



Influences of perfluorooctanoic acid on the aggregation of multi-walled carbon nanotubes

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Received 30 May 2012; revised 28 August 2012; accepted 30 August 2012

Abstract

The aggregation of multi-walled carbon nanotubes (MWCNTs) in the aqueous phase not only inhibits their extensive utilization in various aspects but also dominates their environmental fate and transport. The role of surfactants at low concentration in the aggregation of MWCNTs has been studied, however the effect of perfluorinated surfactants at low concentration is uncertain. To understand this interfacial phenomenon, the influences of perfluorooctanoic acid (PFOA), and sodium dodecyl sulfate (SDS) as a control, on MWCNT aggregation in the aqueous phase were examined by the UV absorbency method. Influences of pH and cationic species on the critical coagulation concentration (CCC) value were evaluated. The CCC values were dependent on the concentration of PFOA, however a pronounced effect of SDS concentration on the CCC values was not observed. The CCC values of the MWCNTs were 51.6 mmol/L in NaCl and 0.28 mmol/L in CaCl₂ solutions, which suggested pronounced differences in the effects of Na⁺ and Ca²⁺ ions on the aggregation of the MWCNTs. The presence of both PFOA and SDS significantly decreased the CCC values of the MWCNTs in NaCl solution. The aggregation of the MWCNTs took place under acidic conditions and was not notably altered under neutral and alkaline conditions due to the electrostatic repulsion of deprotonated functional groups on the surface of the MWCNTs.

Key words: perfluorooctanoic acid; aggregation; multi-walled carbon nanotubes

DOI: 10.1016/S1001-0742(12)60063-1

Introduction

Carbon nanotubes (CNTs) have attracted considerable attention since their discovery due to their unique physico-chemical, mechanical, and optical properties (Iijima, 1991; Mauter and Elimelech, 2008). CNTs, with their rolled-up graphene structures, are divided into single-wall carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Iijima, 1991), depending on how many layers of graphene are present. CNTs have a wide variety of applications, such as energy storage (Cheng et al., 2001), composite construction materials (Vecitis et al., 2011), nanopores and sensors (Tsai et al., 2007), medicine (Prato et al., 2008), and adsorbents (Kabbashi et al., 2009). The extensive manufacture and utilization of CNTs in various

aspects inevitably results in the exposure of CNTs to the natural environment through wastewater discharge, aging of materials containing CNTs and CNT manufacturing industries (Wiesner et al., 2006, 2009). CNTs released into the environment participate in various processes with respect to the aqueous phase, biological species, and geochemical matrices (Jaisi et al., 2008; Navarro et al., 2008). The aggregation state of CNTs, as a crucial property, has a strong influence on their fates, mobility, and risks in the environment (Pan and Xing, 2008). Besides, the aggregation of CNTs in aqueous or organic phases significantly inhibits their widespread application in manufacturing, energy, electronic and pharmaceutical industries (Jiang et al., 2003). Approaches for the dispersion of CNTs, therefore, are currently hot issues for their potential utilization and various aspects of their environmental implications.

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The dispersion of CNTs in aqueous systems has already been well documented (Jiang et al., 2003; Yurekli et al., 2004; Vaisman et al., 2006; Chappell et al., 2009; Kim et al., 2012). To date, the most efficient methods preventing the aggregation of CNTs are to disperse CNTs using surfactants (Jiang et al., 2003; Yurekli et al., 2004) or by the adsorption of organic compounds (Zhao et al., 2003; Chappell et al., 2009), or by introducing functional groups via oxidants and strong acid treatments (Kytotani et al., 2001; Zhang et al., 2003). Modification via oxidation treatments can change their original properties, e.g., the length and defects of CNTs. However, it has been demonstrated that modification with surfactants does not cause damage to the walls of CNTs. CNTs may be encased in a micelle due to the self-assembly structure of a surfactant, or be coated by hemi-micellar surfactants (O'Connell et al., 2001, 2002; Wang et al., 2004). Structureless random adsorption of sodium dodecyl sulfate (SDS) was found to be responsible for the dispersion of CNTs (Yurekli et al., 2004). Ju et al. (2012) found that sodium dodecylbenzene sulfonate efficiently aids the dispersion of CNTs in aqueous media due to the adsorption on the outer surfaces. Improvement of surfactants to assist CNTs dispersion depends on both the surface characteristics and the type of surfactants, and anionic surfactants were found to have a higher dispersion efficiency than that of cationic or non-ionic surfactants (Rausch et al., 2010). However, as opposed to the dispersion of CNTs, the aggregation of CNTs in aqueous phases has rarely been studied, especially after surface modification of CNTs by different approaches. Sano et al. (2001) studied the aggregation of acid-treated SWCNTs in electrolyte solutions containing several cationic species by a turbidity method, showing the different critical coagulation concentration (CCC) values with cationic species of various valences. Saleh et al. (2008; 2010) reported the effects of biomacromolecules, humic acids, pH, monovalent and divalent salts on the aggregation of MWCNTs, monitored by multi-angle light scattering equipment.

