

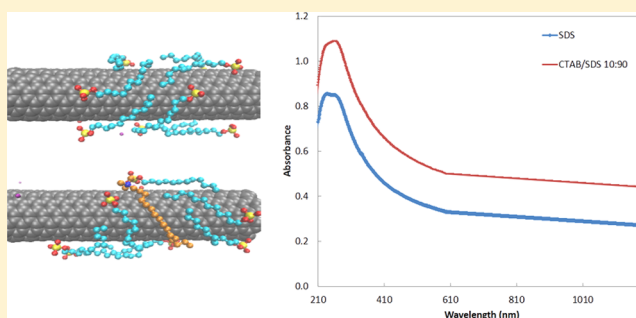
Dispersion of Carbon Nanotubes Using Mixed Surfactants: Experimental and Molecular Dynamics Simulation Studies

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S Supporting Information

ABSTRACT: The ability of cationic-rich and anionic-rich mixtures of CTAB (cetyltrimethylammonium bromide) and SDS (sodium dodecyl sulfate) for dispersing of carbon nanotubes (CNTs) in aqueous media has been studied through both the experimental and molecular dynamics simulation methods. Compared to the pure CTAB and SDS, these mixtures are more effective with the lower concentrations and more individual CNTs, reflecting a synergistic effect in these mixtures. The synergistic effects observed in mixed surfactant systems are mainly due to the electrostatic attractions between surfactant heads. In addition, the surface charge related to the colloidal stability of mixed surfactant-covered nanotubes has been characterized by means of ζ -potential measurements. The results indicate that the hydrophobic interactions between surfactant tails also give rise to the higher adsorption of surfactant molecules. Furthermore, molecular dynamics (MD) simulations have been performed to provide insight about the structure of surfactant aggregates onto nanotubes and to attempt an explanation of the experimental results. The MD simulation results indicate that the random and disordered adsorption of mixed surfactants onto carbon nanotubes may be preferred for a low surfactant concentration. Our research may provide experimental and theoretical bases for using mixed surfactants to disperse CNTs, which can open an avenue for new applications of mixed surfactants.



1. INTRODUCTION

The unique mechanical, electrical, and optical properties of carbon nanotubes (CNTs) suggest their potential in a variety of applications such as nanoelectronics, polymer nanocomposites, coatings, and drug delivery.^{1,2} Unfortunately, the van der Waals tube–tube attraction makes their existence in aggregated bundles and hampers their practical applications because of their poor solubility and dispersibility both in aqueous and organic media.³

To overcome this problem, two different approaches are currently being used to disperse carbon nanotubes, covalent and noncovalent functionalization. Covalent functionalizations involve the bonding of different chemical functional groups on the side walls of carbon nanotubes.⁴ However, such bonding disrupts the intrinsic sp^2 hybridized network that gives rise to exceptional properties of nanotubes.^{4,5} In contrast, the noncovalent functionalizations include the physical adsorption of surfactants and polymers to improve the dispersibility of the CNTs.⁶ The noncovalent approach is superior in the sense that it does not alter the π -electron network of carbon nanotubes, consequently preserving the electrical properties of carbon nanotubes.⁷

Up to now, a wide variety of pure surfactants have been investigated for dispersion of carbon nanotubes, and particular attention has been devoted for selecting the best dispersing

agent in terms of percentage of dispersed CNTs, ratio of dispersing agents vs dispersed CNTs, and stability of the dispersions formed.⁸ Unfortunately, to date, the mechanism by which these surfactant molecules adsorb onto carbon nanotubes is poorly understood. Although some reports have proposed structured adsorption of surfactants on the nanotube surface, Yurekli et al. demonstrated that sodium dodecyl sulfate (SDS) molecules randomly adsorbed without preferential head–tail orientation.^{4,9}

Another possible way of studying the surfactants adsorption onto CNTs is the use of computer simulation methods. Molecular dynamics (MD) simulations provide a natural method to study the self-assembly structure formed onto carbon nanotubes and interactions between surfactant molecules and CNTs.^{10–12} Therefore, MD simulation seems to be a very powerful tool in studying the problem of adsorption mechanism of surfactant molecules onto carbon nanotubes.

The use of mixtures of surfactants is effective in many applications because of synergistic effects that improve surfactant packing on surfaces and modifications of repulsive/ attractive forces. Although there are many relevant researches

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about dispersing CNTs by pure surfactants, mixed surfactants applied in this field are rare. Tan et al. studied the dispersion ability of Surfynol CT324, a commercial blend of anionic and nonionic surfactants, and another similar mixed surfactants, Surfynol CT131.¹³ Excellent performance for Surfynol CT324 and a performance similar to that of dodecylbenzenesulfonic acid sodium salt (NaDDBS) for Surfynol CT131 was observed. However, a mixture of (10%) NaDDBS with (90%) cetyltrimethylammonium p-toluene sulfonate (CTAT) was ineffective in suspending individual nanotubes. Madni et al. found that the mixtures of (50%) cationic surfactant dodecyltrimethylammonium bromide (DTAB) and (50%) anionic surfactant sodium octanoate (SOCT) are able to produce the high dispersed multiwalled carbon nanotubes (MWNTs).¹⁴

In the present study, we examine aqueous dispersions of multiwalled carbon nanotubes using two pure surfactants: sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) and the mixtures of different mixing ratios of SDS/CTAB. The significance of using a particular mixing ratio of mixed surfactants has been established for obtaining a stable nanotube dispersion. Furthermore, we use large-scale (up to 33000 atoms) and all-atomistic MD simulations to study the structure of aggregates formed in both pure and mixed surfactant systems. This study may provide guidance for the application of dispersing CNTs by mixed surfactants.

2. METHODS

2.1. Experimental Details. The MWNTs (length 0.1–10 μm , outer mean diameter 10–15 nm, mean number of walls 5–15) were purchased from Arkema Co., Ltd., prepared by the method of chemical vapor deposition (CVD). The surfactants of sodium dodecyl sulfate (SDS, >99%) and cetyltrimethylammonium bromide (CTAB, 99%) were provided by Merck Chemical Co. that SDS was doubly recrystallized from a ethanol solution and CTAB was used without further purification. All dispersion experiments were carried out with distilled water. To obtain surfactant-stabilized CNT dispersions in aqueous solutions, the following experimental steps were performed. For each experiment 0.1 wt % MWNTs based on the weight of water was mixed with 5 mL of an aqueous solution containing different concentration of SDS and CTAB. For each system SDS–MWNT and CTAB–MWNT, three series of aqueous solutions were prepared: (i) two samples below the critical micelle concentration (cmc) of each surfactant, (ii) one sample at concentration of the cmc of surfactants, and (iii) several solutions above the cmc of each surfactants. The critical micelle concentration of SDS and CTAB are 6 and 0.8 mM, respectively. Investigations have shown that cmc in catanionic mixtures decreases due to attraction between head-groups.

