



Dispersion and aggregation of single-walled carbon nanotubes in aqueous solutions of anionic surfactants*

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Abstract: Understanding the dispersion and aggregation of carbon nanotubes (CNTs) in the aqueous environment are critical for the fate, bioavailability, and the environment and health risk assessment of them because the better suspended CNTs display a higher mobility and could transfer to a longer distance in the environment to possibly pose greater ecological and environmental risks. In this study, we have found that bulk single-walled carbon nanotubes (SWCNTs) could not be dispersed and stably suspended in water and sodium dodecylbenzene sulfonate (SDBS) solution by shaking at 140 r/min, although they could be stably suspended in SDBS solution by sonication. Even through sonication, SWCNTs suspended in SDBS solution do not remain stable at the presence of environmentally relevant cations (e.g., Na⁺, K⁺, Ca²⁺, and Mg²⁺) after dilution. These observations suggest that SWCNTs will not travel long distances in significant concentrations in the natural environment to pose great ecological and environmental risks. We also observed that the re-aggregation of suspended SWCNTs in the presence of cations was dependent on the SDBS concentration rather than the SWCNT concentration in the suspension. Both SDBS and sonication play important roles in the dispersion of SWCNTs, with sonication breaking down large aggregates of SWCNTs, while SDBS adsorbed on the SWCNTs inhibits the coagulation and aggregation by steric/electrostatic repulsion to maintain the stability of the suspension in water.

Key words: Dispersion, Aggregation, Single-walled carbon nanotubes (SWCNTs), Anionic surfactant, Sonication

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1 Introduction

Carbon nanotubes (CNTs), including single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs), have unique and tunable physical and chemical properties that can be exploited in numerous potential applications. However, CNTs have also attracted notoriety for their possible environmental and health effects (Dunphy Guzmán *et al.*, 2006), as they inevitably enter the environment during their

production, transport, handling, use, and disposal (Gottschalk and Nowack, 2011), where they can potentially cause damage to aquatic organisms (Cheng *et al.*, 2007), mammals (Lam *et al.*, 2004), and human cells (Jia *et al.*, 2005). The dispersion and aggregation of CNTs in the aqueous environment are critical behaviors affecting their fate, bioavailability, and potential environmental and health risks (Hyung and Kim, 2008; Saleh *et al.*, 2008); more stably suspended CNTs exhibit a higher mobility and could thus be transported longer distances in the environment, thus posing greater ecological and environmental risks (Hyung and Kim, 2008; Bouchard *et al.*, 2012). Both bulk CNTs and stably suspended CNTs are used in industrial applications and can be released into the natural environment (Dunphy Guzmán *et al.*, 2006). Bulk CNTs are generally aggregated in bundles and

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cannot be dispersed significantly in water or even in organic solvents, owing to the strong van der Waals (vdW) interactions along their primary axes (Islam *et al.*, 2003). Surfactants are widely employed as dispersion detergents to prepare stably suspended CNTs for industrial applications (Islam *et al.*, 2003; Zhang *et al.*, 2004; Lin *et al.*, 2009; 2010). Therefore, for a better understanding of the mobility of CNTs in the environment, it is important to examine (1) whether bulk CNTs can be dispersed and stably suspended in the natural environment (Hyung and Kim, 2008; Lin and Xing, 2008) and (2) whether surfactant-suspended CNTs can retain their stability in the natural environment (Saleh *et al.*, 2008).

It has been widely reported that bulk CNTs can be dispersed and stably suspended in aqueous solutions of surfactants and natural organic matter (NOM) using sonication (Hyung and Kim, 2008; Lin *et al.*, 2009; 2010). Surfactants and NOM are surface active and ubiquitous in the environment. Surfactants are mainly used in households and in industry as detergent formulations and surface cleaners and are discharged into the environment in huge quantities (Matthijs *et al.*, 1999). They are synthesized by bacteria, yeasts, and fungi in the environment (Zajic *et al.*, 1983). NOM is a key component of soils, sediments, and natural water and which originates primarily from the biological degradation of plants as well as animal remains (McRae, 1988). Sonication is a method of vigorously agitating water and is an important process for dispersing or debundling CNT aggregates and bundles (Islam *et al.*, 2003). However, sonication induces more extreme agitation than is encountered in the natural aqueous environment. Therefore, the results of experiments using vigorous sonication are not appropriate for assessing and predicting the dispersion and suspension of bulk CNTs in the aqueous environment. For example, MWCNTs can be dispersed and stably suspended in natural surface water containing dissolved NOM by sonication but not by shaking at 140 r/min (Lin *et al.*, 2010); the latter represents realistic agitation conditions encountered in the natural aqueous environment and is widely used in experiments on the sorption of contaminants by CNTs, sediments, and soils (Yang *et al.*, 2006). Therefore, milder methods, such as shaking, should be employed in experiments on the dispersion and suspension of bulk CNTs in aqueous solutions of surfactants and NOM (Lin and Xing, 2008; Lin *et al.*, 2010).