Perfluorochemicals are a type of anionic surfactants with high-energy C–F bonds that are persistent and widespread in the environment (Giesy and Kannan, 2002). Perfluorooctanoic acid (PFOA), as the major homologue of perfluorochemicals, has been widely detected in environmental matrixes, including air, sediment, sludge, municipal wastewater, coastal water, and even tap water (So et al., 2004; Higgins et al., 2005; Mcmurdo et al., 2008; Mak et al., 2009). The widespread occurrence of PFOA will potentially influence the fate, transport and bioaccumulation of released CNTs in the natural environment when they are present together. To date, the impact of PFOA on the aggregation of CNTs has not been studied in the previous works. Overall, there is a critical need to understand and quantify the influence of PFOA on the aggregation of MWCNTs in the aqueous phase. The CCC of a MWCNT

suspension is a critical parameter for the aggregation of MWCNTs in the medium (Sano et al., 2001; Saleh et al., 2008).

We hypothesized in this work that the CCC values of MWCNT suspensions may be altered by low PFOA concentrations. The objective of this study was to evaluate the effects of PFOA on the aggregation of MWCNTs in the presence of various cations. The aggregation of MWCNT suspensions was determined by a turbidity method at different pH values, in Na⁺ and Ca²⁺ solutions, and in the presence of PFOA. For comparison, SDS was used.

1 Materials and methods

1.1 MWCNTs

MWCNTs were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. The MWCNTs were synthesized by a chemical vapor deposition method, using Ni nanoparticles as metallic catalyst. The manufacturer reported that the MWCNTs had a purity of over 95%, a powder density of 2.1 g/cm³ at 20°C, outer diameter of 20–40 nm, and mean length of 1 μm.

The MWCNT suspension was prepared using a successive batch sonication and clarification protocol (Phenrat et al., 2007). In brief, 50 mg of MWCNT powder was added to 200 mL Milli-Q water (Barnstead). The mixture was ultrasonicated for 30 min (Sonicator, 50–65 kHz). The MWCNTs suspension was quiescently left aside at room temperature for 10 min and the upper suspension was decanted. The collected suspension was sonicated again and the newly formed suspension was collected. This procedure of sonication and suspension collection was repeated five times. The final collected suspension was used as the MWCNT stock solution, which was stable for the duration of all the aggregation experiments.

PFOA with 96% purity was purchased from KMF Laborchemie Handels GmbH, Germany. The stock solution of PFOA was prepared by suspending one gram of PFOA in 1 L Milli-Q water (Barnstead) and ultrasonating for 30 min, and diluting to 60 mg/L. SDS with 99% purity was purchased from Sigma-Aldrich Chemie GmbH, Germany. The SDS stock solution was prepared at 60 mg/L in MQ water.

1.2 Characterization of MWCNTs

The morphology and impurity of the MWCNTs were probed by transmission electron microscopy (TEM). The samples were dispersed in ethanol and deposited on a holey carbon film supported on a copper grid. The microscope was operated at an acceleration voltage of 120 kV. High-resolution electron micrographs of MWCNTs were taken under Scherzer-focus conditions.

