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A Mechanistic Study of the Selective Retention of SDS-Suspended Single-Wall Carbon Nanotubes on Agarose Gels

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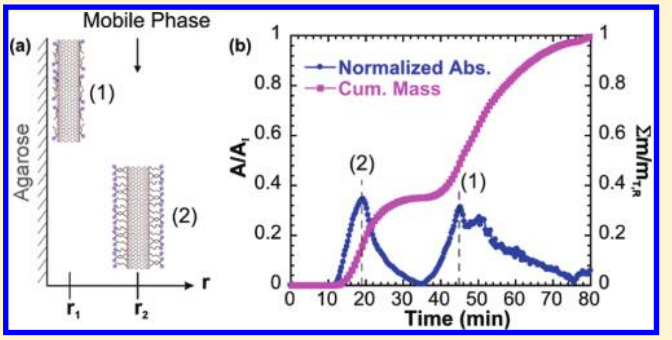
Supporting Information

ABSTRACT: Elution chromatography through columns packed with agarose beads has been used to separate metallic from semiconducting single-wall carbon nanotubes (SWCNTs). Prior studies have attributed the separation to either selective adsorption or size-exclusion (due to selective aggregation) of semiconducting SWCNTs. Initial SWCNT suspensions with different aggregation states were prepared to test these competing theories. Retention characteristics of the SWCNT suspensions were not affected by changes to aggregation state, except when the centrifugation time was short and aggregation excessive. On the other hand, selective adsorption of nanotubes on the agarose matrix is confirmed by modifying the surfactant structure around the SWCNTs without changing the aggregation state of the suspension. In addition, salt-modifiers and solvent-modifiers allow systematic changes to the surfactant aggregation number, orientation, and sidewall coverage. The retention characteristics from these modified SWCNT suspensions suggest that surfactant orientation rather than the exposed regions on the surface of the nanotubes is the dominant factor in the adsorption process.



INTRODUCTION

Single-wall carbon nanotubes (SWCNTs) have physical properties that are enticing for a large number of applications. However, the presence of both metallic and semiconducting SWCNT types prevents their use in many applications. Although progress has been achieved in the synthesis of SWCNTs with a narrow size distribution, postsynthesis methods are still the only route to achieve monodispersity by diameter, length, and type.[1,2]

SWCNTs must be dispersed prior to separation. SWCNTs are typically dispersed in aqueous media through covalent functionalization or using either surfactants,[3,4] DNA,[5,6] or polymers.[7,8] The most promising methods of separation exploit the differences in the surfactant assembly surrounding SWCNTs. For example, density gradient ultracentrifugation (DGU) takes advantage of the difference in buoyant density provided by the specific interactions of the surfactant shell with the SWCNTs.[9] Another interesting method recently developed by Kataura and co-workers is the separation of SWCNTs into metallic (m) and semiconducting (s) species by chromatography with agarose-gel beads as the stationary phase.[10,11] In these separations, the s-SWCNTs are retained by the agarose beads while the m-SWCNTs are eluted. The s-SWCNTs are only released from the column once the sodium dodecyl sulfate (SDS) eluent is replaced with a sodium cholate (SC) solution. Although the chromatographic separation with agarose beads is not yet as effective as DGU, it is more conducive to scale up.

The retention of SWCNTs on agarose gel beads is still not well understood, with two different retention mechanisms being proposed. The first mechanism proposed by Kataura and co-workers is based on the selective adsorption of s-SWCNTs onto the agarose gel.[10−13] The alternative mechanism is that separation is caused by size-exclusion of s-SWCNTs, which was proposed by Moshamer et al.[14] They demonstrated that m-SWCNTs synthesized through the arc-discharge method are better dispersed than their semiconducting counterparts. The authors then proposed that the poorly dispersed and, consequently, larger bundles of s-SWCNTs are retained by the agarose beads. However, the selective retention of s-SWCNTs by virtue of their size is contrary to the principles associated with size-exclusion chromatography, which dictates that larger objects, such as bundled SWCNTs, pass through the column faster because of their inability to diffuse through smaller pores. Only extremely large objects relative to the pore dimensions would be trapped by the beads. Therefore, bundled s-SWCNTs would have to be significantly larger in size than the individualized m-SWCNTs, which is contrary to most analytical reports of these suspensions based on AFM, photoluminescence, absorbance, and Raman spectroscopy.[3,4,14−18]