The effect of cations including Na^+ , K^+ , Mg^{2+} , and Ca^{2+} on the aggregation and deposition of stably suspended CNTs has been widely studied, because these electrolyte ions are ubiquitous in the aqueous environment and are known to coagulate certain colloidal sols (Saleh *et al.*, 2008; Lin *et al.*, 2010; Bouchard *et al.*, 2012). Previous studies have reported that these cations could coagulate and deposit stably suspended CNTs by depressing the electric double layer (Saleh *et al.*, 2008). A certain minimum concentration of a given electrolyte ion is needed to induce the diffusion-limited aggregation of CNTs; this concentration is commonly referred to as the critical coagulation concentration (CCC) (Bouchard *et al.*, 2012). Most reported CCC values (Saleh *et al.*, 2008; 2010; Lin *et al.*, 2010; Bouchard *et al.*, 2012) for Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , although dependent on the physicochemical properties of the CNTs (e.g., surface oxygen-containing functional groups (Smith *et al.*, 2009)) and solution chemistry (e.g., dispersant types (Saleh *et al.*, 2008; 2010; Lin *et al.*, 2010)), were higher than their average concentrations in fresh river water (i.e., 0.22, 0.034, 0.16, and 0.36 mmol/kg (Broecker *et al.*, 1982), respectively) but lower than that in surface seawater (i.e., 470, 10.2, 53, and 10.3 mmol/kg (Broecker *et al.*, 1982), respectively). These findings suggest that stably suspended CNTs can remain stable and be transported long distances in the natural terrestrial ecosystem, and thus pose an unexpected degree of ecological and environmental risk. However, these findings were mostly obtained from experiments that employed higher concentrations of CNTs as well as dispersion detergents (e.g., surfactants and NOM) typical of industrial applications rather than those found in the environment. For example, the reported concentration of the surfactant sodium dodecylsulfate (SDS) for stabilizing CNTs was up to 20 000 mg/L (Islam *et al.*, 2003). The dilution of a stable suspension of CNTs to lower concentrations of dispersion detergents and suspended CNTs occurs as soon as the industrial suspension is released into the surface or ground waters; this phenomenon has not previously been considered in studies on the environmental fate and transport of CNTs. Bouchard *et al.* (2012), investigating the effects of lower surfactant concentrations (SDS 5–500 mg/L) on the CNTs dispersibility, observed that the CCC values increased with the SDS concentration for Na^+ but were almost independent of the SDS concentration

for Ca^{2+} . Therefore, to estimate environmental exposure, the dependence of CCC values on the concentration of CNTs and dispersion of detergents must be investigated with respect to their environmental distribution, fate, and transport.

Therefore, experiments were conducted on the dispersion of bulk SWCNTs in aqueous solutions of an anionic surfactant (sodium dodecylbenzene sulfonate (SDBS)), with and without the use of sonication, to investigate whether shaking at 140 r/min alone, a mild agitation representative of the natural aqueous environment, could cause bulk SWCNTs to be dispersed and stably suspended in the SDBS solution. The effects of environmentally relevant cations, including monovalent (i.e., Na^+ and K^+) and divalent (i.e., Ca^{2+} and Mg^{2+}) ions, and the concentrations of SWCNTs and SDBS on the aggregation (i.e., CCC values) of SDBS-suspended SWCNTs were also investigated to determine whether SDBS-suspended SWCNTs can retain their stability when a stable suspension of CNTs is diluted to lower concentrations. This information will be helpful in estimating the environmental distribution, fate, and transport of CNTs and, thus, the environmental exposure risks.

2 Materials and methods

2.1 Materials

SDBS was obtained from the Tokyo Chemical Industry Co., Ltd., and used as purchased as the dispersion detergent. The purity and critical micelle concentration (CMC) of SDBS was 98% and 963 mg/L, respectively (Yang *et al.*, 2007). SWCNTs, with a purity of 90%, outer diameter of 1–2 nm, and specific surface area of 385 m^2/g , were purchased from the Chengdu Organic Chemistry Ltd., and used in the experiments as received. The specific surface area of the SWCNTs was calculated from the N_2 adsorption isotherm using the multi-point Brunauer-Emmett-Teller method. The N_2 adsorption isotherm of the SWCNTs was obtained at 77 K (Autosorb-1, Quantachrome) after outgassing at 105 °C for at least 24 h.