For mixed surfactant systems, initially we prepared pure solution of CTAB and SDS at 30 mM concentration and then four surfactant concentration levels were prepared: (0.1/0.9), (0.2/0.8), (0.3/0.7), and (0.4/0.6) (cationic/anionic). The same procedure was carried out for preparation of anionic-rich samples. These solutions were prepared at above the cmc point, then 0.005 gr of MWNT was added to these solutions. These samples were ultrasonicated for 1 h in order to get the surfactant-coated MWNTs. Then all samples were centrifuged for 20 min at 1000 rpm to remove the big clusters, and after 24 h, the samples were used for further studies.

UV–vis measurements were performed on a mini 1240 spectrometer. Nano-ZS (MALVERN) using laser Doppler velocimetry and phase analysis light scattering cell was used for ζ -potential measurement. The temperature of the scattering cell was controlled at 298 K. A light scattering angle of 17° was combined with the reference beam, and the data were analyzed with the software supplied for the instrument. Surface tension measurements were carried out at 298 K by the ring method using a Sigma 700 tensiometer under atmospheric pressure.

2.2. Simulation Details. Molecular dynamics simulations of the self-assembly of pure and mixed surfactants on the nanotube surface in aqueous solution were carried out using the GROMACS 4.5 software package.¹⁵ The simulated systems, including the total numbers of CTA⁺, DS[−], counterions, water molecules, and the total number of atoms are reported in Table 1. It should be noted that while the experiments were

Table 1. Simulation Details for the Systems Studied in This Work

models	N_{CTA^+}	N_{DS^-}	N_{Cl^-}	N_{Na^+}	N_{water}	N_{Total}
CNT-pure surfactants	10	0	10	0	10 967	33 643
CNT-mixed surfactants	9	1	9	1	10 970	33 649
CNT-mixed surfactants	1	9	1	9	10 994	33 697
CNT-pure surfactants	0	10	0	10	10 992	33 688

conducted for the MWNT, the simulations were performed for the SWNT because the size of the entire MWNT is much bigger than the accessible scale of the MD simulation. For this reason, a fragment of an armchair type SWNT composed of 532 carbon atoms was used in the simulations. Recent simulations on the SDS–SWNT systems have demonstrated that while SDS surfactants lie parallel to the SWNT of small diameter, they form slanted angles on the larger diameter tubes.¹⁰ However, it has been pointed out by Xu et al. that at low surfactant surface coverage, SDS heads show no preferential orientation arrangement with respect to the SWNT axis for both small and large diameter tubes.¹¹ Since the surfactant surface coverage in our simulations are smaller than those used in ref 10, it was assumed that the nanotube diameter has no strong effect on the results. Note that our MD simulations were aimed at comparing the structure of surfactant aggregates formed on the nanotube of given diameter. Therefore, for all simulated systems, an uncapped (7, 7) single-walled carbon nanotube (with a diameter of 0.95 nm and a length of 4.68 nm) was selected as a representative SWNT. The (7,7) SWNT was generated using TubeGen tool¹⁶ and maintained at the center of simulation box of size $7 \times 7 \times 7 \text{ nm}^3$ which was not allowed to move during the simulations. Because most of the nanotubes were opened after sonication, it is likely that the interior of the nanotube would be accessible to the environment, and potentially filled by the solvent, ions or other molecules. Therefore, the length of the simulation box was chosen to be about 2.3 nm longer than the length of nanotube (4.68 nm) to allow the water molecules or ions to fill the nanotubes. Simulations were all started with a surrounding configuration of surfactant molecules. The PACKMOL program¹⁷ was used to generate these configurations. A snapshot of the initial configuration for anionic-rich system is shown in Figure S1 in the Supporting Information. The initial configurations for the rest of the simulated systems were constructed in a similar manner. It was assumed that sodium dodecyl sulfate completely dissociate into dodecyl sulfate ion

and Na^+ ion and cetyltrimethylammonium bromide was assumed to completely dissociate into cetyltrimethylammonium ion and its counterion. The Cl^- ion was considered as the counterion for the cetyltrimethylammonium ion. It has recently been reported by Suttipong et al. that for the adsorption of SDS on the SWNT surface, an insignificant change in the self-assembled surfactant aggregate morphology is observed when Na^+ ions are substituted with larger Cs^+ at low surfactant surface coverage.¹⁸ Since all MD simulations presented in this study have been conducted at low surfactant surface coverage, we assumed that the substitution of Cl^- for Br^- counterions does not change the surfactant aggregate structure on the nanotube surface. Note that the difference between Cl^- and Br^- ions diameter is smaller than that for Na^+ and Cs^+ ions. It should be pointed out that the four model systems selected in this study are not expected to immediately address experimental research. However, the four model systems could hopefully provide some information on structure of the surfactant aggregates formed onto nanotubes of small diameter at low surfactant surface coverage. The united-atom GROMOS 96 force field¹⁹ was selected to represent all bonded and nonbonded interactions. This force field has been used to simulate surfactant molecules and carbon nanotube as well.^{20–22} Automated Topology Builder (ATB) was used to generate topology and conformation of surfactant molecules.²³ The long-range electrostatic interactions were handled with the particle mesh Ewald (PME) method and the van der Waals interactions (vdW) were treated with a cutoff distance of 1.2 nm.

The equations of motion were integrated with a time step of 2 fs using the Verlet (leap-frog) algorithm.^{24,25} All the simulations were conducted under the NPT ensemble (constant number of atoms, constant pressure of 1.0 bar, and constant temperature of 300 K) in order to best mimic the experimental conditions. Constant temperature and pressure were maintained using the velocity-rescaled Berendsen thermostat²⁶ and a Parrinello–Rahman barostat.²⁷ Periodic boundary conditions were applied in all three directions. Each system was equilibrated for 23 ns, and only the last 4 ns of simulation were used for data analysis. Since it was previously shown that the simulated solvent accessible surface (SAS) area can be used to quantify the dynamics of adsorption and desorption of surfactant molecules on the nanotube surface,¹² we plotted the variation of SAS areas of the CTA^+ and DS^- ions as a function of simulation time (see Figure S2 in the Supporting Information) to show that the simulated systems have reached the stable minimum. SAS area was traced out by a probe sphere which was rolled around the CTA^+ or DS^- ions to identify their solvent accessible surface areas. Furthermore, we performed simulations with two different initial configurations for two of our simulated systems to ensure that the results were not affected by the initial configuration. In Figure S3, we compared the simulation results computed from the new configurations (configuration 2) to those obtained from the primary configurations (configuration 1). For the two systems considered, no significant difference was observed in the radial distribution functions (RDFs) obtained from the two different initial configurations selected here. Visualizations of all molecular configurations were done using VMD.²⁸

