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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 nanofulids. 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 ~20 μm 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 ±1.0%. An ultrasonic technique is used to prepare MWNT nanofluids.

3. Results and discussion

3.1. Absorption of cationic gemini surfactant

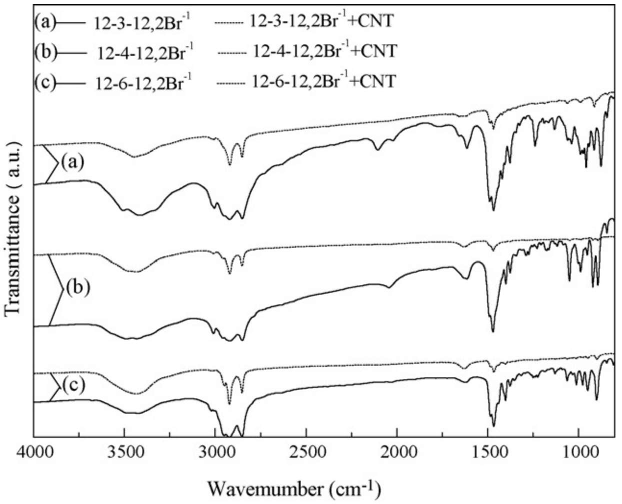

Fig. 1. FT-IR spectra of pure 12-3(4,6)-12,2Br^{-1} and MWNTs with absorbed 12-3(4,6)-12,2Br^{-1} by subtracting the MWNT contribution.

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 –CH$_2$–, respectively. The band at 2960 cm^{-1} is assigned to the asymmetrical stretching of –CH$_3$. The symmetrical and asymmetrical bending vibrations of –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 –CH$_2$– remain a constant. The intensity of the asymmetrical stretching of –CH$_3$ at 2960 cm^{-1} shows a significant decrease. It is different from the bending vibration of –CH$_3$, which also decrease seriously but not eliminate. The still existent intensity of bending vibration of –CH$_3$ should be attributed to the exists of –CH$_3$ in the head groups. All these 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.

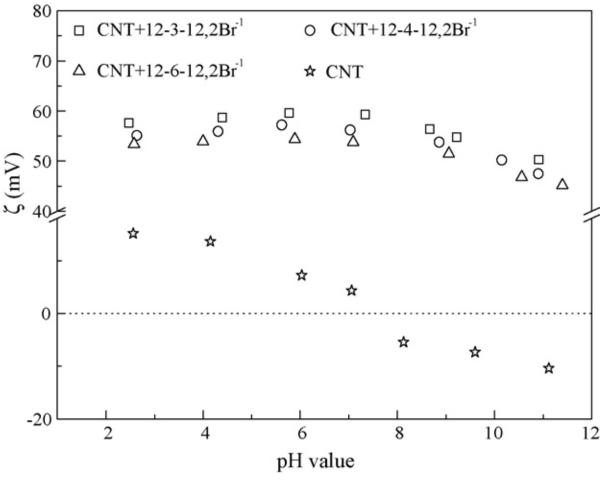

Fig. 2. Zeta potential values of CNT nanofluids stabilized by gemini surfactant with different spacer chain length as a function of pH value.

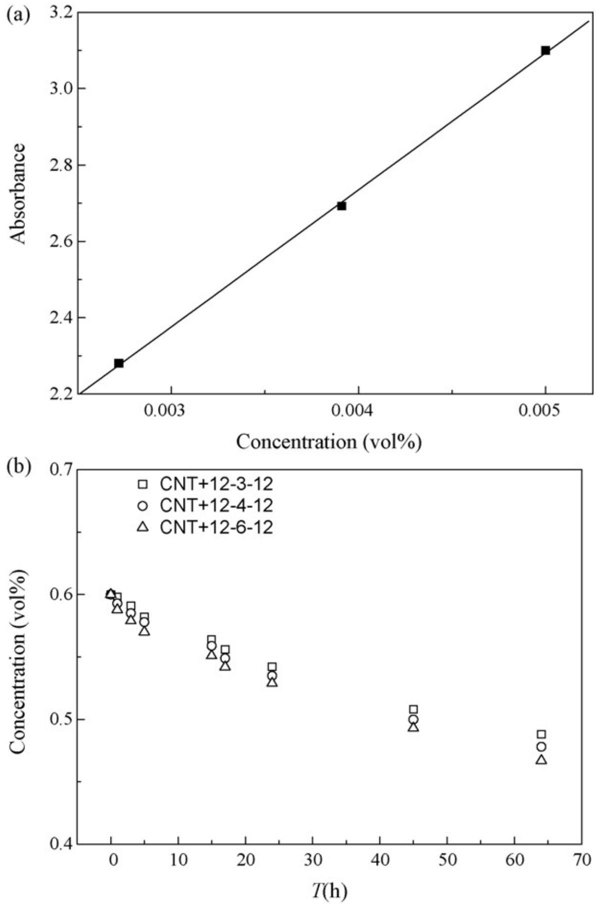

Fig. 3. (a) Linear relationship between light absorption and the concentration of MWNT in water at wavelength of 397 nm. (b) Relative MWNT concentration of nanofluids as a function of sediment times.