2.2 Dispersion and adsorption experiments

SWCNTs (8, 40, or 150 mg) were added to 20 ml vials along with 20 ml of SDBS solution with initial

concentrations of up to 8000 mg/L at neutral pH. The vials were sealed with aluminum-foil-lined Teflon screw caps and sonicated in a bath sonicator (KQ-600KDE, Shumei, China) at a fixed frequency of 40 kHz for 11 h at (25 ± 5) °C or shaken at 140 r/min for 2 d at (25 ± 1) °C. Preliminary experiments indicated that the apparent equilibrium of both the dispersion of the SWCNTs and the adsorption of SDBS on the SWCNTs was reached after sonication for 11 h or shaking for 2 d. After equilibration, the mixtures in the vials were centrifuged at 3000g for 70 min to obtain stable SWCNT suspensions. In previous studies (Lin and Xing, 2008; Bai *et al.*, 2010; Lin *et al.*, 2010), centrifugation was observed to be a more suitable method of obtaining stable suspensions of CNTs compared with settling for 4 d (Hyung *et al.*, 2007; Hyung and Kim, 2008). The stable suspensions of SWCNTs were measured directly with a UV-vis spectrometer (UV-2450, Shimadzu) at 800 nm to quantify the concentrations of SWCNTs in the suspensions (Hyung *et al.*, 2007; Hyung and Kim, 2008) based on that (1) a linear relationship between the absorbance at 800 nm and the CNT concentration was observed in previous studies (Lin and Xing, 2008; Bai *et al.*, 2010; Lin *et al.*, 2010) and in the preliminary experiments of this study, and (2) the SDBS solution was found to exhibit no absorbance at 800 nm in this study. The concentrations of SDBS in the suspensions were also quantified with the UV-vis spectrometer but at 260 nm and after the suspensions were filtered through 0.2- μm poly (tetrafluoroethylene) filters (Millipore). According to previous observations (Lin and Xing, 2008; Bai *et al.*, 2010; Lin *et al.*, 2010), the filter is effective in removing the suspended SWCNTs. The amount of SDBS adsorbed on the SWCNTs was thus calculated from the mass difference between the SDBS in the initial solution and in the suspension.

2.3 Aggregation experiments

SWCNTs (400 mg) in 1 L of SDBS solution with a concentration of 5000 mg/L at neutral pH were sonicated at a fixed frequency of 40 kHz for 11 h, followed by centrifugation at 3000g for 70 min to obtain a stable suspension to serve as the stock SWCNT suspension for the aggregation experiments. This was diluted to four concentrations (the SDBS concentrations in the diluted suspension were 50, 500, 1000, or 2500 mg/L) in 20-ml vials using Na^+ , K^+ ,

Ca²⁺, or Mg²⁺ solutions (made from their chloride salts) with various ion concentrations at neutral pH. Then, the mixtures were shaken at 140 r/min at (25±1) °C for 24 h and subsequently centrifuged at 3000g for 70 min to yield the stable suspensions of SWCNTs; the SWCNT concentrations were then quantified at a UV wavelength of 800 nm. Stable SWCNT suspensions containing 500 mg/L SDBS and 3.7, 5.6, 7.0, or 9.2 mg/L SWCNTs were also prepared through dilution of the stock SWCNT suspension with Ca²⁺ solution at various concentrations to examine the effect of SWCNT concentration on its aggregation by Ca²⁺.

2.4 Characteristics of SWCNT suspension

Zeta potential measurements of SWCNT suspensions were performed on a Zetasizer (ZEN 3690, Malvern). Electron microscopic images of SWCNTs were obtained using an FEI F20 transmission electron microscope (TEM) at 200 kV. A droplet of the diluted SWCNT suspension was air-dried onto a 300-mesh copper grid (T11012, Beijing XXBR Technology Co., Ltd.) for 2 h before observation.

3 Results and discussion

3.1 Dispersion of bulk SWCNTs in SDBS solution

Fig. 1 shows that, with sonication, SWCNTs can be dispersed and stably suspended in the SDBS solution. The amounts of both the stably suspended SWCNTs (Q) and the adsorbed SDBS on SWCNTs (q) increased with the equilibrium SDBS concentration (C_e) to reach asymptotic values of 3500 mg/L and 250 mg/g, respectively, at the equilibrium SDBS concentration of approximately 2500 mg/L (Fig. 1). The addition of more SWCNTs resulted in more SWCNTs being dispersed and stably suspended (Figs. 1 and 2). All three suspension curves for the added SWCNT doses of 400, 2000, and 7500 mg/L showed similar trends, with the adsorption isotherm of SDBS reaching its asymptotic value at an equilibrium SDBS concentration of around 2500 mg/L. The plateau values of the concentration of stably suspended SWCNTs at doses of 400, 2000, and 7500 mg/L were approximately half the dose, i.e., 200, 1000, and 3500 mg/L, respectively (Figs. 1 and 2). The amount of stably suspended SWCNTs increased

with the amount of SDBS adsorbed on the SWCNTs (Fig. 3), indicating that the adsorption of SDBS plays an important role in the dispersion of SWCNTs. However, only shaking at 140 r/min, SWCNTs cannot be stably suspended in SDBS solution, even when the SDBS concentration and the amount of adsorbed