Thermogravimetry of the MWCNTs was conducted using a simultaneous thermal analyzer 429 (Netzsch,

Gerätebau GmbH, Germany). Generally, 80–100 mg of dry MWCNTs was weighed on a thermobalance, the heating rate was 1 K/min and the maximal temperature was 1000 K. The electrophoretic mobility of the MWCNT suspension was measured with a Zetasizer Nano series (Malvern) after ultrasonication for 10 min (Sonicator, 50–65 kHz).

1.3 Preparation of coated MWCNTs

MWCNTs stock solution (25 mL) was transferred into 100 mL-volumetric flasks. Afterwards, aliquot volumes of PFOA or SDS were added into the flasks, and 50 mL of suspension was made up with MQ water. The final concentrations of PFOA or SDS in the original solution were 200, 600 and 1000 $\mu\text{g/L}$ in the Milli-Q water system. The equilibrium was reached by horizontally shaking at 150 r/min for 48 hr under ambient conditions. The equilibrium suspensions of MWCNTs were thus used as the suspension of MWCNTs coated by PFOA or SDS, respectively, to study their aggregation characteristics.

1.4 Measurement of CCC of MWCNT suspension

A turbidity method (Sano et al., 2001) was adapted to determine the CCC of MWCNTs coated with PFOA or SDS surfactants in NaCl and CaCl₂ solutions. Briefly, 2 mL of suspension of MWCNTs coated by surfactants and 6 mL of a defined concentration of NaCl or CaCl₂ were mixed, ultrasonicated for 1 min, and left undisturbed for 15 hr. The suspension was then centrifuged for 15 min at 5000 r/min. Aliquots of supernatant were taken for measurement of the absorption at 880 nm using a UV-Visible spectrophotometer (Beckman Coulter DU-800, USA). Treatments without PFOA and SDS in the system were utilized as controls. All treatments were conducted in duplicate. The calculation of the normalized amount of

dispersed CNTs in aqueous phase was performed such that the absorption value at various salinities was normalized by that of treatments without PFOA or SDS in the pure aqueous system, and used for quantifying the CCC values.

1.5 Effects of solution pH on CCC of MWCNTs suspension

The effect of solution pH on the critical coagulation concentration for MWCNT suspension was studied at pH 2.4, 3, 4, 5, 6, 7, and 8 in sodium phosphate-citric acid buffer with constant ionic strength of 25 mmol/L (Elving et al., 1956). The determination of CCC at different pH values were performed as described above.

2 Results and discussion

2.1 Characterization of MWCNTs

2.1.1 TEM images

Representative TEM images of MWCNTs are presented in **Fig. 1**. The internal and external diameters of the MWCNTs were 5–10 nm and 20–30 nm, respectively, similar to that reported by the manufacturer. **Figure 1a** depicts that the MWCNTs were sinuous and always entangled. The black circular spots in the central part of MWCNTs were most likely metal catalyst particles. These catalyst particles are occasionally present inside the nanotube structure as well as being terminal features (Tessonier et al., 2009). These results indicate that the MWCNTs were not completely pure, as verified by thermogravimetry. The silky substances on the outer surfaces of the MWCNTs observed at high resolution were free amorphous carbon (**Fig. 1b**). The stacked aromatic layers in the MWCNTs were not always parallel to the tube axis (**Fig. 1b**) and several layers of graphene were perpendicular to the tube axis (**Fig. 1b**). The internal diameters of MWCNTs were