Greater electrostatic force can also lead to form more free particles by increasing particle–particle distance, so that the distance exceeds the hydrogen bonding range between particles and further reduces the probability of particle coagulation and settling [8]. Maximum zeta potential value appearing at pH 7 extends the application regions of MWNT nanofluid. The tendency is that the zeta potential values show augmentation with decrease of surfactant spacer chain length. This phenomenon indicates that the MWNT nanofluid with gemini surfactant 12-3-12,2Br^{-1} would have better stability. The reason may be that the Br^{-} ions, for the cationic gemini surfactant with longer spacer chain length, easily enter into the absorbed layer. It reduces the net charges of MWNT surfaces and makes the absolute value of zeta potential decrease, resulting in weak dispersion system. The MWNT suspension without cationic gemini surfactants aggregates seriously. Its zeta potential values are between −30 and +30 mV, which also indicates that the system is in poor stability.

3.3. UV–vis method study on the stability of CNT nanofluid with gemini surfactant

In this study, the UV–vis spectrophotometer was used to estimate the suspension concentration of MWNTs with increasing sediment times. The absorbance of MWNTs at 397 nm has been obtained with different MWNT concentrations of the suspensions. Fig. 3(a) shows a linear relation between the MWNT concentration and the absorbance of suspended MWNTs. According to the linear relations, the relative stability of the MWNT nanofluids was estimated with sediment times and the results are shown in Fig. 3(b). In which the stability of MWNT nanofluids stabilized by cationic gemini surfactant with different spacer chain length at different sediment times was depicted. It can be seen that the MWNT nanofluids stabilized by gemini surfactant with longer spacer chain length show poor stability with increasing sediment times. This result agrees well with that from the zeta potential measurements. As the spacer chain length of gemini surfactant is relative shorter, the MWNT suspension shows excellent stability. It is that, compared with the initial concentration, the relative concentration is still being maintained over 85% even the sediment time is increased to 64 h. Fibrous morphology and non-polar surfaces of MWNTs make it easily agglomerate and precipitate in water based fluid. The addition of cationic gemini surfactant help to improve stability of MWNTs in water. Because the hydrophobic surfaces of MWNTs are modified to be hydrophilic by the adsorption of gemini surfactants on the MWNT surfaces, increasing the repulsion forces between the suspended MWNTs due to the increase of zeta potential which reflects the surface charge of particles in a fluid [20].

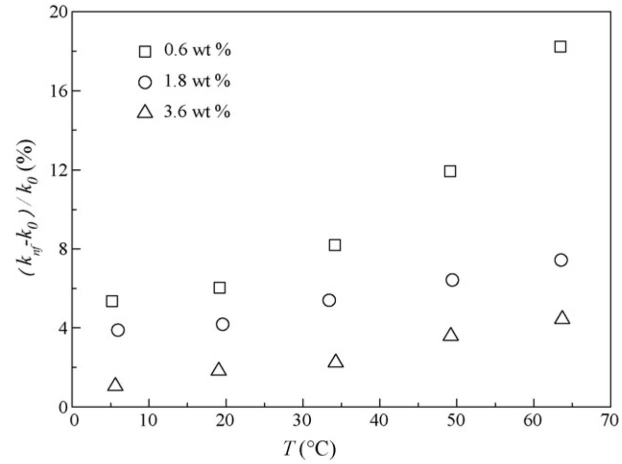

Fig. 4. Thermal conductivity of 0.1 vol% MWNT nanofluid with different 12-3-12,2Br^{-1} concentrations.

