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Adsorption and Conformation of a Cationic Surfactant on Single-Walled Carbon Nanotubes and Their Influence on Naphthalene Sorption

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Surfactants are used in synthesis and dispersion of carbon nanotubes (CNTs) and can thus be released into the environment with CNTs. In this study, it was observed that the coupled release of surfactants and CNTs altered the sorption of organic contaminants on the CNTs. The cationic surfactant, cetylpyridinium chloride (CPC), decreased naphthalene sorption on single-walled carbon nanotubes (SWCNT). In the most dramatic example, the adsorption capacity of naphthalene on SWCNT was reduced from 240 to 61.1 mg/g. The decrease of naphthalene sorption could be largely attributed to the competition of adsorbed CPC cations (i.e., $C_{21}H_{38}N^+$) with naphthalene by occupying the SWCNT surface as surfaces decreased from 737 to 88.9 m^2/g after the coating of CPC. However, the adsorbed CPC may form hemimicelles and result in a favorable media for naphthalene partition to counteract the decrease in naphthalene sorption. Configuration changes of adsorbed CPC hemimicelles might occur because the naphthalene partition into the adsorbed CPC decreased with the increase of adsorbed CPC. A partition−adsorption model was introduced to describe the partition fraction of naphthalene into adsorbed CPC hemimicelles as well as the adsorption fraction of naphthalene on unoccupied surfaces of SWCNT.

Introduction

Adsorption of toxic chemicals by carbon nanotubes (CNTs) is a critical process for the environmental application of CNTs as superior sorbents (*1, 2*) and for the environmental risk assessment of toxic chemicals and CNTs once they are released to the environment (*2−6*). Single-walled carbon nanotubes (SWCNT), a category of the most remarkable CNTs, exhibit adsorption comparable with activated carbon for toxic organic pollutants (i.e., phenanthrene) because of their large surface area (*3*). Thus, they are potential superior sorbents for organic contaminants. However, high rates of organic contaminants adsorbed to SWCNT may result in increased environmental exposure risks from the contaminant or SWCNT and could alter their fate and bioavailability in the environment (*3*).

Surfactants have been employed to synthesize carbon nanomaterials (*7−9*). Moreover, most applications of CNTs require large-scale manipulation of their stable suspensions in high weight fractions. The insolubility of CNTs in either water or organic solvents greatly limits their actual applications, which has led to research efforts to understand their dispersion by surfactants (*10−14*). Therefore, surfactants used both in synthesis and dispersion of CNTs may be released into the environment along with CNTs. Surfactants have the ability not only to disperse CNTs but also to alter their sorption for organic chemicals, which would affect the transport, fate, and environmental risks of CNTs and organic contaminants simultaneously. For example, two anionic surfactants, sodium dodecyl sulfate and sodium dodecylbenzene sulfonate, were found to enhance the sorption of benzene, toluene, *n*-undecane, and phenanthrene on CNTs from solvents including methanol, ethanol, and *n*-heptane (*15, 16*). Surfactants, including anionic, nonionic, and cationic species, have been found to alter the sorption of organic contaminants onto solids such as soils (*17, 18*), clays (*19−21*), and activated carbons (*22, 23*) from water. In these cases, the adsorbed surfactants on the solids are effective media for contaminant sorption, while the surfactants in water are effective media for contaminant solubilization (thus decreasing sorption). The influence of surfactants on the sorption of organic contaminants by CNTs from water has not yet been investigated. This will be important, however, as the aqueous system is especially of environmental importance.

In this study, a cationic surfactant, cetyl pyridinium chloride (CPC), was employed to investigate its effects on the sorption of an organic contaminant (naphthalene) by SWCNT from water. The objectives of this study were to examine (1) how and to what extent surfactants (e.g., CPC) can alter the sorption of organic contaminants (e.g., naphthalene) on CNTs and (2) the role of adsorbed surfactants and their configurations on sorption. A partition−adsorption model was introduced to describe and predict the sorption of organic contaminants on CNTs in the presence of surfactants. This information may help to estimate the behaviors and risks of both CNTs and organic contaminants when in the presence of surfactants used in synthesis and dispersion.

Materials and Methods

Chemicals and SWCNT. Cetylpyridinium chloride monohydrate (CPC), with a purity of >99.0%, was purchased from China Medicine (Group) Shanghai Reagent Co. The molecular formula, molecular weight, and critical micelle concentration (cmc) of CPC are $C_{21}H_{38}NCl \cdot H_2O$, 358 g/mol, and 320 mg/L (i.e., $C_{21}H_{38}N^+$), respectively. In aqueous systems, CPC exists as its cationic species (i.e., $C_{21}H_{38}N^+$). Naphthalene, with a purity of >98%, was purchased from Acros Organics (Geel, Belgium). The molecular weight, water solubility, and octanol−water partition coefficient (log K_{ow}) of naphthalene are 128.2 g/mol, 32.3 mg/L, and 3.36 (*3*), respectively. SWCNT was purchased from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. This SWCNT has a purity of >90%, carbon content of >96.3%, length of 10−50 μm, outer diameter of 1−2 nm, and inner diameter of 0.8−1.6 nm.