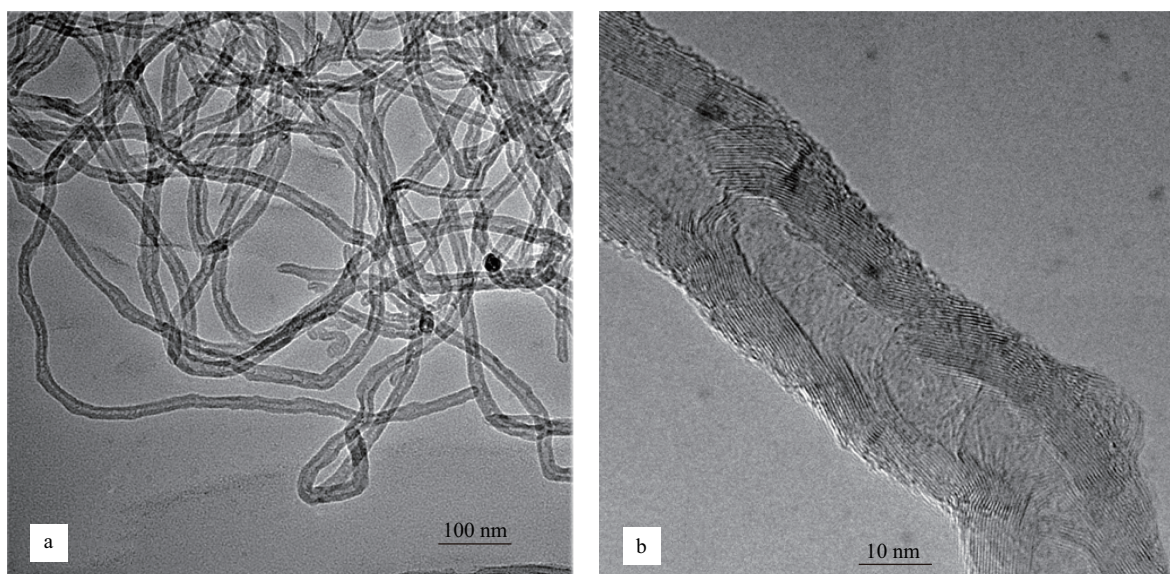


Fig. 1 TEM images of tested MWCNTs.

not always identical. A similar structure of MWCNTs at high resolution was defined as a “fish bone” structure (Tessonnier et al., 2009).

2.1.2 Thermogravimetry of MWCNTs

MWCNTs were characterized by simultaneous thermal analysis and the thermogravimetry. The thermogravimetry curve of the MWCNTs is presented in Fig. 2. The major onset of oxidation of MWCNTs occurred at 350°C. The plateau beyond 1000°C indicates a residual mass of 3.5% of the total mass, which can be attributed to the metal oxide catalyst in the MWCNTs sample.

A significant mass decrease of the MWCNTs was observed at less than 350°C. Saleh et al. (2008) also pointed out that MWCNTs had a small peak (0.7% of the total integrated area under the peaks) near 300°C with respect to the thermogravimetry curve of MWCNTs, indicative of amorphous carbon. The mass loss in the low temperature range (less than 350°C) generally is attributed to the evaporation of water contained in the MWCNTs and the amorphous carbon combustion on the surface of the MWCNTs.

2.2 Aggregation behavior of MWCNTs

2.2.1 CCC of MWCNTs in NaCl and CaCl₂ solutions

The CCC values of the MWCNTs were determined in NaCl and CaCl₂ solutions by a turbidity method (Sano et al., 2001). The results are presented in Fig. 3. The salt concentration was taken as the CCC value when the normalized dispersive amount of the MWCNTs in the solution was 0.5 (Sano et al., 2001). Our results showed that the CCC values of the MWCNTs were 51.6 mmol/L and 0.28 mmol/L in the NaCl and the CaCl₂ solutions, respectively. Saleh et al. (2008) reported that the CCC value of as-grown MWCNTs was 25 mmol/L NaCl and 2.6 mmol/L CaCl₂ as measured by dynamic light scattering. Sano et al. (2001) studied the aggregation of acid-treated SWCNTs and obtained a CCC of 37 mmol/L NaCl. The previously reported CCC values of CNTs are generally

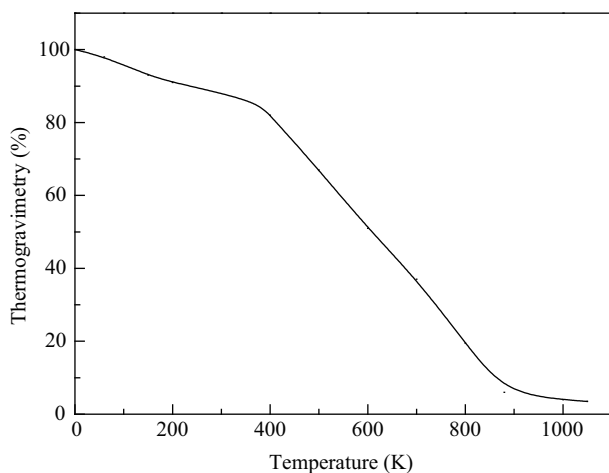


Fig. 2 Thermogravimetry of tested MWCNTs.