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In this paper, we explore the mechanism of chromatographic separation of SWCNTs in agarose columns. Experiments are designed to probe each potential mechanism. The size exclusion of aggregated s-SWCNTs is tested by analyzing the retention characteristics of SDS−SWCNT suspensions that have been ultracentrifuged for varying lengths of time. Alternatively, gum arabic (GA), which is a sugar-based surfactant with structural similarities to agarose, is added to the initial SDS−SWCNT suspension to alter the surface of the nanotubes. This surfactant adsorbs onto the surface of SDS-coated SWCNTs without changing their aggregation state and prevents their adsorption onto the beads, confirming that selective adsorption is responsible for the separation of s- from m-SWCNTs. Finally, the features of the surfactant shell that enable adsorption are investigated as well as the nature of an active adsorption site on the SWCNT surface.

METHODS

Reagents. Deionized water was used in all experiments. Sodium dodecyl sulfate (SDS) (≥99%), sodium cholate (SC) (≥99%), gum arabic, and double-stranded DNA from salmon testes were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. HiPco SWCNTs were obtained from Rice University (Rice HPR 162.3) and used as received. Carbon tetrachloride (99.9%) and *o*-dichlorobenzene (99%) were purchased from Sigma-Aldrich. Benzene (99.5%) and *p*-xylene (99.7%) were purchased from Fluka and Fisher Scientific (Pittsburgh, PA), respectively. All solvents were used as received.

Aqueous SWCNT Suspensions. Aqueous suspensions of nanotubes were prepared by mixing 60 mg of raw SWCNTs with 200 mL of a 1 wt % SDS solution. High-shear homogenization (IKA T-25 Ultra-Turrax) for 30 min and ultrasonication (Misonix S3000) for 10 min (120 W) were used to aid all dispersions. After ultrasonication, the mixture was ultracentrifuged at 20 000 rpm (53 000*g*) for 4 h (Beckman Coulter Optima L-80 K, SW 28 rotor). The DNA-coated SWCNTs were prepared by mixing 50 mg of SWCNTs and 50 mg of DNA in 60 mL of water. The suspension was sonicated for 5 min (32.5 W) and ultracentrifuged for 2 h at 20 000 rpm. Before sonication, the size of the DNA strands is between 500 and 10 000 base pairs. Gel electrophoresis showed that the DNA size is reduced to about 500 base pairs after sonication.

Column Experiments. The column experiments were performed using low-pressure chromatography columns from Bio-Rad (see Figure S1 in Supporting Information). The columns were made of glass and had an inner diameter of 1.5 cm. The columns were packed with agarose beads (Sepharose 6B, 45−165 μm in diameter) up to 9 cm in height. A flow adapter connected an Econo gradient pump (Bio-Rad) to the column. A typical experimental sequence consisted of first stabilizing the column with at least two column-volumes (CV), approximately 32 mL, of 1 wt % SDS solution. One-half of a column-volume of either the initial or the surfactant-modified suspension was then injected into the column. The early fractions of SWCNTs were eluted with one CV of SDS solution followed by two CVs of 2 wt % SC solution to remove the retained SWCNTs from the column.

Density Gradient Ultracentrifugation. Linear density gradients were formed by layering aqueous solutions of iodixanol (bought as OptiPrep from Sigma-Aldrich) in centrifuge tubes (38 mL thick-wall polycarbonate from Beckman-Coulter). Volumes of 1.5, 3.75, and 10 mL of 60, 40, and 30% (w/v) iodixanol, respectively, were sequentially added to the tube followed by 10 mL of DI water. The SWCNT suspensions (3.75 mL) were inserted on top of the 30% iodixanol layer using a syringe pump. Prior to insertion, the SDS−SWCNT suspension was adjusted to 20% (w/v) in iodixanol. The SDS concentration was 1 wt % throughout the tube. The centrifuge tubes were allowed to rest for at least 5 h to establish the linear gradient. The samples were then ultracentrifuged for 17 h at 27 000 rpm (96 507*g*).