CPC Sorption Experiments. The isotherm of CPC on SWCNTs was obtained using a batch equilibration technique at 25 ± 1 °C and pH 6.0 ± 0.2 in 20 mL vials. Ten milligrams of SWCNT was added to 20 mL CPC solutions (25−1500 mg/L) in the vials. Then the vials were sealed with screw caps and placed on a shaker for 36 h to reach the apparent equilibrium. After centrifugation (3000*g* for 20 min), $C_{21}H_{38}N^+$ concentrations in supernatant were determined by a UV-

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TABLE 1. Selected Properties of Free and CPC-Coated SWCNT

sorbents	m_{CPC}[a] (g)	Q_{CPC}[b] (mg/g)	f_{ss}[c]	A_{surf}[d] (m^2/g)	A_{cal}[e] (m^2/g)	$A_{occupied}$ (m^2/g)	Q_A[f] (mg/m^2)	D[g] (μm)
SW0	0	0	0	737	737	0	0	18.2 ± 2.7
SW1	0.109	84.6	0.0846	392	675	283	0.299	19.7 ± 3.1
SW2	0.217	156	0.156	275	622	347	0.450	22.3 ± 4.5
SW3	0.381	244	0.244	171	557	386	0.632	19.3 ± 3.7
SW4	0.550	318	0.318	88.9	502	413	0.770	25.1 ± 5.2

[a] m_{CPC} is the added doses of CPC with 1 g of SWCNT for the preparation of CPC-coated SWCNTs. [b] Q_{CPC} is the adsorbed CPC (i.e., $C_{21}H_{38}N^+$) amount per gram of CPC-coated SWCNTs, calculated by the following equation: $Q_{CPC} = 304/358 \times m_{CPC}/(1 + 304/358 \times m_{CPC})$, where 304 and 358 are the molecular weight of $C_{21}H_{38}N^+$ and CPC ($C_{21}H_{38}NCl \cdot H_2O$), respectively. [c] f_{ss} is the adsorbed CPC (i.e., $C_{21}H_{38}N^+$) content in CPC-coated SWCNTs, calculated by the following equation: $f_{ss} = Q_{CPC}/100$. [d] A_{surf} is the surface area measured through the adsorption–desorption isotherm of N_2 at 77 K with the multipoint BET method. [e] A_{cal} is the calculated surface area from the surface area of SW0 (737 m^2/g) and the adsorbed CPC content by the following equation: $A_{cal} = 737 \times (1 - f_{ss})$; $A_{occupied}$ was calculated by the difference of A_{cal} and A_{surf} (i.e., $A_{occupied} = A_{cal} - A_{surf}$), representing the surface area occupied by adsorbed CPC. [f] Q_A, representing the density of adsorbed CPC on occupied SWCNT surface, was calculated by the following equation: $Q_A = Q_{CPC}/A_{occupied}$. [g] D is the particle size, presented as the mean ± standard deviation (at 95% confidence level supposed as the normal distribution) of at least 98 particles, taken from the horizontal and vertical span of particles in the optical microphotographs (Figure S1 of the Supporting Information).

spectrophotometer at a wavelength of 259 nm. The adsorbed CPC (i.e., $C_{21}H_{38}N^+$) was calculated by the mass difference of $C_{21}H_{38}N^+$ between the initial and residual solutions. The supernatants were also measured by a UV-spectrophotometer at 660 nm to determine the turbidity and represents the suspension of SWCNT.

Preparation of CPC-Coated SWCNTs. To prepare the CPC-coated SWCNTs, CPC was dissolved into water and mixed with 1 g of the SWCNTs. The added doses of CPC ranged from 0 to 0.550 g (Table 1). The mixtures were shaken at 25 ± 1 °C for 36 h and centrifuged (3000g for 20 min) to collect CPC-coated SWCNTs. Then, the collected CPC-coated SWCNTs were washed with distilled water repeatedly until free of chloride ions, as indicated by $AgNO_3$, dried at 60 °C, and stored for further experiments. The residual CPC amounts in supernatants, measured by a UV-spectrophotometer at 259 nm, were very negligible relative to the adsorbed CPC and were therefore assumed to be zero. Thus, the adsorbed $C_{21}H_{38}N^+$ amounts of CPC-coated SWCNTs were calculated from the added dose of $C_{21}H_{38}N^+$. The free and CPC-coated SWCNTs were labeled as SW0, SW1, SW2, SW3 and SW4, respective to the CPC dose used for coating (Table 1). Surface area values of the free and CPC-coated SWCNTs in Table 1 were determined by nitrogen adsorption–desorption isotherms at 77 K.

