



# Properties of carbon nanotube nanofluids stabilized by cationic gemini surfactant

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## ABSTRACT

Stable water based nanofluids containing multi-walled carbon nanotubes (MWNTs) were prepared using cationic gemini surfactant as stabilizer. Zeta potential measurements and Fourier transformation infrared spectra were employed to study the absorption mechanisms of the surfactants on the MWNT surfaces. The stability of the nanofluids was obtained using UV–vis absorption method. Results of thermal conductivity indicate that higher concentration of cationic gemini surfactant is a negative factor in improving the thermal conductivity of nanofluids. Increase of spacer chain length of cationic gemini surfactant gives rise to the sediment of MWNTs in the nanofluids, resulting in decrease of thermal conductivity enhancement of MWNT nanofluids. Mechanical ball-milling technology would be a new method to pretreat the pristine MWNTs, and using this method nanofluids with optimized thermal properties can be obtained.

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## 1. Introduction

Heat transfer fluids play an important role in a number of industrial sectors including power generation, chemical production, air-conditioning, transportation and microelectronics. Preparation of heat transfer fluids with high thermal conductivity arise the researcher's interests to satisfy the requirements of high heat flux applications. Early studies are about the suspensions of millimeter or micrometer sized particles, which, although showed some enhancement, exhibited problems such as abrasion and channel clogging due to poor suspension stability particularly in the case of mini- and/or micro-channels [1]. Nanofluids have recently gained significant interests because of their properties of enhanced thermal conductivity, excellent stability, and little pipe wall abrasion, which can be obtained by the incorporation into the base liquid with thermally conductive particulate solids such as metals or metal oxide [2–4]. Carbon nanotubes (CNTs) have attracted much attention in thermal management applications because of their ultra-high thermal conductivity [5]. Without the help of surface functionalization of CNTs, it is very difficult to disentangle or disperse the CNTs in the hydrophilic fluids such as water and ethylene glycol [6,7], mainly due to the hydrophobic surfaces of CNTs. Addition of chemical surfactant is a convenient method to disperse the CNTs to get homogenous and stable CNT nanofluids. However, excess addition of chemical surfactant will decrease the nanofluid stability and further be an obstacle of thermal conductivity enhancement of nanofluids [8]. Hence, it is desirable to prepare

stable CNT nanofluid with little amount of addition of the chemical surfactant. Many researches have been preformed on preparation of CNT nanofluids using relative higher amount of conventional surfactants [9–12]. There is a report that the optimum amounts to obtain a stable homogeneous CNT suspension are about 0.5 wt% CNTs and 2.0 wt% sodium dodecyl sulfate [11]. The maximum thermal conductivity enhancement was 34% for a 0.6 vol% CNT suspension in water with cetyltrimethyl ammonium bromide as surfactant [12]. Though the stability of nanofluid is very important for its application, there is a little study on estimating the stability of the nanofluid. Jiang et al. have used the UV–vis spectrophotometric method to quantitatively characterize colloidal stability of the dispersions [11]. This advantage of the method can be applied to all base fluid. Recently, our lab has successfully prepared CNT nanofluids using a new type cationic gemini surfactant as stabilizer [13]. This surfactant has superior interfacial properties compared with conventional surfactants [14,15]. The advantage of using gemini surfactant as dispersant is to decrease the addition amount. It can decrease the influence of thermal resistance, between the chemical surfactants and the CNTs, on the thermal conductivity enhancement.

In this study, the effects of the spacer chain length and concentration of cationic gemini surfactants on the stability and thermal conductivity enhancement of nanofluids are presented. The stable and adsorption mechanisms of CNT nanofluids with gemini surfactants also have been proposed according to the results of zeta potential values and Fourier transmission infrared spectroscopy (FT-IR). Furthermore, the stability of MWNT nanofluids is estimated with UV–vis spectrophotometer. A transient short hot wire method was used to measure the thermal conductivity of the MWNT nanofluids containing cationic gemini surfactants. The results are

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expected to provide guidance to design nanofluids with excellent performances.

## 2. Experimental

### 2.1. Materials

The MWNTs were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. The MWNTs' average length and diameter are  $\sim 20\ \mu\text{m}$  and 30–50 nm, respectively. Mechanical milling technology is employed to cut MWNT into different length. The cationic gemini surfactant (12-3(4,6)-12,2Br $^{-1}$ ) was synthesized by a single-step reaction, in which two dodecyl trimethyl ammonium bromide molecules react with one 1,3(4,6)-dibromopropane molecule to generate one 12-3(4,6)-12,2Br $^{-1}$  molecule. The detailed description of the reactions can be found in Ref. [16]. The inorganic salts including sodium chloride, hydrochloric acid and sodium hydroxide are analytic agents. Distilled water was used as dispersed phase in all the experiments.

### 2.2. Experimental method

Zeta potential and FT-IR measurements were employed to study the stable mechanisms of the MWNT nanofluid stabilized by gemini surfactant with different spacer chain length and concentration. The experimental method has been depicted in detail in our previous study [13]. UV–vis absorption of MWNTs was used to estimate the suspension concentration with increasing sediment time. The peak absorbance of MWNTs in water based suspensions appears at 397 nm. Hence, a linear relation between the known concentration and the absorbance of suspended MWNTs can be obtained. The relative stability of MWNT nanofluids can be estimated by measuring the UV–vis absorption of the MWNT nanofluids at different sediment times. From the above relation between MWNT concentration and its UV–vis absorbance value we can obtain the concentration of the MWNT nanofluids at different sediment times. The measured nanofluids should be diluted to obtain measurable absorbance values. A transient short hot wire method for measuring the thermal conductivity of the nanofluids has been applied [17]. The uncertainty of this measurement is estimated to be within  $\pm 1.0\%$ . An ultrasonic technique is used to prepare MWNT nanofluids.