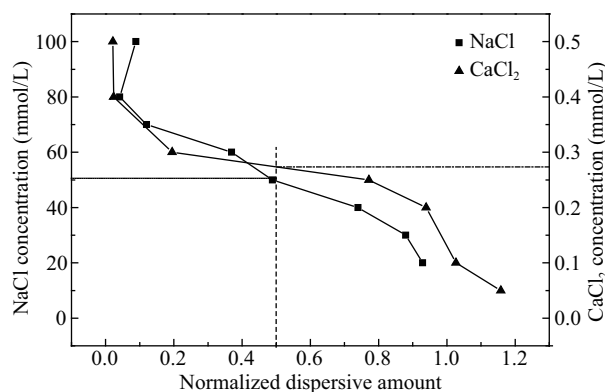


Fig. 3 Aggregation behaviors of MWCNTs as a function of salinity.

consistent with the values observed in this study, except for that in CaCl₂ solution. The effects of monovalent and divalent electrolyte counter-ions on the CCC value of MWCNTs were consistent with the Schulze-Hardy rule.

2.2.2 Effect of PFOA on CCC of MWCNT suspension

The effects of surfactants on the aggregation of the MWCNTs were evaluated with MWCNTs coated by different concentrations of PFOA and SDS and the results are shown in Fig. 4. PFOA shifted the curve of normalized dispersive amount from higher concentration to lower concentration in NaCl solution (Fig. 4a), and the CCC value of the MWCNTs decreased with increasing concentration of PFOA (Table 1). In comparison with the control treatment, the CCC values were reduced by 11.6%, 23.6%, and 31.3% in 200, 600, and 1000 µg/L of PFOA solution in NaCl solution, respectively. This indicated that the concentration of PFOA played a negative role in the aggregation of MWCNTs. Generally, our results are consistent with the observation that SDS reduced the dispersion of MWCNTs at low SDS concentrations in 5 mmol/L NaNO₃ solution (Chappell et al., 2009).

The presence of SDS pronouncedly altered the curve in NaCl solution (Fig. 4b), like that of PFOA. The CCC value diminished by 30.1%–32.9% in the presence of SDS compared with the control treatment (Table 1). Nevertheless, no significant shifting of the curves among different tested SDS concentrations was observed (Fig. 4b). In contrast, in the CaCl₂ solution, PFOA and SDS did not significantly alter the CCC value (Table 1), which ranged from 0.27 to 0.29 mmol/L. These results suggest that Ca²⁺ ions

Table 1 Critical coagulation concentration (CCC) values of MWCNTs coated by PFOA and SDS in NaCl and CaCl₂ solutions

Surfactant concentration (µg/L)	NaCl (mmol/L)		CaCl ₂ (mmol/L)	
	PFOA	SDS	PFOA	SDS
0	51.58 a	51.58 a	0.28 a	0.28 a
200	45.58 b	35.50 b	0.27 a	0.28 a
600	39.38 c	36.04 b	0.27 a	0.27 a
1000	35.42 d	34.61 b	0.28 a	0.29 a

Different letters in the column refers to the significance ($p < 0.05$).