Naphthalene Sorption Experiments. Naphthalene isotherms were determined by the batch equilibration technique at 25 ± 1 °C and pH 6.0 ± 0.2 in 20 mL vials, as described in our previous work (*3*). Briefly, naphthalene in methanol was added to 20 mL suspension, which contained 1.6 mg of free SWCNT or 2.0–7.5 mg of CPC-coated SWCNTs in the vials. Then, the vials were sealed and mixed for 36 h to reach apparent equilibrium. After centrifugation (3000g for 20 min), the supernatant was characterized by a fluorospectrophotometer at the excitation and emission wavelengths of 280 and 328 nm, respectively. Experimental uncertainties were evaluated in vials without sorbents, which is less than 2% of the initial concentrations. Therefore, adsorbed naphthalene amounts were calculated directly through the mass difference between the initial and equilibrium concentrations.

The Dubinin–Ashtakhov (DA, eq 1) and Freundlich (eq 2) models were employed for isotherm data fitting (*3*–*5*).

$$q_e = \frac{Q^0}{10^{(\varepsilon/E)^b}} \tag{1}$$

$$q_e = K_f C_e^{\,n} \tag{2}$$

where q_e (mg/g) is the equilibrium adsorbed concentration; Q^0 (mg/g) is the saturated adsorption capacity; ε (kJ/mol) $= RT\ln(C_s/C_e)$ is the effective adsorption potential, where C_e (mg/L) is the equilibrium aqueous concentration, C_s (mg/L) is the water solubility, R [8.314×10^{-3} kJ/(mol·K)] is the universal gas constant, and T (K) is the absolute temperature; E (kJ/mol) is the "correlating divisor"; and b is the fitting parameter. K_f [(mg/g)/(mg/L)^n] is the Freundlich affinity coefficient, and n is the Freundlich exponential coefficient.

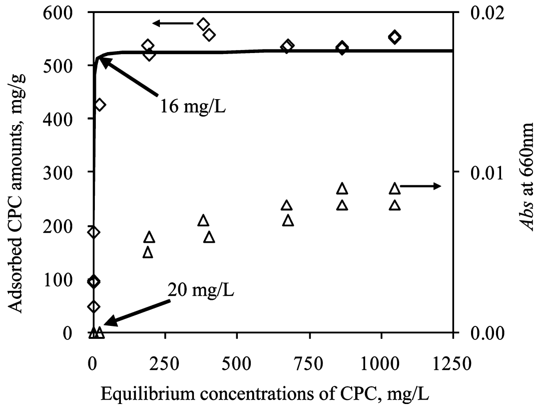

FIGURE 1. Adsorption isotherm of CPC (i.e., $C_{21}H_{38}N^+$) on SWCNT and the absorbance (Abs) at 660 nm of the supernatants.

Results and Discussion

Adsorption of CPC on SWCNT. The isotherm of CPC (i.e., $C_{21}H_{38}N^+$) on SWCNT showed a steep initial slope at low concentrations and then reached a plateau at an elevated equilibrium concentration (Figure 1), which followed a typical Langmuir-type behavior. According to the isotherm fitting using the Langmuir model, the adsorption maximum of $C_{21}H_{38}N^+$ on SWCNT is approximately 530 mg/g at an equilibrium $C_{21}H_{38}N^+$ concentration of 16 mg/L (Figure 1). Adsorption of $C_{21}H_{38}N^+$ results in a significant decrease of the SWCNT surface area (Table 1), suggesting the occupancy of SWCNT surface sites by $C_{21}H_{38}N^+$. In addition, at the equilibrium $C_{21}H_{38}N^+$ concentrations lower than 20 mg/L, no dispersion of SWCNT in the surfactant solution was observed due to the zero absorbance at 660 nm of the supernatants (Figure 1). The high adsorption of $C_{21}H_{38}N^+$ on SWCNT while lacking dispersion of SWCNT at the equilibrium $C_{21}H_{38}N^+$ concentrations below 20 mg/L (Figure 1) indicates that the dispersion of CNTs by surfactant solutions (*12*–*14*) cannot be the result of adsorption of surfactants on CNTs.