3.4. Thermal conductivity enhancement of MWNT nanofluids stabilized by cationic gemini surfactant

The critical micelle concentration of 12-3-12,2Br^{-1} is reported as $9.6 \pm 0.3 \times 10^{-4}$ mol/L at room temperature [21]. Ten times critical micelle concentration of 12-3-12,2Br^{-1} is 0.6 wt%. Solutions of 12-3-12,2Br^{-1} with different concentrations (0.6, 1.8 and 3.6 wt% at room temperature) were selected to prepare MWNT suspensions. The MWNTs used to prepare nanofluid were milled by a ball-milling machine for 35 h. The MWNT concentration is 0.1 vol%. The thermal conductivity of the prepared MWNT nanofluid was measured at different temperatures. Fig. 4 shows that the thermal conductivity enhancement decreases with increase of 12-3-12,2Br^{-1} loading at different measured temperatures. At 65 °C the thermal conductivity enhancement of nanofluid containing 0.1 vol% MWNTs is 18.2 when the 12-3-12,2Br^{-1} concentration is 0.6 wt%. The obtained MWNT nanofluid has better thermal conductivity than that in the report that the thermal conductivity enhancement of 0.6 vol% CNT suspension in water was only 34% [12]. The 12-3-12,2Br^{-1} added in the nanofluid act as stabilizer, and the more 12-3-12,2Br^{-1} addition can improve the stability of the MWNT nanofluid. However, the more 12-3-12,2Br^{-1} addition hinders the improvement of the thermal conductivity enhancement of the MWNT nanofluids. In this study, the lowest 12-3-12,2Br^{-1} concentration is 0.6 wt% in order to obtain stable nanofluid containing 0.6 vol% MWNTs. The amount of added stabilizer is lower than that in the report that 2.0 wt%

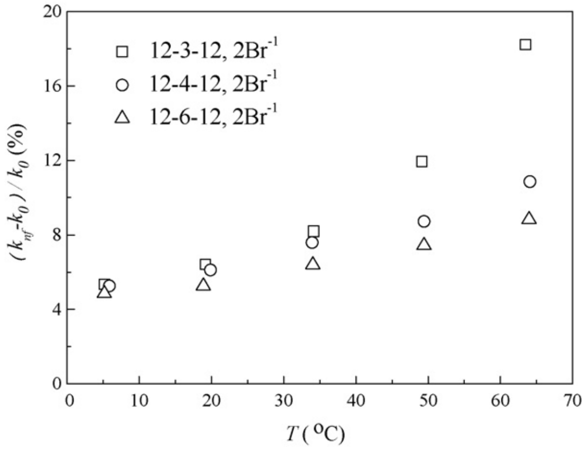

Fig. 5. Effect of surfactant structures on the thermal conductivity enhancement of MWNT nanofluids.

sodium dodecyl sulfate is needed to obtain 0.5 wt% CNTs suspension [11]. Though the thermal conductivity enhancement depends on the thermal conductivity of both particles and the base fluid, the effect of the added stabilizer on the thermal conductivity of nanofluid cannot be ignored. Liu et al. reported that the thermal conductivity of carbon nanotube-synthetic engine oil suspensions with conventional surfactants is higher compared with that of same suspensions without the addition of surfactant. The presence of surfactant as stabilizer has positive effect on the carbon nanotube-synthetic engine oil suspensions [22]. It is similar to the result of our study. The interfacial thermal resistance between the MWNTs and the base fluids, arising from the absorption of surfactants on the surfaces of MWNTs, strongly decreases the thermal conductivity enhancement of nanofluids [23]. The excess addition of chemical surfactant will improve the interfacial thermal resistance. Furthermore, the viscosity of the nanofluid increases with the fraction of the excess surfactant [12]. The increasing viscosity will significantly decrease the heat transfer capacity of nanofluids because the thermal conductivity enhancement of the nanofluids has relation to the Brown motion of added particles. And increased viscosity will decrease the Brownian motion of the added particles, and further decrease the heat transfer capacity of nanofluids [24]. It results in the decrease of the thermal conductivity enhancement of nanofluids. Our previous study also demonstrated that the viscosity of the nanofluid containing surfactants decreased with the improvement of temperatures, and the less addition of surfactants accelerates the decrease of nanofluid viscosities [13]. Therefore, the thermal conductivity enhancement increases significantly with improvement of temperatures when the addition quantity of the surfactant is lower.

Fig. 5 depicts the effect of the structures of cationic gemini surfactant molecules on the thermal conductivity enhancement of MWNT nanofluids. In the experiments the concentration of MWNTs and cationic gemini surfactant is 0.1 vol% and 0.6 wt%, respectively. The spacer chain length of the cationic gemini surfactant increase from 3 methylenes to 6 methylenes. It is observed in Fig. 5 that the thermal conductivity enhancement of MWNT nanofluid increases with the decrease of spacer chain length of cationic gemini surfactant. The measurement of zeta potential indicates that the MWNT nanofluid stabilized by gemini surfactant with shorter spacer chain length has better stability. Therefore, increase of spacer chain length of surfactant gives rise to sediments of MWNTs in the nanofluid, resulting in the decrease of thermal conductivity enhancement of MWNT nanofluid. This effect is especially obvious at higher temperatures.