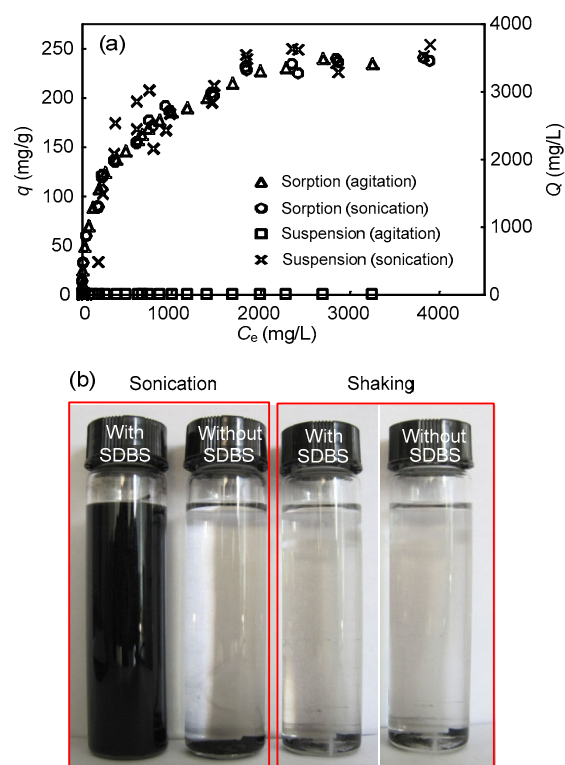


Fig. 1 Amounts of stably suspended SWCNTs and adsorbed SDBS on SWCNTs versus the equilibrium SDBS concentration after the SWCNTs (with an initial dose of 7500 mg/L in solution) sonicated for 11 h or shaken for 2 d (a) and images of the dispersion of SWCNTs in 0 and 5000 mg/L SDBS solutions after sonication and shaking (b)

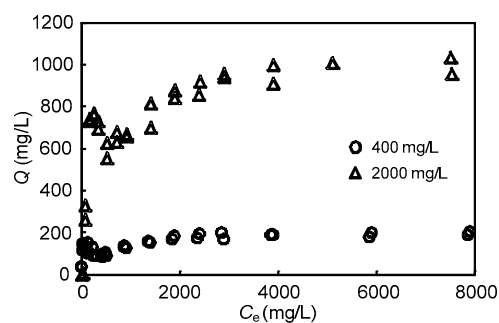


Fig. 2 Amounts of stably suspended SWCNTs at the SWCNT doses of 400 and 2000 mg/L versus the equilibrium SDBS concentration after sonication for 11 h

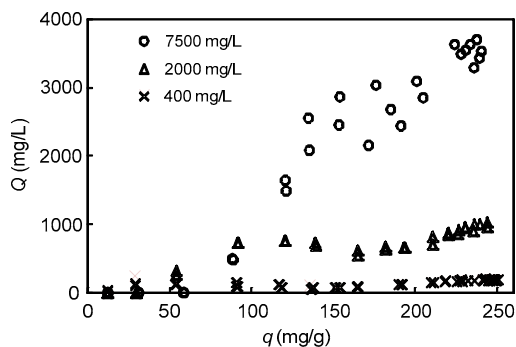


Fig. 3 Amounts of stably suspended SWCNTs at three doses of SWCNTs (i.e., 400, 2000, and 7500 mg/L) versus the amount of SDBS adsorbed on the SWCNTs

SDBS were up to 5000 mg/L and 250 mg/g (i.e., the plateau value of adsorbed SDBS), respectively (Fig. 1). However, the adsorption isotherm of SDBS on the SWCNTs after sonication at 40 kHz for 11 h overlaps with that after shaking at 140 r/min for 2 d (Fig. 1). These findings indicate that (1) sonication plays an important role in the dispersion of SWCNTs in SDBS solution and (2) bulk SWCNTs cannot be dispersed, stably suspended, or transported long distances at significant concentrations in the environment, even when mixed with ubiquitous surfactants and NOM after being released into the environment; this is because mild shaking at 140 r/min is reflective of the natural aqueous environment, whereas extreme agitation by sonication is not.