SWCNT Characterization. The effluent from the column was characterized by absorbance and fluorescence spectroscopy using an Applied NanoFluorescence Nanospectralyzer (Houston, TX) with excitation from 662 and 784 nm diode lasers. The effluent was continuously characterized in situ using a fluorometer flow cell from Starna Cells. Typically, absorption spectra were taken every 20 s while the effluent flowed through the cell. In some cases, a Bio-Rad fraction collector (Model 2110) was used to obtain samples every 1/3 CV during elution.

RESULTS AND DISCUSSION

Retention Behavior of As-Prepared SDS−SWCNT Suspensions. The retention profile of an SDS-coated (1 wt %) SWCNT suspension was measured to establish the elution characteristics of the initial suspension. As observed by others, a significant fraction of nanotubes is initially retained on the agarose beads while the rest of the nanotubes are eluted out of the column with 1 wt % SDS. Figure 1a shows the elution curve (chromatogram) of these SWCNT suspensions as they pass through the column. The first peak is observed at ∼20 min. The visible absorbance spectra at the first peak in Figure 1b shows that the relative concentration of metallic species (400−600 nm) has increased but the suspension still consists of both m- and s-SWCNTs. This result is likely because of the large volume of suspension loaded into the column. This high loading was done intentionally for these experiments so that the differences in retention behavior described below could be easily observed. The remaining nanotubes in the column cannot be eluted with SDS. The retention of these SWCNTs is reversible once the eluent is switched from 1 wt % SDS to 2 wt % SC after 24 min. A second peak in the elution curve of the suspension is then observed at approximately 48 min, as shown in Figure 1a. This peak is broader and less smooth than the first peak. The much lower relative absorbance between 400 and 600 nm in Figure 1b shows that the species eluting in this peak are mainly s-SWCNTs. In this particular sample, the second peak accounts for 65% of all the nanotubes that are eluted, as observed from the cumulative mass curve. In general, 62 ± 3% of the nanotubes are recovered in the second peak. Due to the irreversible retention of some nanotubes, the cumulative mass curve has been normalized to the total amount of SWCNTs that are recovered, as explained in the Supporting Information. For as-prepared SWCNT suspensions in SDS, the amount of nanotubes that are irreversibly retained in the column is very small, so most of the injected nanotubes are recovered (i.e., recovery of 99 ± 10%).

Probing Size-Exclusion as a Mechanism for Selective Retention of s-SWCNTs. In an ideal size-exclusion separation, samples are eluted isocratically; in other words, there is no need to change the eluents or buffer. Furthermore, all the sample components should elute in approximately one CV.[19] However, the elution of SWCNTs from the column requires more than one CV (Figure 1a) of eluent and the change from SDS to SC

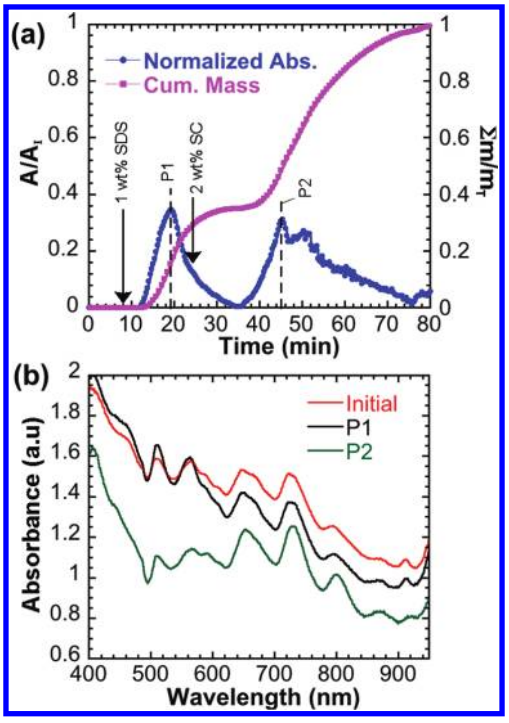

Figure 1. General retention behavior of SWCNTs suspended in 1 wt % SDS. (a) Elution and cumulative mass curves. The elution curves are presented in terms of the absorbance of the effluent normalized by the absorbance of the initial suspension. All absorbance data points are at λ = 763 nm. Details of the calculations for the cumulative mass curves are provided in the Supporting Information. (b) Absorbance spectra from the initial sample and the effluent at the first (P1) and second (P2) peaks of the elution curve, which are shown as dashed lines in part (a). The SWCNT suspension is injected at time zero. The plot also shows the times at which the eluents, SDS and SC solutions, are injected.