TABLE 2. DA and Freundlich Model Fitted Sorption Isotherms of Naphthalene on Free and CPC-Coated SWCNTs[a]

model	parameter	SW0	SW1	SW2	SW3	SW4
DA	Q^0 (mg/g)	240 ± 11	204 ± 5	132 ± 6	81.3 ± 1.9	66.1 ± 3.1
	E (kJ/mol)	16.2 ± 0.4	10.8 ± 0.2	9.17 ± 0.31	7.88 ± 0.12	7.51 ± 0.02
	b	1.26 ± 0.06	1.07 ± 0.02	0.916 ± 0.032	0.920 ± 0.014	0.898 ± 0.022
	r^2	0.995	0.999	0.997	0.999	0.999
Freundlich	K_f [(mg/g)/(mg/L)^n]	80.2 ± 2.5	34.2 ± 1.4	11.1 ± 0.9	5.36 ± 0.47	4.65 ± 0.26
	n	0.347 ± 0.011	0.522 ± 0.014	0.722 ± 0.025	0.778 ± 0.028	0.740 ± 0.018
	r^2	0.995	0.997	0.994	0.993	0.997
Q^0_{cal} (mg/g)[b]		240	220	203	181	164
Q^0_{SA} (mg/m^2)[c]		0.326	0.520	0.480	0.475	0.744

[a] values are presented as mean ± standard deviation. [b] Q^0_{cal} is the calculated maximum adsorption capacity from the maximum naphthalene adsorption capacity of free SWCNTs (240 mg/g) with the SWCNT content $(1 - f_{ss})$ of CPC-coated SWCNTs, i.e., $Q^0_{cal} = (1 - f_{ss}) \times 240$. [c] Q^0_{SA} is the surface area normalized saturated adsorbed capacity ($Q^0_{SA} = Q^0/A_{suf}$).

Moreover, the adsorption of surfactants on CNTs may result in the lower surfactant concentrations in solution to disperse CNTs. Although surfactants have been used to disperse CNTs (*12−14*), the concentrations used were extremely high and unusual in the natural environment. Therefore, the dispersion and transport of CNTs in the environment could not be promoted significantly by surfactants due to their adsorption loss. The only exception would be cases with extremely high surfactant concentrations.

Sorption of Naphthalene on Free and Coated SWCNTs. Isotherms representing the sorption of naphthalene by free and coated SWCNTs are nonlinear and well fitted by both DA and Freundlich models (Table 2). CPC coating increased the linearity of the naphthalene isotherms, as indicated by the increased Freundlich exponential coefficient n ($n \rightarrow 1$, Table 2). CPC-coated SWCNTs have notably lower naphthalene sorption than the free SWCNTs (Table 2). As listed in Table 2, the DA model fitted capacity, Q^0, substantially decreased from 240 mg/g for free SWCNT (SW0) to 66.1 mg/g for SW4 with the increase in adsorbed CPC content (f_{ss}). However, the surface area normalized saturated adsorbed capacity (Q^0_{SA}) values of CPC-coated SWCNTs are higher than that of the free SWCNT (Table 2). This suggests that additional naphthalene sorption may occur besides sorption on the surface of CPC-coated SWCNTs. The adsorbed CPC could be responsible for the additional naphthalene sorption.

The lower naphthalene sorption on CPC-coated SWCNTs than on the free SWCNT (Table 2) may be partly a result of the lower SWCNT mass $(1 - f_{ss})$ in CPC-coated SWCNTs (Table 1). However, the calculated maximum adsorption capacity (Q^0_{cal}) of CPC-coated SWCNTs (Table 2) calculated from the maximum naphthalene adsorption capacity of free SWCNT (240 mg/g) with the SWCNT content in CPC-coated SWCNTs $(1 - f_{ss})$, i.e., $Q^0_{cal} = (1 - f_{ss}) \times 240$ mg/g, is significantly higher than their respective Q^0 (Table 2). Moreover, the difference between Q^0_{cal} and Q^0 gets bigger for SWCNTs with more CPC coating (Table 2). Therefore, SWCNT content alone cannot explain the lower naphthalene sorption of CPC-coated SWCNTs. Additional mechanisms such as competition of adsorbed CPC to decrease naphthalene sorption should be taken into account for CPC-coated SWCNTs.

Adsorption of naphthalene by SWCNT may be attributed to a $\pi-\pi$ electron interactions (*5, 16, 24, 25*) and a hydrophobic mechanism (*5, 25*). With the hydrophobic mechanism, CPC could decrease naphthalene adsorption by enhancing naphthalene solubility in solution (*17, 26*). However, this solubilization occurs commonly at surfactant concentrations higher than the cmc (*17, 26*). In this case, concentrations of CPC in the residual solutions are far lower than their cmc because of the adsorption of CPC by SWCNT (Figure 1). Thus, the solubilization effect on the decrease of naphthalene adsorption should be negligible. Since the maximum adsorption capacity (Q^0) of organic chemicals depends on the available hydrophobic sites on carbon nanotube surfaces (*3, 5*), CPC may also decrease the naphthalene adsorption by occupying the available surfaces of SWCNT due to its adsorption (Figure 1), which is called "competition". Moreover, adsorbed CPC on SWCNT may possibly provide a favorable media for naphthalene partitioning. This has been observed for surfactant-modified sorbents (*18−23*). Competition and partitioning of naphthalene by adsorbed CPC is discussed in detail below. In addition, dispersion of SWCNT aggregates into smaller ones by surfactants may result in more surface sites for SWCNT to be exposed for naphthalene sorption (*15, 16, 27*). This possible dispersion and the surface exposure enhancement of SWCNTs by CPC and their influence on naphthalene sorption can be negligible because the particle sizes of CPC-coated SWCNTs have no significant difference with that of the free SWCNTs (Table 1).