3. RESULTS AND DISCUSSION

3.1. Comparison of Dispersing Power of Pure and Mixed Surfactants Using UV–Vis Spectroscopy. The

evaluation of the degree of dispersion of CNTs in aqueous media can be achieved by recording the UV–vis spectra of the dispersions.⁶ Because individualized CNTs are active in the UV–vis region and exhibit characteristic bands corresponding to additional absorption due to 1D Van Hove singularities.^{29–32} However, bundled CNTs are hardly active in the wavelength region between 200 and 1200 nm. Therefore, it is pertinent to compare the amount of individually dispersed CNTs in the solution through the absorption intensity. The UV–vis spectra of aqueous CNT dispersions using different SDS and CTAB concentrations are measured to ascertain their optimal concentration (C_{opt}). Figure 1 shows the evolution of

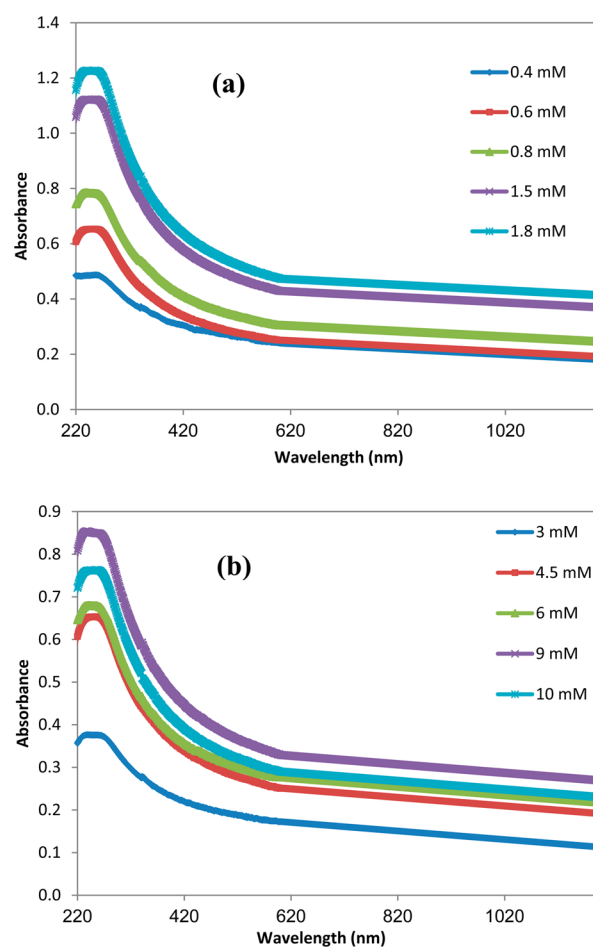


Figure 1. UV–vis spectra of an aqueous (0.1 wt %) CNT dispersions using different surfactant concentrations: (a) CTAB and (b) SDS.

absorbance for different CTAB and SDS concentrations. As shown in Figure 1, the increase of CTAB and SDS concentrations up to concentration of 1.5 and 9 mM for CTAB and SDS, respectively, lead to the increase of the absorbance intensity; however, a further increase of CTAB and SDS concentrations cause the reduction in absorbance intensity. Thus, the values of C_{opt} for CTAB and SDS are determined to be 1.5 and 9 mM, respectively, which are higher than their critical micelle concentration (cmc). Therefore, it is assumed that most surfactants in the suspensions adsorbed onto the surfaces of the MWNTs. Further increase of CTAB and SDS concentrations above the C_{opt} result in wasting materials and may lead to undesired results. Similar results have been reported by Shin et al.³³ and Dong et al.,³ who found that

the values of C_{opt} are slightly higher than the cmc of surfactants. It is worth mentioning that among CTAB and SDS surfactants, CTAB can suspend the nanotubes better than SDS at its optimal concentration, because it has a longer alkyl chain length, which in turn, would lead to the stronger hydrophobic interactions between the MWNT and CTAB.

To compare the dispersing power of CTAB/SDS mixtures, we measure the UV-vis spectra of aqueous CNT dispersions for both cationic-rich and anionic-rich mixtures. As shown in Figure 2a, with increasing the CTAB mole fraction in the

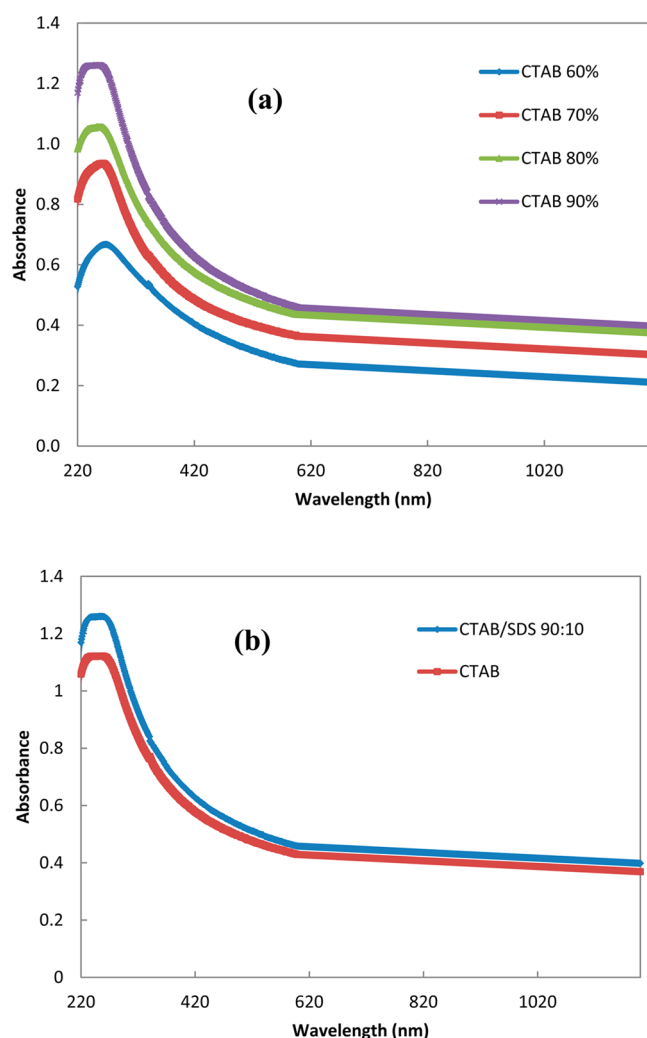


Figure 2. UV-vis spectra of an aqueous (0.1 wt %) CNT dispersions using (a) cationic-rich mixtures and (b) pure CTAB and CTAB/SDS 90:10.