Suspension of CNTs in surfactant solutions with the assistance of sonication has been explained by the “Unzipping” theory postulated by Strano *et al.* (2003) or alternatively by the “Cutting” theory of Liu *et al.* (1998). The “Unzipping” theory suggests that gaps or spaces can be created at bundle ends of CNTs in the high-shear environment of the sonicated solution, and then surfactant adsorption and diffusion can enlarge this space along the bundle length, thereby creating separate individual nanotubes (Strano *et al.*, 2003). The “Cutting” theory postulates that microscopic domains of high temperature are produced by the collapse of cavitation bubbles during sonication, leading to localized sonochemistry that attacks the surface of CNTs, leaving an open hole in the tube side, before cutting them cleanly at the points of damage and separating the pieces from the other tubes in the bundles (Liu *et al.*, 1998). However, the “Unzipping” theory, i.e., the debundling mechanism, cannot

reasonably interpret the dispersion of SWCNTs in the SDBS solution, because the observed adsorption isotherms of SDBS on SWCNTs using shaking and sonication overlap with each other, but the dispersion of SWCNTs in SDBS solution was not observed in the case of shaking and was noticeably different from that of the case of sonication (Fig. 1). If the debundling mechanism captures the dispersion of SWCNTs in SDBS solution, the sorption of SDBS on the dispersed SWCNTs (i.e., after sonication) would be much higher than that on the undispersed SWCNTs (i.e., after shaking). This is because after debundling, a large fraction of the area of the bundled nanotubes that was previously inaccessible for the adsorption of SDBS would become accessible (Strano *et al.*, 2003; Yang and Xing, 2010). Moreover, the stably suspended SWCNTs would exist in the SDBS solution as individual tubes owing to the debundling mechanism, rather than as the small aggregates observed in the TEM investigation (Fig. 4b). The “Cutting” theory also cannot explain the observed dispersion of SWCNTs in the SDBS solution because SWCNTs cannot be dispersed and stably suspended in water without SDBS (Fig. 1). From the TEM images (Fig. 4), we observed that the large aggregates of SWCNTs (Fig. 4a), composed of entangled smaller aggregates (Yang and Xing, 2007), are broken down into small aggregates (Fig. 4b) during the sonication process, as observed in previous studies (Lecoanet *et al.*, 2004; Yudasaka *et al.*, 2005). Moreover, after sonication, the separated smaller aggregates in the water coagulated quickly to re-form as large aggregates and precipitate because of the strong vdW forces between SWCNTs with smaller outer diameters (Lin and Xing, 2008; Lin *et al.*, 2009); in SDBS solution, however, they remain in solution to form a stable suspension (Fig. 1). Therefore, we suggest that

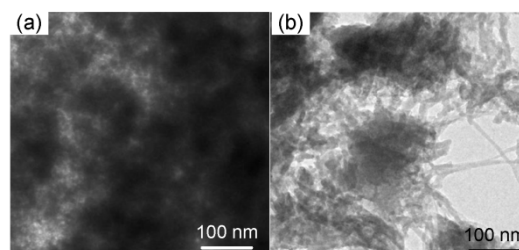


Fig. 4 TEM images of SWCNT aggregates before (a) and after (b) sonication

a possible mechanism of suspension is that (1) the large aggregates of SWCNTs are broken down and separated into smaller ones by sonication and (2) the coagulation and aggregation of the smaller aggregates are inhibited by the steric/electrostatic repulsion between the SDBS molecules adsorbed on the SWCNTs, and thus, the small aggregates retain their stability in solution. The steric/electrostatic repulsion between the adsorbed SDBS molecules is demonstrated by the decrease in the zeta potential values with the increase in the amount of adsorbed SDBS (Fig. 5). This mechanism, in which the adsorbed surfactants induce electrostatic and/or steric repulsions to counterbalance the vdW attraction between nanotubes and thus maintain the stability of suspended CNTs, has also been suggested in previous studies (Lin and Xing, 2008; Lin *et al.*, 2009; 2010). In contrast to SWCNTs, MWCNTs could be dispersed and stably suspended in NOM and tannic acid solutions by mild agitation such as shaking or magnetic stirring (Hyung *et al.*, 2007; Hyung and Kim, 2008; Lin and Xing, 2008). The most plausible reason for this difference is that SWCNTs have smaller outer diameters and thus higher vdW attractions between tubes than MWCNTs (Lin and Xing, 2008; Lin *et al.*, 2009), i.e., more energy is needed to break down and separate SWCNT aggregates. Therefore, MWCNTs with larger outer diameters (20.9, 27.8, 42.7, and 70.1 nm), rather than those with smaller diameters (9.4 nm) and SWCNTs (1.4 nm), can be stably suspended in tannic acid solutions by shaking, resulting in the increase in the amount of suspended MWCNTs with the increase in the outer diameter (Lin and Xing, 2008).

3.2 Stabilization of SDBS-suspended SWCNTs in the presence of cations

Fig. 6 shows that SDBS-suspended SWCNTs in 2500 mg/L SDBS solution are destabilized and re-aggregated by the addition of cations, exhibiting similarly shaped aggregation curves, i.e., the SDBS-suspended SWCNTs largely retain their stability at low ion concentrations up to a threshold value, and then they re-aggregate and are deposited suddenly when the ion strength exceeds the threshold value. As indicated by the increase in the zeta potential values of SDBS-suspended SWCNTs with the increase in the concentration of the cations (e.g., Ca^{2+} , as a representative ion), as shown in Fig. 7 and suggested in our

previous paper (Lin *et al.*, 2009), the aggregation and deposition of SWCNTs above the threshold value can be attributed to the depression of the electric double layer by the added ions, which suppresses the electrostatic repulsion between suspended aggregates.