Competition of Adsorbed CPC with Naphthalene. In our previous study (*4*), competition between polycyclic aromatic hydrocarbon (PAH) chemicals on CNTs was reported. It was observed that the nonlinear isotherm of a given PAH would be more linear if competitive PAHs were added (*4*). In this case, competition by adsorbed CPC may also be reasonable for the decreased sorption of naphthalene on CPC-coated SWCNTs, as supported by the increased linearity of naphthalene isotherms and the decreased maximum adsorption capacity (Q^0, in Table 2) with the increase of adsorbed CPC amounts (Table 1). Competition of naphthalene by CPC occurs because adsorbed CPC may previously occupy the hydrophobic sites of SWCNT surfaces (*3−6*). This surface occupying process is supported by the significant decrease of surface area (A_{surf}) with adsorbed CPC amounts as well as the significantly lower A_{surf} than the respective A_{cal} (Table 1). The lower A_{surf} relative to A_{cal} indicates that the decrease of surface area (i.e., A_{surf}) with increased f_{ss} resulted from the surface occupancy of CPC on SWCNTs in addition to the possible decrease from the lower SWCNT content $(1 - f_{ss})$ of CPC-coated SWCNTs.

It should be noted that the competition by adsorbed CPC decreased the maximum adsorption capacity (Q^0) of naphthalene on SWCNTs (Table 2 and Figure 1). This differs from the observed competition phenomena for PAH chemicals on CNTs (*4*), in which the Q^0 for a given PAH chemical mostly remained constant when other PAH chemicals were added as competitors. This difference could be attributed to the different molecular structures between CPC and PAHs as well as the structural influence on the available CNT surface area for sorption. For a CPC molecule, there is a long flexible aliphatic chain (cetyl) on the aromatic pyridine ring. This is in contrast to PAH molecules, which only have aromatic rings. Relative to the aliphatic chains, aromatic rings are hard and inflexible. If the surfaces of the CNTs are covered by hard and inflexible PAH molecules, the exposed surface of adsorbed PAH molecules can be utilized by other molecules

TABLE 3. The Partition−Adsorption Model Fitted Naphthalene Isotherms on CPC-Coated SWCNTs[a]

parameters	SW1	SW2	SW3	SW4
K_p (L/g)	2.54 ± 0.10	1.65 ± 0.07	0.952 ± 0.076	0.978 ± 0.037
Q^{0*} (mg/g)[b]	128	89.6	55.7	28.9
E^* (kJ/mol)	13.1 ± 0.6	10.8 ± 0.6	9.14 ± 0.52	9.53 ± 0.57
b^*	1.21 ± 0.07	0.807 ± 0.046	0.770 ± 0.067	1.12 ± 0.10
r^2	0.997	0.997	0.996	0.997
K_{ss} (L/g)[c]	30.0	10.6	3.90	3.07

[a] Values are presented as the mean ± standard deviation. [b] Q^{0*} is the saturated adsorbed capacity on unoccupied SWCNT surface, which as calculated simply from the Q^0 value of naphthalene on free SWCNT (240 mg/g) and the ratios of unoccupied surface area of CPC-coated SWCNTs (i.e., A_{surf} in Table 1) to the surface area of free SWCNT (737 m^2/g) by the following equation, $Q^{0*} = 240A_{surf}/737$. [c] K_{ss} represents the partitioning ability of adsorbed CPC, which was calculated by normalizing the partition coefficient (K_p) with adsorbed CPC content (f_{ss}), i.e., $K_{ss} = K_p/f_{ss}$.

(*4*). Therefore, the Q^0 for a given PAH chemical on CNTs remains constant when other PAH chemicals were added as competitors (*4*). If the surface of a CNT is occupied by CPC, however, the adsorbed CPC molecules may not provide surfaces for adsorption of other molecules because of the flexibility of the cetyl chain. This hypothesis is supported by the decreased surface area of CPC-coated SWCNTs (Table 1). Other evidence for this hypothesis was observed in other studies (*21, 28*) where the surface area values of coated clays with cationic surfactants were far smaller than that of the uncoated clays. Therefore, the decrease of naphthalene sorption with adsorbed CPC can be attributed to the occupancy of CPC on SWCNT surfaces, which decreased the exposed surface area of SWCNTs. Furthermore, the measured surface area value (A_{surf}, in Table 1) of CPC-coated SWCNTs represents their unoccupied surface area, while the difference between A_{surf} and A_{cal} (Table 1) represents the occupied surface area ($A_{occupied}$, in Table 1) of SWCNTs by CPC.