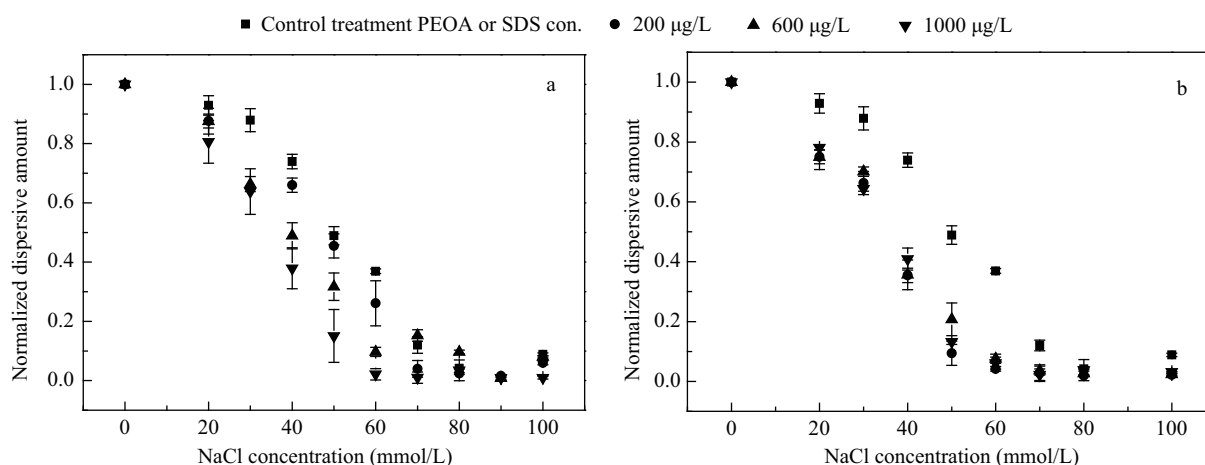


Fig. 4 Aggregation curve of MWCNTs coated by PFOA (a) and SDS (b) in NaCl solution.

play a more crucial role in the aggregation of MWCNT suspensions than the modification by PFOA and SDS.

Previous studies demonstrated that ionic surfactants, for instance SDS (O'Connell et al., 2002; Moore et al., 2003; Tummala and Striolo, 2009) and dodecyl-benzene sodium sulfonate at high concentration (Islam et al., 2003), were efficient in enhancing the dispersive stability of CNTs in aqueous systems. The adsorbed amounts of SDS on the surface of MWCNTs significantly depend on the diameter of MWCNTs and the concentration of SDS (Tummala and Striolo, 2009). The SDS adsorbed on graphite at low surface coverage (i.e., high surface area per head group) preferentially lies parallel to other SDS molecules or parallel to the nanotubes axis, and consequently reaches a maximal number of contacts between the surfactant tail and the carbon atoms in graphite due to the hydrophobic interactions (Sammalkorpi et al., 2008). However, the destabilizing effect of sorbed surfactant on MWCNTs suspension is observed herein, because the surface coverage of the MWCNTs by PFOA was about 1% in 10 mmol/L NaCl solution (Li, 2011), calculated from the molecular size of PFOA (1.08 nm²) using the MOLDEN software (Schafteenaar and Noordik, 2000).

2.2.3 Effect of solution pH on the CCC of MWCNTs

The influence of solution pH on the CCC of MWCNT suspensions was investigated in the range of pH 3–8 using sodium phosphate-citric buffer with 25 mmol/L ionic strength. The results are shown in Fig. 5. At pH > 4, the effect of pH on the aggregation of MWCNTs were very small. As pH decreased from 4 to 3, the coagulation of fractal MWCNTs took place. The probable reason is that the acidic pH value was close to the point of zero charge of the MWCNTs, and the functional groups of the MWCNTs were protonated, so that the electrostatic repulsion among the particles became weak. Consequently, the van der Waals attraction forces became dominant, finally resulting in the coagulation of MWCNTs, according to the Derjaguin-Landau-Verwey-Overbeek theory (Chen