solution, the absorbance in the characteristic wavelength region changes to higher values, indicating that the amount of individually dispersed MWNTs increases. Hence, according to our experimental results, the dispersing power of the CTAB/SDS mixtures follows the trend

$$\text{CTAB/SDS}(60:40) < \text{CTAB/SDS}(70:30) < \text{CTAB/SDS}(80:20) < \text{CTAB/SDS}(90:10) \\ \text{dispersing power} \rightarrow$$

The reason for this experimentally observed trend may be that the increase of SDS ratio in the CTAB/SDS mixture leads to the increase of the amount of SDS adsorbed on the MWNT surfaces. Because the two surfactants have opposite charges,

when both molecules adsorb onto nanotube, the charge neutralization between heads of opposite charge leads to a reduction in the electrostatic repulsions between isolated tubes and, therefore, the amount of individually dispersed MWNTs decreases. Figure 2b that a 90:10 mixture of CTAB/SDS is able to disperse the MWNTs better than the pure CTAB at its optimal concentration. This can be attributed to the synergistic effect of the surfactant mixture which results in stronger CTAB adsorption onto MWNT surface. The synergistic effect observed in a 90:10 mixture arises mainly from the electrostatic attractions between headgroup of surfactants. Note that compared to other cationic-rich mixtures, mixed surfactant-coated nanotubes in a 90:10 mixture of CTAB/SDS have a higher effective surface charge which stabilize the MWNTs against the aggregation. The same trend is observed for the anionic-rich mixtures, as can be seen in parts a and b of Figure 3. Thus, the dispersing power of mixed surfactants depends on

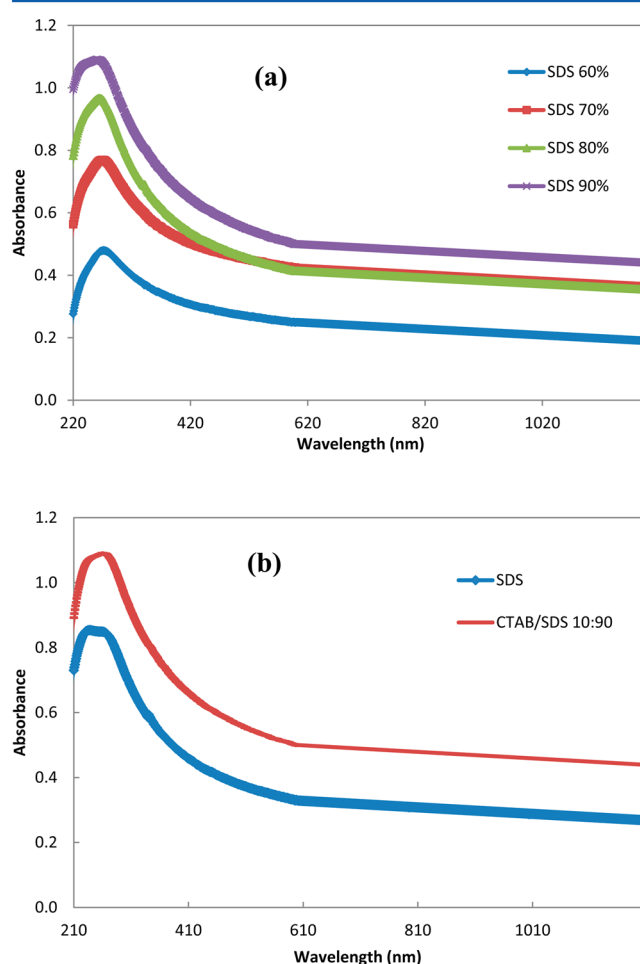


Figure 3. UV-vis spectra of an aqueous (0.1 wt %) CNT dispersions using (a) anionic-rich mixtures and (b) pure SDS and CTAB/SDS 10:90.

the mixing ratio of two surfactants and it is maximum for the 90:10 cationic-rich and anionic-rich mixtures. In the following sections, we will focus on these two mixtures and make a comparison between these mixtures and pure surfactants in dispersion of MWNTs. It is worth pointing out that the difference of absorption intensity between pure anionic (SDS) and anionic-rich (10:90 CTAB/SDS) is larger than that between pure cationic (CTAB) and cationic-rich mixture

(90:10 CTAB/SDS). This means that the synergistic effect due to the addition of 10% CTAB surfactant to the SDS–MWNT dispersion is stronger than addition of the same amount of SDS molecules to the CTAB–MWNT dispersion (compare Figures 2b and 3b). The difference in the synergistic effect between anionic-rich and cationic-rich mixtures reveals that hydrophobic interactions between the (longer) tail of CTAB and the tail of SDS contribute to the dispersing power of mixed surfactants, in addition to the head–head attractions.

3.2. Comparison of Adsorption of Pure and Mixed Surfactants on the MWNTs. In order to compare the amount of pure and mixed surfactants adsorbed on the nanotube surface, surface tension measurements of colloidally stable, dispersed MWNTs solutions containing either pure or the 90:10 and 10:90 mixtures of CTAB/SDS (cationic-rich and anionic-rich mixture) are performed. These measurements are similar to those that are typically conducted on a series of aqueous solutions with different surfactant concentrations to find the cmc of the surfactant considered. In a system consisting of only surfactant molecules in water, below the cmc the surfactant molecules are located either in the water phase, at the walls of the container or at the air–water interface. In this region, the surface tension decreases linearly with the logarithm of the surfactant concentration. For surfactant concentration above the cmc, the surfactants aggregate into micelles and as a result, in this region, the surface tension becomes almost constant. In a system consisting of carbon nanotubes and surfactants, a dynamic equilibrium exists between the free surfactant molecules in solution, surfactant molecules located at the air–water interface, and the surfactants adsorbed on the nanotube surfaces. Here, below the cmc, an increase in the surfactant concentration results in an increase in the concentration of surfactant at the air–water interface as well as an increase in the fraction of solubilized nanotubes.³⁴ Plausibly, at the apparent cmc both surface adsorptions saturate for similar reasons. Consequently, the cmc values of a system containing both surfactants and carbon nanotube differ from a system composed only of surfactant molecules. The difference between the cmc values in the present (cmc') and absence of carbon nanotube (cmc) is a measure of the surfactant adsorption on the nanotube surface.