Partitioning of Naphthalene to Adsorbed CPC. Partitioning, presented as a linear isotherm, is an important process for sorption of organic pollutants by surfactant-coated sorbents, i.e., organobentonite (*18−21*), in which adsorbed surfactants act as a favorable media for solute partitioning. Besides competition, the increased linearity of naphthalene isotherms (Table 2) may also be a result of increased partitioning of naphthalene into adsorbed CPC. The surface area normalized adsorbed naphthalene capacity (Q^0_{SA}) values of CPC-coated SWCNTs are higher than that of the free SWCNT (Table 2), indicating additional partitioning of naphthalene into the adsorbed CPC. Since adsorbed CPC molecules cannot provide surfaces for adsorption of other molecules, as mentioned above, the total sorption of naphthalene by CPC-coated SWCNTs may be considered as the combination of a partitioning fraction of naphthalene into adsorbed CPC and an adsorption fraction of naphthalene on unoccupied SWCNT surfaces. The partitioning fraction can be described by a linear equation (*24−27*), while the adsorption fraction on unoccupied SWCNT surfaces can be described by a DA equation (*3−5*). Therefore, a partition−adsorption model (eq 3), combining the linear and DA equations, was developed here to describe the naphthalene sorption by CPC-coated SWCNTs and to separate the partitioning and adsorption fractions from the total sorption.

$$q_e = K_p C_e + \frac{Q^{0*}}{10^{(\varepsilon/E^*)^{b^*}}} \tag{3}$$

where K_p (L/g) is the partition coefficient, representing the partitioning fraction of naphthalene into the adsorbed CPC; Q^{0*} (mg/g) is the saturated adsorption capacity on unoccupied SWCNT surfaces; E^* (kJ/mol) is the “correlating divisor”; and b^* is the fitting parameter for the adsorption on unoccupied SWCNT surfaces. Since adsorption on CNTs is a surface-dominated process in which the saturated adsorbed capacity is dominated by the surface area of CNTs (*3, 4*), Q^{0*} values of naphthalene by CPC-coated SWCNTs (Table 3) could be calculated simply from the Q^0 value of naphthalene on free SWCNT (240 mg/g) and the ratios of unoccupied surface area of CPC-coated SWCNTs (i.e., A_{surf} in Table 1) to the surface area of free SWCNTs (737 m^2/g) by the following equation: $Q^{0*} = 240A_{surf}/737$.

The good fitting results of the partition−adsorption model (eq 3), using the calculated Q^{0*} values, for naphthalene isotherms of CPC-coated SWCNTs are listed in Table 3. The partitioning fraction of naphthalene into adsorbed CPC (K_p, in Table 3) decreased with adsorbed CPC (f_{ss}, in Table 1). This should be attributed to the possible decrease of the partitioning ability of adsorbed CPC. The partitioning ability of adsorbed CPC (K_{ss}, in Table 3) could be obtained by normalizing the partition coefficient (K_p) with adsorbed CPC content (f_{ss}), i.e., $K_{ss} = K_p/f_{ss}$. A phenomenon unique to surfactants in solution is the aggregation, i.e., the self-assembly of surfactant molecules (monomers) into dynamic clusters called micelles (Figure 3a), when concentrations of surfactants are higher than their cmc values (*29*). Surfactant aggregation may also occur at the solid−water interfaces. With the increase of surfactant concentrations, surfactant monomers adsorbed on solid surfaces begin to aggregate and form micelle-like structures called hemimicelles (*29*). Surfactant micelles and hemimicelles are mainly responsible for the solute partitioning in the surfactant solution and adsorbed surfactants, respectively (*17−20, 26, 29, 30*), while the solute partitioning into the surfactant monomers may largely be negligible. As shown in the solubility curve of naphthalene in CPC solutions (Figure 2a), naphthalene partitioning into CPC monomers could be largely neglected at CPC concentrations (C_{CPC}) below its cmc (320 mg/L). However, naphthalene partitioning into CPC micelles is significant at CPC concentrations (C_{CPC}) above its cmc, exhibiting sharply increased naphthalene solubility (S^*, mg/L) with the increase of C_{CPC} (Figure 2a). The partitioning ability of CPC micelles (K_{mc}, L/mg), therefore, can be calculated with the following equation

$$K_{mc} = [(S^* - C_s)/C_s]/(C_{CPC} - \mathrm{cmc}) \tag{4}$$

where $(S^* - C_s)/C_s$ is the naphthalene partition coefficient between aqueous CPC micelles and water; $(C_{CPC} - \mathrm{cmc})$ is the CPC micelle concentrations, mg/L; and C_s is the naphthalene solubility in water, 32.3 mg/L. Figure 2b shows a linear relationship between $(S^* - C_s)/C_s$ and CPC micelle concentrations $(C_{CPC} - \mathrm{cmc})$, in which the slope of the linear relationship (0.00415 L/mg, i.e., 4.15 L/g) is the K_{mc}. Surfactant hemimicelles may form on the surface of carbon nanotubes (*10, 14, 31, 32*). The increase of adsorbed CPC amounts per unit of occupied surface area (Q_A, in Table 1) with the increase of adsorbed CPC content (f_{ss}, in Table 1) is evidence of the