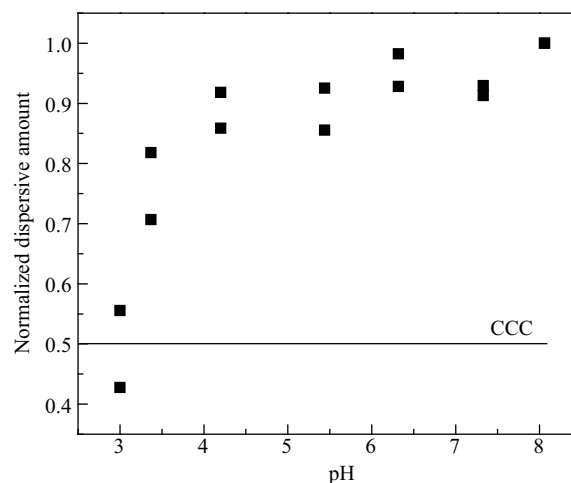


Fig. 5 Effect of solution pH on the CCC of MWCNT suspension at 25 mmol/L ionic strength in sodium phosphate-citric buffer.

and Elimelech, 2006; Saleh et al., 2008).

2.2.4 Effect of PFOA on electrophoretic mobility of MWCNTs

The influences of PFOA and SDS on the electrophoretic mobility of the MWCNTs are shown in Fig. 6. The adsorption of PFOA and SDS on the surface of the MWCNTs increased the electrophoretic mobility of the MWCNTs particles, while there was no significant difference between PFOA and SDS. In addition, their effects on the electrophoretic mobility were independent of the concentrations of PFOA and SDS in the tested range of 200–1000 µg/L. These results thus indicated that the adsorption of surfactant decreased the net Zeta potential of MWCNTs. At high concentration of SDS (1000 µg/L), the adsorption of SDS on CNTs made the Zeta potential more negative (Jiang et al., 2003). In the high concentration range, surfactants alter the specific self-organization morphology of surfactant molecules to some extent, with structures such as cylindrical micelles (Moore et al., 2003), hemimicelles (Moore et al., 2003), and helices or double helices

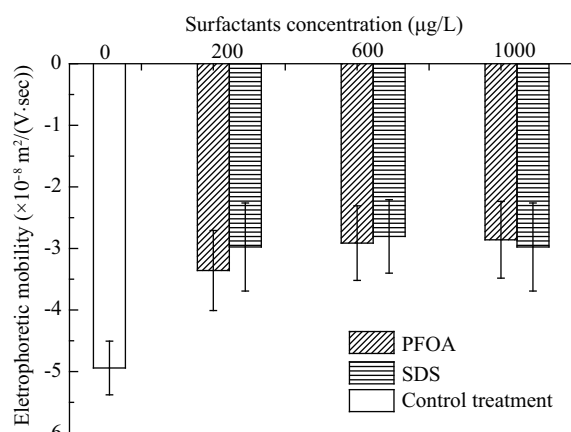


Fig. 6 Electrophoretic mobility of MWCNTs coated by PFOA and SDS.

(O'Connell et al., 2002). In the low concentration range, SDS molecules lay predominantly flat on the surfaces of or parallel to the axes of nanotubes due to hydrophobic interactions (Tummala and Striolo, 2009). In our case, the low adsorbed amounts of PFOA and SDS respectively reduced net Zeta potential of MWCNTs, resulting in an enhanced aggregation. This effect was attributed to the decreased repulsive forces between the MWCNTs.

3 Conclusions

The application of low PFOA and SDS concentration, respectively, destabilized the MWCNT suspensions. The CCC values of MWCNT suspensions in NaCl solution decreased with increasing PFOA concentration. No effect of PFOA on the CCC in CaCl₂ solution was observed. SDS also increased the aggregation of MWCNTs, but no dependence on SDS concentration was observed in NaCl or CaCl₂ solution. The change of aggregation derived from the reduced electrostatic repulsion due to the adsorption of PFOA on the surface of the fractal MWCNTs. The stability of MWCNT suspensions in acidic aqueous media was sensitive to the medium pH because of the carboxylic and phenolic groups associated on the surface of MWCNTs. The decreased dispersion of MWCNTs by low concentration of PFOA will diminish their environmental risks.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20977043, 20777033) and the Opening Funding of State Key Laboratory of Pollution Control and Resource Reuse (No. PCRRF12012). The author is grateful for a scholarship from the Deutscher Akademischer Austausch Dienst.

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