moreover, the electrostatic repulsive force of apperant micelle gave more electrostatic effect to stabilize TiO<sub>2</sub> in nanofluid. The same behavior of nanofluid was observed for nanofluid containing TiO<sub>2</sub> 3% and 6% (v/v). However, the concentration of CTAB at CMC may reduce the stability of nanofluid containing TiO<sub>2</sub> 6% (v/v) due to the electrostatic repulsive force of apperant micelle may cause a narrow distance between particles resulting in stronger electrostatic repulsive force that overcomes gravitational force to stabilize nanoparticles in the fluid. This is in good agreement with the highest stibility of nanofluid containing TiO<sub>2</sub> 6% (v/v) without CTAB. The amount of TiO<sub>2</sub> higher than 6% (v/v) brought about the lower stability in the absense of CTAB. On the other hand, the effect of CTAB molecule can render decreasing in electrostatic repulsive force in the case of nanofluid containing TiO<sub>2</sub> 9% (v/v) so as to the highest stability of nanofluid was found at the concentration of CTAB  $1.92 \times 10^{-4}$  mol/L. Nevertheless, the concentration of CTAB at CMC may reduce nanofluid stability because of electrostatic repulsive force that occurred after desorption of CTAB molecules from TiO<sub>2</sub> surafce to form micelle. The effect of CTAB concentration on nanofluid stability containing various amounts of TiO<sub>2</sub> at 90 °C was exhibited as same as the pattern in Fig. 5. The same trend was observed.



**Fig4.** Stability of nanofluid containing various TiO<sub>2</sub> concentrations at 30°C



**Fig5.** Stability of nanofluid containing various TiO<sub>2</sub> concentrations at 90°C

### 3.5 Effect of operation temperature on nanofluid stability

Temperature seems to give significant effect on nanofluid stability in the two ranges of  $\text{TiO}_2$  concentration i.e. i) 1-3% (v/v) and ii) 6-9% (v/v). Increase of temperature can decrease nanofluid stability at 1-3%(v/v) since higher kinetics energy of  $\text{TiO}_2$  particles enhance can enhance collision rate of particles leading to agglomeration and sedimentation. Influence of temperature seems to be negligible at 6-9% (v/v)  $\text{TiO}_2$ . This is probably due to higher viscosity arising from higher concentration of  $\text{TiO}_2$  particles[8]. That may retard the particle collision rates that would have been increased according to higher energy as shown in Fig. 4-5.

## 4. CONCLUSION

The experiments reveal that the stability of nanofluid is dependence on three factors i.e. (i) amount of  $\text{TiO}_2$ /water (% v/v), (ii) concentration of CTAB and (iii) nanofluid temperature. The nanofluid can be stabilized at  $\text{TiO}_2$  concentration up to 6%(v/v) without CTAB. Additional CTAB concentrations lower than critical micelle concentration decrease the nanofluid stability at 1-6% (v/v), in contrast nanofluid stability increase at 9% (v/v). Increase of temperature can decrease nanofluid stability at 1-3%(v/v); however the effect is negligible at higher  $\text{TiO}_2$  concentration.

## 5. ACKNOWLEDGEMENT

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## REFERENCES

- [1] Waste Heat Recovery Technology and Opportunities in U.S. Industry Prepared by BCS, Incorporated March 2008.
  - [2] S.K.Das, S.U.S.Choi, W.YU,T.Pradeep, "Nanofluids Science and Technology" pp. 40-43, 2007.
  - [3] W. Duangthongsuk, S. Wongwises, "Heat transfer enhancement and pressure drop characteristics of  $\text{TiO}_2$ -water nanofluid in a double tube counter flow heat exchanger", International Journal of Heat Mass Transfer 52 pp. 2059-2067, 2009.
  - [4] S.M.S. Murshed, K.C. Leong, C. Yang, "Enhanced thermal conductivity of  $\text{TiO}_2$ -water based nanofluids", International Journal of Thermal Sciences 44, pp. 367-373, 2005.
  - [5] E.Chibowki, L. Holysz, K.Terpilowski, A.E. wiacek, "Influence of Ionic Surfactants and Lecithin on Stability of Titanium Dioxide in Aqueous Electrolyte Solution", CROATICA CHEMICA ACTA 80, pp.395-40, 2007.
  - [6] K. D. Dobson, A. D. Roddick-Lanzilotta, A. J. McQuillan, "An in situ infrared spectroscopic investigation of adsorption of sodium dodecylsulfate and of cetyltrimethylammonium bromide surfactants to  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Ta}_2\text{O}_5$  particle films from aqueous solutions", Vibration Spectroscopy 24, pp.287-295, 2000.
  - [7] X. Li, D. Zhu, X. Wang, "Evaluation on dispersion behaviour of the aqueous copper nano-suspensions", Journal of Colloid and Interface Science 310, pp. 456-463, 2007.
  - [8] S. Bobbo, L. Fedele, A. Benetti, L. Colla, M. Fabrizio, C. Pagura, S. Barison "Viscosity of water based SWCNH and  $\text{TiO}_2$  nanofluids", Experiment Thermal and Fluid Science 36, pp. 65-71, 2012.
- T. Meesuppung, photograph and biography not available at the time of publication.
- P. Ngaotrakanwivat, photograph and biography not available at the time of publication.