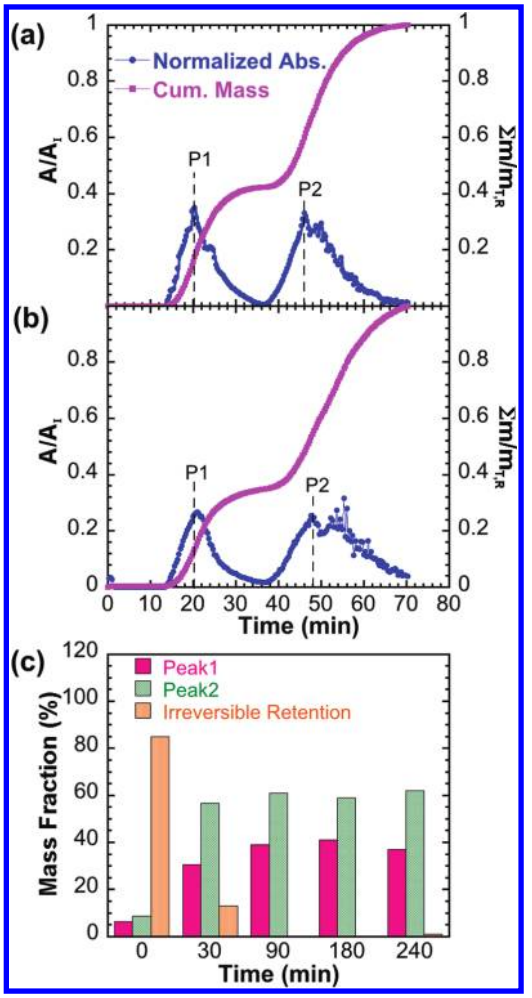

Figure 2. Retention behavior of 1 wt % SDS−SWCNT suspensions prepared with different aggregation states. Elution and cumulative mass curves for the SWCNT suspensions subjected to (a) 240 and (b) 30 min of ultracentrifugation. (c) Mass fraction of SWCNTs that are eluted in Peak 1 (P1) and Peak 2 (P2) as well as those that are irreversibly retained within the column.

solutions. These general observations point to the fact that s-SWCNTs are selectively retained due to adsorption.

To further explore the possible selective retention due to aggregation of s-SWCNTs and subsequent size-exclusion, experiments were conducted on suspensions with different degrees of aggregation, which were prepared using different ultracentrifugation times. Figure S2 in Supporting Information shows that the suspensions ultracentrifuged the longest have the most distinct features. These spectral changes indicate that more aggregated SWCNTs are removed with longer ultracentrifugation times.[20,21] Figures 2a and 2b show that the elution curves for suspensions after 240 and 30 min of ultracentrifugation are very similar. The retention behavior of the suspensions ultracentrifuged between 240 and 30 min is also similar (see Figure 2c and Figure S3 in Supporting Information). However, Figure 2c shows that the suspension subjected to 30 min of ultracentrifugation has some irreversible retention, which can be visually observed in the column after the experiment. The amount of irreversible retention increases dramatically for noncentrifuged suspensions. In this case, approximately 80% of the nanotubes injected are irreversibly retained in the column. The absorbance spectra in Figure S3 also show that aggregation affects the quality of the separation. All of the suspensions ultracentrifuged for less than 240 min show a higher metal fraction in the second peak, which is likely because aggregates are formed with both m- and s-SWCNTs.