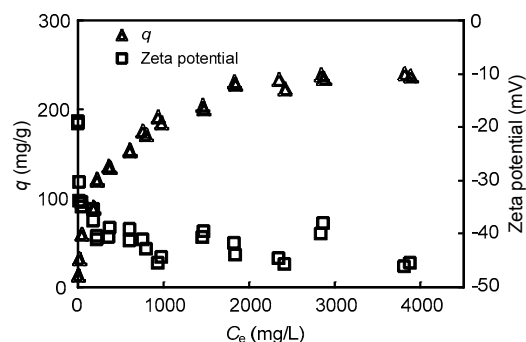


Fig. 5 Zeta potential values of SWCNT suspension in the SDBS solution at the SWCNT dose of 7500 mg/L and the amount of SDBS adsorbed on the SWCNTs versus the equilibrium SDBS concentration after sonication for 11 h

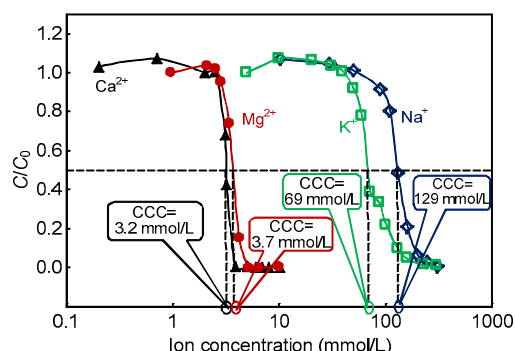


Fig. 6 SWCNT stabilization in 2500 mg/L SDBS solution as a function of ionic strength
 C/C_0 : ratio of stably suspended SWCNT concentration in solution at a given ion concentration to the initial stably suspended SWCNT concentration

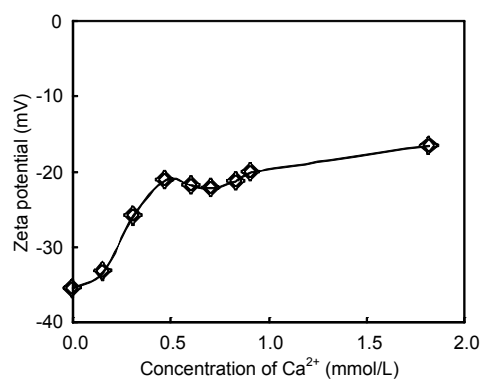


Fig. 7 Effect of Ca^{2+} concentration on the zeta potential values of an SWCNT suspension in 50 mg/L SDBS solution

When the SWCNT surface charge is rapidly screened by the increasing ionic concentration, the electrostatic repulsion between them is completely suppressed, and hence, the energy barrier to aggregation is eliminated and every collision results in attachment of SWCNT sol (Lin and Xing, 2008; Lin *et al.*, 2009). The CCC values of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} for re-aggregation of suspended SWCNTs in 2500 mg/L SDBS solution were approximately 129, 69, 3.2, and 3.7 mmol/L, respectively (Fig. 6). The CCC values of divalent ions were an order of magnitude lower than those of monovalent ions, indicating that divalent ions are more effective counter-ions (Bouchard *et al.*, 2012). All of the CCC values were much higher than the average concentrations of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} in fresh river water (i.e., 0.22, 0.034, 0.16, and 0.36 mmol/kg, respectively) but lower than those in surface seawater (i.e., 470, 10.2, 53, and 10.3 mmol/kg, respectively) (Broecker *et al.*, 1982).

After the stable SWCNT suspension was diluted, the CCC values of the cations for re-aggregation of

the suspended SWCNTs decreased significantly (Fig. 8a). Fig. 8a, for example, shows the effect of the Ca^{2+} concentration on the aggregation of stably suspended SWCNTs in a 2500 mg/L SDBS solution and the three diluted suspensions of SWCNTs with SDBS concentrations of 50, 500, and 1000 mg/L. This decrease in the CCC values indicates that stably suspended SWCNTs do not retain environmental stability that would allow them to be transported long distances at significant concentrations, because, as soon as they are released into the environment, dilution will occur and environmentally relevant cations will coagulate and re-aggregate the diluted suspension of SWCNTs.