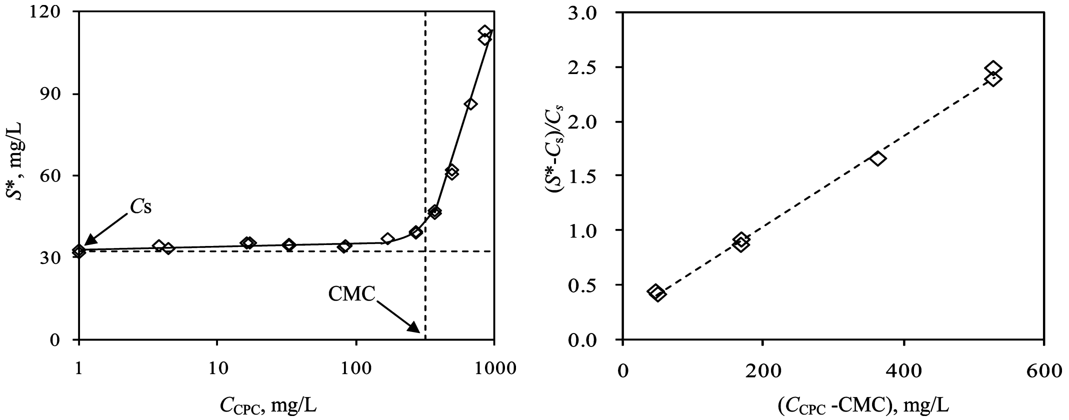

FIGURE 2. Solubility curve of naphthalene in CPC solution at 25 °C (a) and linear relationship between $(S^* - C_s)/C_s$ and CPC micelle concentrations (C_{CPC} − cmc) (b).

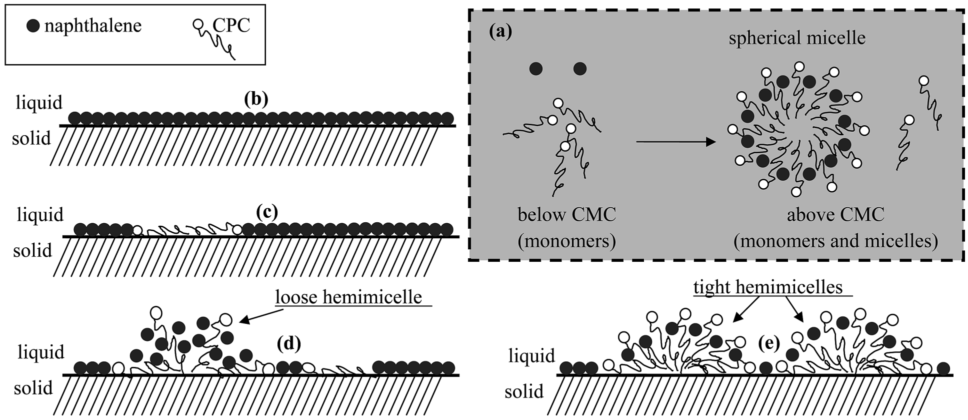

FIGURE 3. Possible scheme of the CPC micellization in solution as well as the adsorption and conformation changes of CPC on SWCNT and its influence on naphthalene adsorption and partitioning.

formation of CPC hemimicelles on SWCNTs. Relative to aqueous CPC micelles with a K_{mc} of 4.15 L/g, adsorbed CPC hemimicelles have a higher partitioning ability (K_{ss}, in Table 3) for naphthalene, especially for the coated SWCNTs with lower CPC content. With the increase of adsorbed CPC amounts, however, the K_{ss} decreased sharply to approach the K_{mc} (Table 3), i.e., the partitioning ability of the adsorbed CPC hemimicelles approaches that of the aqueous CPC micelles.

Adsorbed CPC (especially for its hemimicelles) may be a favorable media for solute (e.g., naphthalene) partitioning and may result in the solute sorption enhancement. However, the apparent decrease of naphthalene sorption with the increase of adsorbed CPC content (Figure 1 and Table 2) indicated that the naphthalene sorption amounts that were enhanced by the partitioning into adsorbed CPC were less than the apparent decrease due to competition of adsorbed CPC. According to the partition−adsorption model and its fitted parameters listed in Table 3, one can estimate the sorption contribution from naphthalene partitioning into adsorbed CPC or from the naphthalene adsorption on unoccupied surfaces of SWCNT.