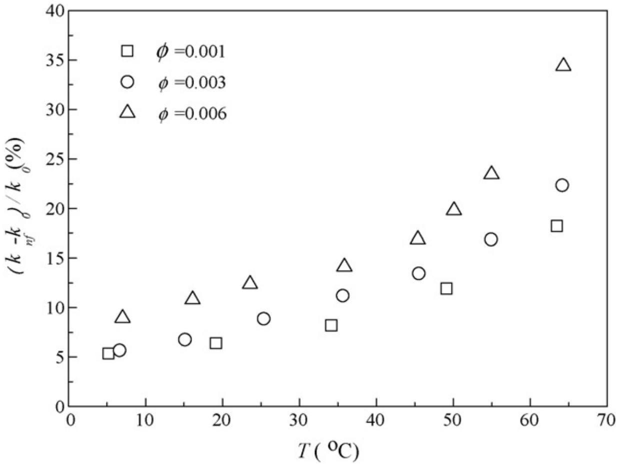

Fig. 6. Thermal conductivity enhancement of nanofluids stabilized by 12-3-12,2Br^{-1} with different concentrations.

Fig. 6 shows the thermal conductivity enhancements of MWNT nanofluids as a function of the volume fraction of MWNTs at different temperatures. ϕ is the volume fraction of MWNTs. The concentration of 12-3-12,2Br^{-1} was 0.6 wt% with respect to water to obtain excellent stability of MWNT nanofluids. The used MWNTs are milled for 35 h. The results clearly show that MWNT nanofluids have noticeably higher thermal conductivity than the base fluid. The enhanced thermal conductivity ratios increase with the increase of volume fraction of MWNTs. This result is similar to that reported previously [1]. Fig. 6 shows that at 65 °C, the thermal conductivity is increased by 34.3% at a volume fraction of 0.6%. But at 5 °C, the thermal conductivity is increased by only 5.6% at the same volume fraction. These results imply that temperatures strongly affects on the thermal conductivity enhancement of water based MWNT nanofluids stabilized by the cationic gemini surfactants. The enhancement of the thermal conductivity shown in Fig. 6 is slightly lower than that reported by Ding et al. [1]. This discrepancy may be associated with thermal properties of the employed MWNTs, and liquid-MWNT interfacial thermal resistance arising from the different kinds and quantities of the added surfactants.

Fig. 7 shows the thermal conductivity enhancements of MWNT nanofluids as a function of ball-milling time at three MWNT concentrations. The results were all obtained at 65 °C. The concentration of the added 12-3-12,2Br^{-1} was 0.6 wt%. It can be seen that the thermal conductivity enhancement increases firstly and then decreases

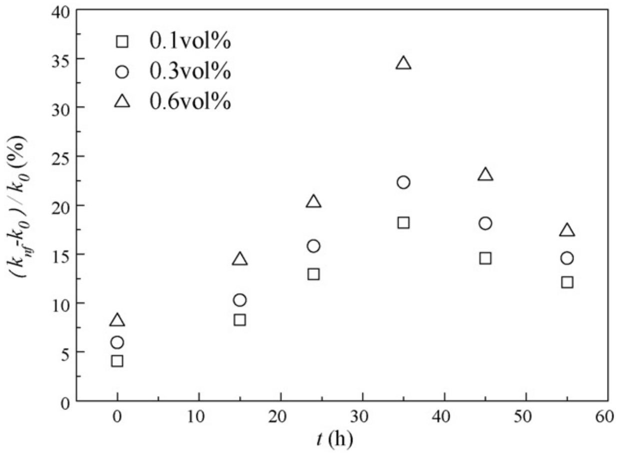

Fig. 7. Thermal conductivity enhancement of nanofluids stabilized by 12-3-12,2Br^{-1} as a function of the ball-milling time.

with increasing ball-milling time, and the ball-milling time of 35 h is the crossover point. It is expected that the aspect ratio of the MWNT decreases with ball-milling time. At the crossover point the aspect ratio of the MWNT, being demonstrated to be a positive factor in improving thermal conductivity of nanofluid [25–27], attained an optimal value. The effect of aspect ratio of MWNTs on thermal conductivity of MWNT nanofluids has also been discussed in our previous study [28]. The treatment to the pristine MWNTs using ball-milling provides a method for preparing nanofluid with optimized thermal properties.

4. Conclusion

Cationic gemini surfactants can be used as stabilizers to prepare stable water based MWNT nanofluids. The hydrophobic chains of gemini surfactants absorb on the MWNT surfaces to make MWNTs disperse well in base fluid. To improve the thermal conductivity of MWNT nanofluids the quantity of the added surfactants should be appropriate. Decrease of spacer chain length of gemini surfactants contributes to improve stability of MWNT nanofluids and further to improve their thermal conductivity. The enhanced thermal conductivity ratios increase with the increase of volume fraction of MWNTs. Compared with pristine MWNTs, pretreated MWNTs using mechanical ball-milling technology dispersed well in base fluid. The mechanical ball-milling technology provides a method to prepare nanofluid with optimized thermal properties.

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