The concentrations of both SWCNTs and SDBS were reduced by the dilution of the SDBS-suspended SWCNTs. However, the decrease in the CCC values of the cations for the re-aggregation of suspended SWCNTs was a result of the decrease in the SDBS concentration rather than the decrease in the SWCNT concentration (Figs. 8b–8d). The CCC values of

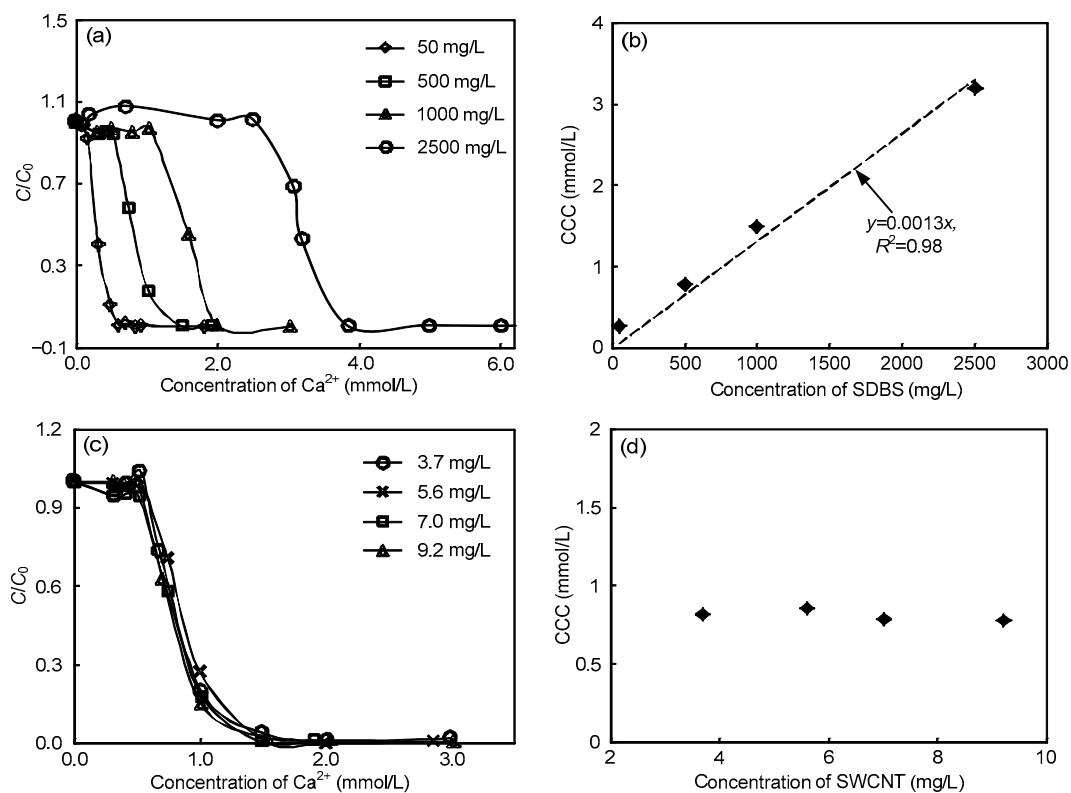


Fig. 8 Stability of SDBS-suspended SWCNTs at four SDBS concentrations (a) and at four SWCNT concentrations (c) as a function of ionic strength (Ca^{2+}), and the CCC values of Ca^{2+} for the aggregation of suspended SWCNTs as a function of SDBS (b) and SWCNT (d) concentrations

SDBS-suspended SWCNTs were independent of the concentration of stably suspended SWCNTs (Figs. 8c and 8d). There was a linear relationship between the CCC values of Ca^{2+} ions and the SDBS concentrations in the suspension (Fig. 8b). Similar phenomena were observed by Bouchard *et al.* (2012) for the CCC values of Na^+ for re-aggregation of suspended MWCNTs and the SDS concentration in the suspension. Yang *et al.* (2013) also observed that the aggregate dimensions of stably suspended SWCNTs were not changed with the added SWCNT dose and SDBS concentrations, although a higher concentration of SWCNTs dispersed in the SDBS solution was observed when more SWCNTs or SDBS was added. Therefore, SWCNT dose and SDBS concentration cannot alter the CCC values of stably suspended SWCNTs because they cannot alter their aggregate dimensions. The CMC of SDBS was 963 mg/L (Yang *et al.*, 2007). Molecular conformations of SDBS molecules above and below CMC will be significantly different as monomer at below CMC and micelle at above CMC (Yang *et al.*, 2007). The linear relationship in the SDBS concentration ranging from 50 to 2500 mg/L (Fig. 8b) indicates that molecular conformations of SDBS molecules also cannot alter the CCC values of stably suspended SWCNTs. The observed dependence of the CCC values on the SDBS concentration could be attributed to (1) the steric/electrostatic repulsion between the adsorbed SDBS molecules on the SWCNT surface, which is responsible for the retention of the stability of suspended SWCNTs in solution (Matarredona *et al.*, 2003; Lin and Xing, 2008; Lin *et al.*, 2009; 2010), and (2) the cationic suppression of the electrostatic repulsion by depressing the electric double layer to destabilize and re-aggregate the suspended SWCNTs (Lin and Xing, 2008; Lin *et al.*, 2009).