Parts a and b of Figure 4 indicate surface tension as a function of logarithm of the surfactant concentration in the absence and presence of MWNTs. Whether in the presence or in the lack of CNTs, the value of surface tension decrease linearly upon increasing the surfactant concentration and then reaches a plateau region. The concentration of the breakpoint corresponds to the cmc of the system where micelles begin to form in solution and the concentration of either pure CTAB or the 90:10 mixture of CTAB/SDS at the air–water interface becomes constant. In both systems (pure and mixed) the difference is obvious after the addition of MWNTs. These differences confirm the adsorption of surfactant molecules on nanotube, resulting in a decrease of the effective surfactant concentration in bulk solutions, and thus, higher concentrations will be needed to reach the cmc. The same results are observed for the surface tension measurements of pure SDS and a 10:90 CTAB/SDS (anionic-rich) mixture, as shown in Figures 5a and 5b.

In order to compare quantitatively the surfactant adsorption for both pure and mixed systems, we determine the cmc values for the systems containing pure CTAB and SDS in the absence (cmc) and presence (cmc') of MWNTs as well as for the 90:10

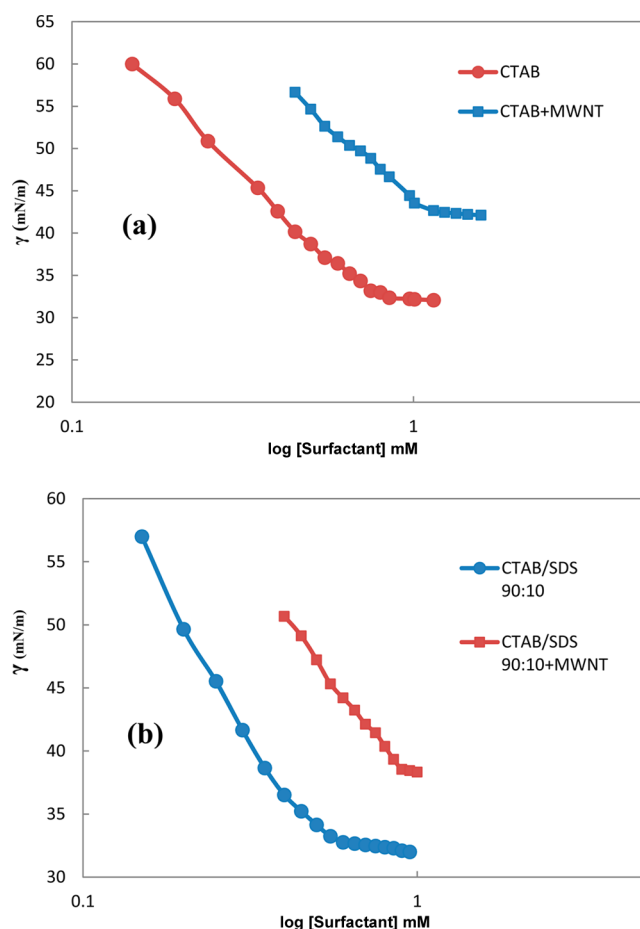


Figure 4. Variation of the surface tension with the logarithm of the total concentration of (a) pure CTAB and (b) CTAB/SDS 90:10.

and 10:90 CTAB/SDS mixtures in the absence (cmc) and presence (cmc') of MWNTs. As can be seen in Table 2, the difference between cmc' and cmc values for the systems containing both cationic-rich and anionic-rich mixtures are larger than those for the systems containing pure surfactant molecules. This suggests that the larger amounts of surfactant molecules have been adsorbed on the nanotube surface in mixed systems. The main reason appears to be the fact that the synergistic effects between two surfactant heads of opposite charge in the mixture improve surfactant packing on the MWNT surfaces and modify the repulsive/attractive forces between surfactant molecules; thus, the surfactant adsorption on the nanotube surface increases. Note that the value of cmc'–cmc for the 10:90 mixture of CTAB/SDS is much larger than that for the 90:10 mixture of CTAB/SDS, showing that mixing the high ratio of SDS with the low ratio of CTAB molecules increases the surfactant adsorption significantly onto MWNTs. This fact proposes that the tail–tail interactions also have an effect on the amount of surfactants adsorbed. This observation is consistent with our UV–vis results (see Figures 2b and 3b).

3.3. Variation of Surface Charge on MWNTs with Pure and Mixed Surfactants Adsorption. The ζ -potential is usually used to obtain the surface charge and is an index of the magnitude of electrostatic interaction between colloidal particles and thus can serve as a measure for the stability of the dispersion. Particles with a ζ -potential smaller than -15 mV or higher than $+15$ mV are considered to be stable by

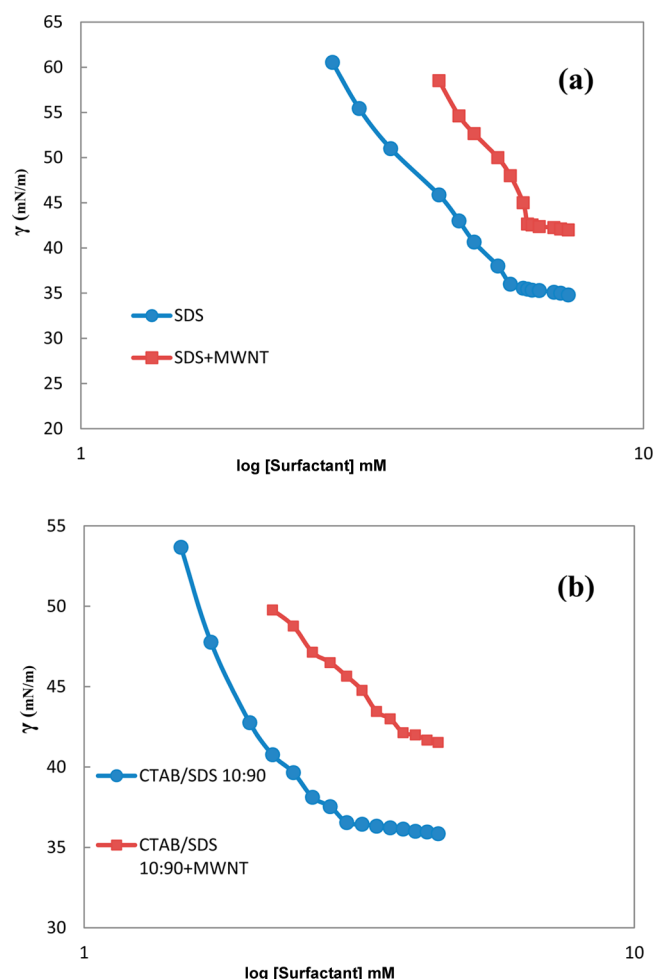


Figure 5. Variation of the surface tension with the logarithm of the total concentration of (a) pure SDS and (b) CTAB/SDS 10:90.