Possible Conformation of Adsorbed CPC on SWCNTs and Its Influence on Naphthalene Adsorption and Partitioning. The decrease of K_{ss} with the increase of adsorbed CPC suggested that conformational changes of adsorbed CPC hemimicelles may occur. The decrease in K_{ss} could not be a result of additional adsorbed CPC with a lower partitioning ability than the previously adsorbed CPC because the partition coefficient (K_p) decreased as adsorbed CPC increased. If the configuration of previously adsorbed CPC hemimicelles had not changed, additional adsorbed CPC may result in an increase of K_p. According to the Q_A (Table 1), the configuration of adsorbed CPC hemimicelles, at small quantities of adsorbed CPC, should be more loose than those at larger quantities of adsorbed CPC, i.e., CPC monomers in a given hemimicelle are fewer for the loose hemimicelles relative to the tight hemimicelles. The loose configuration of adsorbed CPC hemimicelles would have more spaces for naphthalene partitioning (Figure 3d) than the tight configuration (Figure 3e), exhibiting higher K_{ss} (i.e., partitioning ability) values.

Figure 3 shows the possible scheme of adsorption and conformational change of CPC on SWCNTs and its influence on naphthalene adsorption and partitioning. There are three steps in the process of CPC adsorption on SWCNTs that may affect the sorption of naphthalene by SWCNTs (*10, 14, 31, 32*): (i) Adsorption of CPC monomers on SWCNTs to occupy the SWCNT surface and prohibit naphthalene sorption by competition (Figure 3c); (ii) once CPC monomers are adsorbed on the SWCNTs, they may rapidly form loose hemimicelles for naphthalene partitioning (Figure 3d); (iii) with more CPC adsorbed, additional CPC may not only form additional CPC hemimicelles to occupy the SWCNT surfaces and for naphthalene partitioning but also add CPC monomers into the previously adsorbed and loose hemimicelles, which will result in a more tight configuration of hemimicelles with lower partitioning ability until the complete tight hemimicelles are formed (Figure 3e). Relative to the configurations of CPC hemimicelles, the lower and constant K_{mc} implies that CPC in water can form tight micelles only.

Environmental Implication and Prospect. Surfactants used both in the synthesis and dispersion of CNTs (*7−14*) could be released into the environment with CNTs. Though surfactants can be used to prompt dispersion of CNTs (*10−14*), they may also be adsorbed by CNTs in the environment, especially for cationic surfactants such as CPC. As was observed in this study, adsorption of CPC by CNTs would result in a reduction in the ability for cationic surfactants to disperse the CNTs. Therefore, the transfer of CNTs in the environment could not be promoted significantly by surfactants except for when surfactant levels are extremely high. The adsorption of surfactants on CNTs may alter the sorption of other organic pollutants such as naphthalene by competition and partition of adsorbed surfactants. Adsorbed surfactants on CNTs may form different configurations, i.e., loose and tight hemimicelles that have various partitioning abilities for organic pollutants. Although the partitioning of adsorbed surfactants can enhance the sorption of organic pollutants by CNTs, this sorption enhancement would be offset by the sorption decrease from the competition of adsorbed surfactants. This shows an apparent decrease in sorption as the amount of adsorbed surfactant increases. Organic pollutant sorption by CNTs influences their environmental behaviors as the presence of surfactants apparently decreases organic pollutant sorption. Understanding the effects of surfactants on sorption of organic pollutants by CNTs and on dispersion of CNTs will help us to estimate the behaviors and risks of both CNTs and organic contaminants in the environment. It has been observed that the amounts of CPC adsorbed on solids such as silica decreased with the increase of pH and ionic strength, though the partition ability of the adsorbed CPC for solute is independent of pH and ionic strength (*33*). Thus, pH and ionic strength could change the sorption of organic contaminants by CNTs through changing the adsorbed amounts of surfactants by CNTs, as needs to be addressed. Besides cationic surfactants, anionic and nonionic surfactants have also been employed to synthesize and disperse CNTs (*7−14*). Compared with cationic surfactants, these surfactants could have different sorption on CNTs and thus different effects on sorption of organic contaminants by CNTs. Moreover, the adsorption of surfactants on CNTs and its effects on organic contaminant sorption may depend on the various structures and functional groups of CNTs. Therefore, research using different types of surfactants and CNTs is urgently needed to examine the adsorption effects of surfactants on sorption of organic contaminants.

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Supporting Information Available

Solubilization experimental procedures, particle size measurements, optical microphotographs of free and CPC-coated SWCNTs, DA model and Freundlich model fitted sorption isotherms of naphthalene on free and CPC-coated SWCNTs, and partition−adsorption model fitted naphthalene isotherms on CPC-coated SWCNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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