4 Conclusions

We observed that bulk SWCNTs could not be dispersed and stably suspended in SDBS solution by shaking at 140 r/min, although this can be achieved by sonication. Even SDBS-suspended SWCNTs do not retain their stability at environmental levels of relevant cations after dilution. These observations indicate that SWCNTs cannot be transported long

distances at significant concentrations in the natural environment, thus posing potential ecological and environmental risks for the following reasons: (1) shaking at 140 r/min is a mild and typical agitation condition encountered in natural aqueous environments, whereas the agitation induced by sonication is not; and, (2) as soon as the suspensions are released into the environment, dilution occurs and environmentally relevant cations coagulate and re-aggregate the diluted suspension of SWCNTs. We also observed that the re-aggregation of suspended SWCNTs in the presence of the environmentally relevant cations was dependent on the SDBS concentration and not on the SWCNT concentration, with the CCC values of the Ca^{2+} for re-aggregation of SDBS-suspended SWCNTs decreasing with the decrease in the SDBS concentration in the diluted suspension. Both dispersion detergents and sonication play important roles in the dispersion of SWCNTs in water. The vigorous agitation by sonication breaks down the large aggregates of SWCNTs to smaller ones in the dispersion process, while the dispersion detergents (e.g., SDBS), especially the adsorbed fraction on the SWCNT surface, inhibit coagulation and aggregation through steric/electrostatic repulsion between the adsorbed SDBS molecules to maintain the stability of the suspension. This information is important for understanding the distribution and fate of SWCNTs in the environment and for estimating environmental exposure risks.

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中文摘要:

本文题目: 单壁碳纳米管在阴离子表面活性剂溶液中的分散悬浮和团聚沉降性能研究

Dispersion and aggregation of single-walled carbon nanotubes in aqueous solutions of anionic surfactants

研究目的: 纳米颗粒在水中的悬浮和团聚性能是决定它们在环境中迁移行为及潜在健康和环境风险影响范围的关键。表面活性剂不仅在环境中普遍存在,而且是工业制备纳米颗粒稳定悬浮液的主要分散剂。本文以单壁纳米碳管为代表,研究震荡扰动及稀释等模拟环境条件下其在阴离子表面活性剂溶液中的分散悬浮和团聚沉降性能,为评价纳米颗粒排放进入环境后的潜在风险提供依据。

创新要点: 现有研究认为,纳米颗粒由于能在水中稳定悬浮,其排放到环境中会产生长距离迁移并存在造成大范围污染的可能性和生态健康风险。在本文中,震荡扰动及稀释等模拟环境条件的研究表明,单壁碳纳米管在环境中长距离迁移并造成大范围污染的可能性和风险较小。

研究方法: 通过比较震荡扰动(模拟环境条件)和超声辅助两种分散悬浮方式及有无添加十二烷基苯磺酸钠(SDBS)阴离子表面活性剂条件下的单壁碳纳米管在水中的悬浮性能(图1),研究单壁碳纳米管能否在环境中被分散悬浮。通过研究 Na^+ , K^+ , Ca^{2+} 和 Mg^{2+} 等环境主要阳离子存在时SDBS稳定悬浮的单壁碳纳米管悬浮性能及与SDBS浓度等的相关性(图6和8),探明稳定悬浮的单壁碳纳米管能否在环境稀释过程中和环境阳离子存在下保持稳定悬浮。

重要结论: 在超声辅助下,单壁碳纳米管可以在SDBS阴离子表面活性剂溶液中稳定分散悬浮,但不能在水中稳定分散悬浮。在无超声辅助、仅通过机械震荡的情况下,单壁碳纳米管无法在水中和SDBS溶液中稳定分散悬浮。对于已经在SDBS溶液中稳定悬浮的单壁碳纳米管,它们在 Na^+ , K^+ , Ca^{2+} 和 Mg^{2+} 等环境主要阳离子存在时也会脱稳形成团聚沉降,且该团聚沉降行为取决于悬浮溶液中SDBS的浓度。当SDBS稳定悬浮的单壁碳纳米管在环境中被稀释时,SDBS浓度被稀释降低,会迅速导致单壁碳纳米管团聚沉降。因此,单壁碳纳米管很难在环境中被分散悬浮,即使是已经稳定分散悬浮的单壁碳纳米管,也会在环境稀释和环境阳离子的作用下快速团聚沉降。由此可见,单壁碳纳米管在环境中长距离迁移并造成大范围污染的可能性和风险较小。

关键词组: 分散悬浮; 团聚沉降; 单壁碳纳米管; 阴离子表面活性剂; 超声