Table 2. Values of cmc Obtained by Surface Tension Measurements for Pure and Mixed Surfactant Systems

system	cmc (mM)	cmc' (mM)	cmc' – cmc (mM)
pure CTAB	0.8	1.1	0.3
CTAB/SDS (90:10)	0.5	0.9	0.4
CTAB/SDS (10:90)	3	3.8	0.8
pure SDS	6	6.2	0.2

electrostatic repulsion interactions.³ However, particles with ζ -potential between -15 and $+15$ mV can still be stable if they are stabilized sterically.³⁵ In the case of nanotube dispersions it can be related to the potential in the vicinity of the bound ions at the surface of the carbon nanotubes. Although the main purpose of this paper is to study the ability of mixed surfactants for dispersing and stabilizing dispersions containing carbon nanotubes, how the surface charge of surfactant-covered nanotube can be affected by the surfactant tail length and its headgroup size has also been investigated. White et al. have correlated the ζ -potential of surfactant-wrapped individual carbon nanotubes dissolved in water to the dispersion stability.³⁵ They also showed that the ζ -potential increases when reducing the chain length of the anionic alkyl sulfate surfactants because of the greater packing possible for the smaller molecules; whereas, Wang et al. have shown that the cationic gemini surfactant hexyl- α,β -bis (dodecyldimethylam-

monium bromide) ($\text{C}_{12}\text{C}_6\text{C}_{12}\text{Br}_2$) have much stronger adsorption ability than its relative single-chain cationic surfactant dodecyltrimethylammonium bromide.³⁶ In this study, we have attempted to clarify the role of the length of surfactant tail on the stabilization of carbon nanotube suspensions. Table 3 shows the ζ -potential values of the

Table 3. ζ -Potentials of Surfactant–MWNT Suspension for Pure and Mixed Surfactant Systems

system	ζ -potential (mV)
pure CTAB	+47.15
CTAB/SDS (90:10)	+38.25
CTAB/SDS (10:90)	–38.94
pure SDS	–30.19

aqueous MWNTs solution dispersed by pure surfactants at their optimum concentrations as well as by the 90:10 cationic-rich and anionic-rich mixtures. As shown in Table 3, the values of ζ -potential of MWNT suspension for CTAB and a 90:10 CTAB/SDS mixture are higher than 15 eV, as well as for SDS and a 10:90 CTAB/SDS mixture are less than -15 eV, underlining the excellent stability of surfactant–MWNT colloidal dispersion. The magnitude of surface charge for CTAB–MWNT is higher than that for SDS–MWNT. This is due to the much stronger adsorption ability of CTAB on MWNTs, as expected from the results of the UV–vis and surface tension measurements. The stronger adsorption of CTAB onto MWNTs can be attributed to the fact that it has a longer hydrocarbon tail which increases the tail–tail and tail–nanotube hydrophobic interactions and makes favorable the adsorption of a greater amount of CTAB on the MWNTs. In addition, surfactant–MWNT in the anionic-rich mixture shows higher negative surface charge than SDS–MWNT. This is because the presence of the CTAB molecules with a longer tail increases the hydrophobic interactions between surfactant tail particles which lead to an increase in amount of adsorbed SDS on the MWNTs (see Table 2). Whereas, the SDS presence in the CTAB–MWNT solution improves the CTAB adsorption to a lesser degree and as a result the ζ -potential value for the cationic-rich mixture is smaller than that for CTAB–MWNT. Thus, our results for both pure and mixed systems propose that the hydrophobic interactions among tail–tail and tail–carbon of nanotube can affect the amount of adsorbed surfactants as well as the stability of carbon nanotube dispersion. This will be discussed in more detail in the next section.

3.4. Pure and Mixed Surfactants Adsorption on the Nanotube: MD Simulation. In order to investigate whether or not the mixing of surfactants has an effect on the structure of aggregates formed on the nanotube surface, we performed self-assembly simulations of either pure or the 90:10 and 10:90 CTAB/SDS mixture at around the SWNT (7,7). For this purpose, we positioned either 10 pure surfactant molecules (CTA^+ or DS^- along with their counterions) or 10 mixed surfactant molecules (9 of cationic along with 1 anionic or vice versa) around the nanotube. Note that we chose to simulate the same total number of surfactant molecules for both pure and mixed systems to study the structure of surfactant aggregates formed on a nanotube of given diameter under the same circumstances. Having 10 surfactant molecules on a (7, 7) SWNT of 4.68 nm long in our simulations corresponds to a linear packing density of 2.14 surfactants per nm of the SWNT. For comparison, the experimentally estimated linear packing

density of SDS³⁴ is 4.5 ± 1.0 molecule/nm, which is about two times larger than our simulated value. Therefore, our simulations correspond to a low surfactant surface coverage (total low concentration around 48 mM), which is close to the surfactant surface coverage used in recent simulation studies.^{11,37} One limitation typical for all atomistic MD simulations is one due to the currently available computational resources, it is impossible to simulate large enough systems to obtain the adsorption isotherm of surfactants on SWNTs. For this reason, the numbers of surfactant molecules near the carbon nanotube are considered as an input parameter in the simulations. Then the simulations are conducted for a time sufficiently long to evaluate the equilibrium structure for the adsorbed aggregates. Representative simulation snapshots of pure and mixed surfactants adsorbed on a (7, 7) SWNT are shown in Figure 6. As can be observed in Figure 6, surfactant tail-groups in both pure and mixed systems either wrap around the nanotube or lie flat on the nanotube surface, similar to what has been observed for adsorption of SDS and CTAB onto nanotubes.^{10,37} These orientations increase the number of