## 3. Results and discussion

### 3.1. Absorption of cationic gemini surfactant

Fig. 1 shows the FT-IR spectra of MWNTs. The absorption manner of cationic gemini surfactants 12-3(4,6)-12,2Br $^{-1}$  on the MWNT surfaces was investigated by FT-IR spectra method. There is no difference about the concentration of 12-3(4,6)-12,2Br $^{-1}$  in the MWNT suspensions. For the curves of pure 12-3(4,6)-12,2Br $^{-1}$ , the strong bands at 2925 and 2850 cm $^{-1}$  are due to asymmetrical and symmetrical stretching of  $-\text{CH}_2-$ , respectively. The band at 2960 cm $^{-1}$  is assigned to the asymmetrical stretching of  $-\text{CH}_3$ . The symmetrical and asymmetrical bending vibrations of  $-\text{CH}_3$  are represented at 1380 and 1470 cm $^{-1}$  [11]. The peak at 950 cm $^{-1}$  is associated with C–N vibrations. In the curves for the MWNT suspension with 12-3(4,6)-12,2Br $^{-1}$  (the suspension is dried before measuring), the asymmetrical and symmetrical stretching vibrations and bending vibrations of  $-\text{CH}_2-$  remain a constant. The intensity of the asymmetrical stretching of  $-\text{CH}_3$  at 2960 cm $^{-1}$  shows a significant decrease. It is different from the bending vibration of  $-\text{CH}_3$ , which also decrease seriously but not eliminate. The still existent intensity of bending vibration of  $-\text{CH}_3$  should be attributed to the exists of  $-\text{CH}_3$  in the head groups. All these

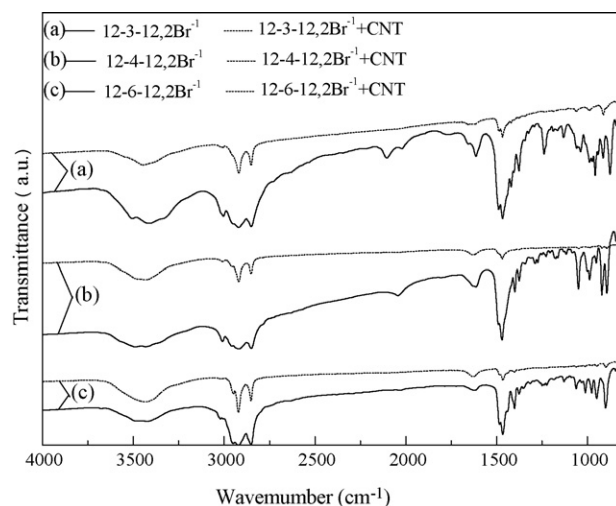


Fig. 1. FT-IR spectra of pure 12-3(4,6)-12,2Br $^{-1}$  and MWNTs with absorbed 12-3(4,6)-12,2Br $^{-1}$  by subtracting the MWNT contribution.

changes indicate that the hydrophobic chains of the 12-3(4,6)-12,2Br $^{-1}$  molecules absorb on the MWNT surfaces. This result will be identified from the following zeta potential measurements.

### 3.2. Zeta potential method study on the stability of CNT nanofluid with different gemini surfactant

The stability of water based MWNT nanofluid has close relation to its electro-kinetic properties. High surface charge density of MWNTs will generate strong repulsive forces, which help to obtain well-dispersed and stable MWNT suspension. Therefore, the measurement of the zeta potential has been done to study the electrophoretic behavior and further to understand the dispersion behavior of MWNTs in water [18,19]. Zeta potential values of MWNT nanofluid stabilized by gemini surfactant with different spacer chain length have been measured. Fig. 2 shows the changes of zeta potential for MWNT suspensions with different gemini surfactant as a function of pH values. In the MWNT suspension with the cationic gemini surfactant, the MWNTs are positive charged in the whole pH ranges. At pH of about 7, the absolute value of zeta potential is the maximum, and the maximum excess 50 mV. It means that the force of electrostatic repulsion between MWNTs is high enough to overcome the attraction force between particles.

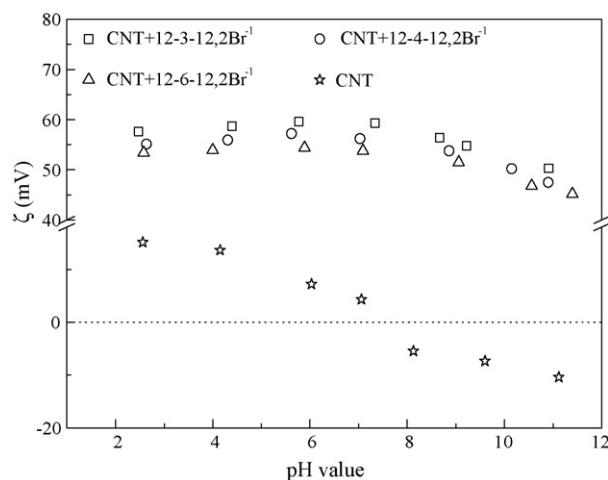


Fig. 2. Zeta potential values of CNT nanofluids stabilized by gemini surfactant with different spacer chain length as a function of pH value.

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