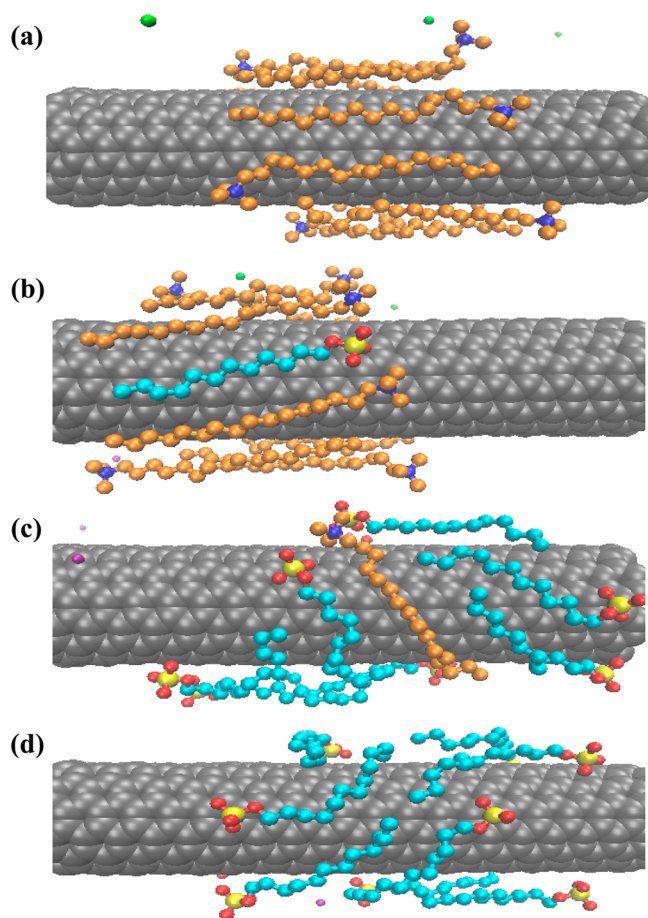


Figure 6. Representative simulation snapshots of a (7,7) SWNT in aqueous solutions of (a) pure cetyltrimethylammonium chloride, (b) a 90:10 mixture of cetyltrimethylammonium chloride/sodium dodecyl sulfate, (c) a 10:90 mixture of cetyltrimethylammonium chloride/sodium dodecyl sulfate, and (d) pure sodium dodecyl sulfate. Water molecules are not shown for clarity. Color code: blue, nitrogen; green, chloride counterion; orange, carbon atoms in cetyltrimethylammonium ion; red, oxygen; yellow, sulfur; purple, sodium counterion; cyan, carbon atoms of dodecyl sulfate ion; silver, carbon atoms in the SWNT. All snapshots are at the 23 ns in the MD simulations.

contacts between surfactant tail and carbon of the SWNT, which in turn, would enhance the hydrophobic interactions between the surfactant tail and SWNT. Therefore, it seems that CTAB molecules with longer tails are able to interact stronger with the SWNT surface. Most of surfactant head-groups are located near the nanotube surface and only a small fraction of surfactant heads in the systems containing either pure cationic or cationic-rich mixture are extended far into the aqueous phase. The hydrocarbon tail in CTA⁺ contains four CH₂ groups more than DS[−] and, therefore, is significantly more hydrophobic, which results in an increase the repulsion between tail–head neighboring surfactant molecules. In addition, the steric hindrance of the heads and head–head repulsions for CTA⁺ is expected to be larger than that for DS[−] because of its larger headgroup size. Thus, the higher repulsive force between tail–head and head–head of the CTA⁺ along with the steric hindrance of the heads may be involved in protrusion of a small fraction of CTA⁺ heads from the nanotubes. It should be pointed out that the orientation of heads toward water molecules in cationic or cationic-rich mixture increases their interactions with water molecules and improves the nanotube dispersion. In addition to the stronger interactions between CTAB tail and the SWNT surface, such orientation of CTAB heads aids in explaining why the dispersing power of cationic and cationic-rich mixture is larger than those of anionic and anionic-rich mixture. It is important to note that a shared feature of snapshots in Figure 6 is that the adsorbed surfactant molecules prefer to self-assemble next to each other instead of being distributed evenly on the nanotube surface. Presumably this occurs so that surfactant molecules are able to maximize their tail–tail interactions. This organization of surfactant molecules has been observed in the case of SDS and CTAB molecules.^{10,37} The binding or condensation of counterions contribute also in shielding some portions of the electrostatic repulsion between surfactant heads and keep the molecules next to each other (for details see Figure S3 in the Supporting Information). Similar results have been reported for the SDS and CTAB adsorption onto SWNTs.^{10,37} We also note that the number of SDS tails around the CTAB tail is higher than CTAB tails which can be found close to the SDS tail (see Figure 6, parts b and c). This indicates that due to the longer length, CTAB tail is able to interact with a greater number of SDS tails. This may explain why the magnitude of ζ -potential value for anionic-rich mixture is higher than that for cationic-rich mixture.

To study mixed surfactants adsorption mechanism on the nanotube surface and compare with the pure surfactant adsorption mechanism, we plot the radial distribution function (RDF) of tail and head segments with respect to the axis of the tube for both pure and mixed systems. As can be seen in Figure 7, all four tail segment RDF curves display one strong peak at ~ 0.9 nm, indicating the surfactant tails adsorb on the nanotube surfaces and form an adsorption monolayer on it as well. This result is consistent with observations in recent MD simulations of SDS and CTAB self-assembly on the nanotube surface.^{10,37} For the pure cationic and cationic-rich mixtures, parts a and b of Figure 7 illustrate that a majority of CTA⁺ heads are positioned adjacent to the nanotube surface and CTA⁺ tails, as can be noticed from the obvious peak at around 1 nm at which overlaps with the tail segments profile. As can be realized with the shoulder found at ~ 1.2 nm, only a small fraction of the CTA⁺ heads are located further and extended to the aqueous environment. However, in the case of anionic and anionic-rich

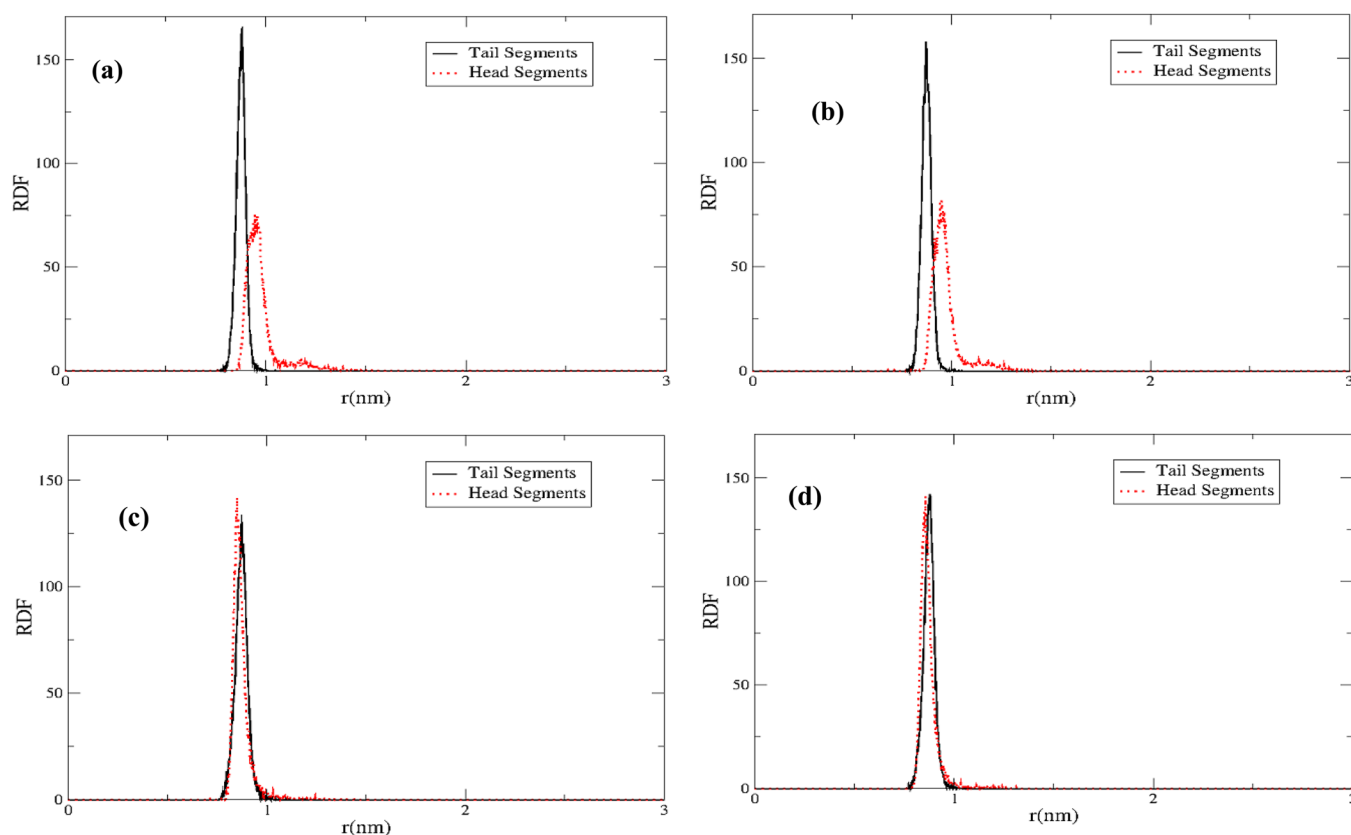


Figure 7. Simulated radial distribution functions (RDFs) of surfactant tail and head segments around the CNT as a function of the distance from the axis of the tube (a) pure cetyltrimethylammonium chloride, (b) a 90:10 mixture of cetyltrimethylammonium chloride/sodium dodecyl sulfate, (c) a 10:90 mixture of cetyltrimethylammonium chloride/sodium dodecyl sulfate, and (d) pure sodium dodecyl sulfate.

mixtures the head segments RDF profiles demonstrate that almost all DS^- heads are adsorbed at the same position of DS^- tails on the nanotube surface. The reason for this difference seems to be the fact that the CTA^+ has a longer tail and larger head which both of them increase the steric hindrance of the heads, the tail–head and head–head repulsions and make a small fraction of CTA^+ heads to be protruded toward the aqueous phase. Therefore, our simulations suggest that upon increasing the headgroup size or tail-group length, a greater number of surfactant heads protrude toward the water. Note that almost all DS^- heads are located near the SWNT surface, whereas previous MD simulations on the SDS–SWNT systems have shown that some of SDS heads protrude toward the water molecules. The reason seems to be the fact that SDS surface coverage in our simulation is lower than those used in previous MD simulations.¹⁰ The same position of most of the surfactant heads and tails on the nanotube surface at low surfactant packing density for both pure and mixed studied systems seems to be qualitatively consistent with the random and disordered adsorption model proposed by Yurekli et al.⁹ and obviously cannot be explained in terms of the ordered micellar structures. In addition, our simulation results indicate that the mixing of surfactant molecules has no effect on the structure of surfactant aggregates on the nanotube of given diameter at low surfactant packing density. The random adsorption of pure SDS and CTAB on SWNT surface have been reported previously by the experiments and MD simulations as well.^{9–11,37} In future work with surfactant mixtures, it would be useful to compute the potential of mean force (PMF) between two nanotubes covered with mixed surfactants to compare the stabilization

of surfactant–SWNT system in cationic-rich and anionic-rich mixtures to those obtained for pure surfactants.

4. CONCLUSIONS

A comparative study that combines experiments and MD simulations was carried out to understand the effects of the mixing of surfactants on the amount of surfactants adsorbed, structure of surfactant aggregates, and colloidal stability of carbon nanotube suspensions. Mixtures of CTAB and SDS surfactants with different mixing ratio were considered to find the best composition for dispersing of MWNTs. We demonstrated that the 90:10 cationic-rich and anionic-rich of CTAB and SDS are able to disperse the MWNTs well at lower concentration as compared to pure CTAB or SDS. This could be attributed to the synergistic effect in these mixtures as well as the high effective surface charge of mixed surfactant-covered nanotubes. The synergistic effects observed in mixed surfactant systems arise mainly from the electrostatics attractions between surfactant heads of opposite charge. We showed that the hydrophobic interactions among surfactant tails also contribute to the adsorption of surfactant molecules onto nanotubes in both pure and mixed systems. Moreover, we used MD simulations to probe both pure and mixed surfactants adsorption onto nanotubes. Our results indicate that at low surfactant concentration all surfactant molecules either lie flat on the nanotube surface or wrap around the nanotubes and only a small fraction of surfactant heads in pure cationic or cationic-rich mixtures are extended toward the water. Of the commonly used models for surfactant adsorption onto

nanotubes, the random adsorption model is in qualitative agreement with our simulation results.

■ ASSOCIATED CONTENT

■ Supporting Information

Figures of (i) initial configuration of surfactant molecules in a 10:90 anionic-rich mixture around a (7,7) SWNT (Figure S1), (ii) variation of solvent accessible surface (SAS) area of CTA⁺ and DS[−] ions or both (for mixtures) as a function of simulation time (Figure S2), (iii) comparison of the simulated radial distribution functions (RDFs) of the surfactant tail and head segments around the CNT between the two different initial configurations (Figure S3), and (iv) simulated radial distribution functions (RDFs) of counterions (Na⁺ for cationic and cationic-rich mixture and Cl[−] for anionic and anionic-rich mixture) around the CNT as a function of the distance from the axis of the tube (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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