These results show that while aggregation and size-exclusion do have some impact on the elution characteristics, it is not responsible for the selective retention of s-SWCNTs. If size exclusion were responsible for selectivity, then the second peak in the elution curve should decrease as more SWCNT aggregates are removed at longer ultracentrifugation times. However, Figure 2c shows no significant changes to the elution characteristics between 30 and 240 min. Instead, irreversible retention is observed once the aggregates reach a threshold size and are not able to flow through the space between the beads, which is consistent with the principles of size-exclusion chromatography.

Probing Selective Adsorption as a Mechanism for Selective Retention of s-SWCNTs. Although nonfunctionalized agarose beads (Sepharose) are mainly designed for size-exclusion chromatography, it is known that they can present strong nonselective adsorption of analytes. These effects are detrimental to separation but in some cases can be used advantageously.[22,23] If selective adsorption of s-SWCNTs to agarose is the primary mechanism for separation in the column, then retention characteristics can be modified by disrupting this adsorption process. This can be achieved by adding a compound that acts similar to

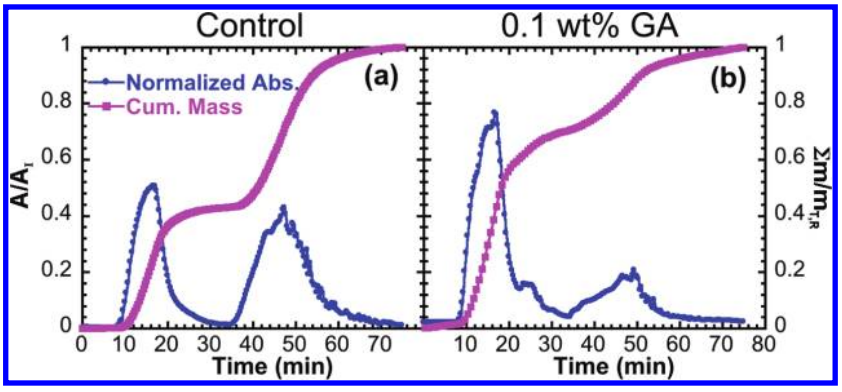

Figure 3. Retention behavior of SDS−SWCNT suspensions modified with 0.1 wt % of GA. Elution and cumulative mass curves for the (a) initial and (b) GA-modified SWCNT suspensions.

agarose in binding with the SWCNTs. Once this compound is added, the adsorption sites on the nanotube−surfactant complex would not be available to interact with the agarose column. Therefore, the retention characteristics should be dramatically altered and the nanotubes should pass through the column with significantly lower retention.

The structure of gum arabic (GA) is complex; however, both GA and agarose have carbohydrates, in particular galactose, as their main structural units.[24] Although the data above show that aggregation mainly affects irreversible retention, the suspension was titrated with GA to observe the changes to the optical spectra (see Figure S4 in Supporting Information) and ensure that the SWCNTs do not aggregate. The results show that GA concentrations below 0.3 wt % significantly increases the PL intensity of large diameter SWCNTs, which is attributed to better coverage of the nanotubes, without inducing aggregation.[25,26] Furthermore, the pronounced red-shift in the emission peaks indicates that the polarity of the medium surrounding SWCNTs has changed.[27] As shown in Figure 3a and 3b, the retention characteristics are significantly altered when 0.1 wt % GA is added to the 1 wt % SDS−SWCNT suspension. The amount of SWCNTs retained in the column has fallen from approximately 58% to 30% with a small amount of GA. The absorbance spectra shows the SWCNTs retained are still predominantly s-SWCNTs (see Figure S5 in Supporting Information). These dramatic changes indicate that the interactions with the column media have been substantially reduced after adding GA, strongly suggesting that selective adsorption of SWCNTs is responsible for the selective retention of SDS−SWCNTs on agarose gel beads.

Effect of Surfactant Structure on the Selective Interaction of s-SWCNTs with Agarose. The total interaction between SWCNTs and the agarose beads will be dependent on the van der Waals forces between the SWCNTs and agarose as well as the steric and electrostatic interactions from the surrounding surfactant layer. Although there is still a debate on how the surfactants assemble on the SWCNT surface, theoretical calculations have shown that SDS molecules tend to lie flat along the axial length of the SWCNT sidewall at low surface density (approximately 1 molecule/nm^2).[28,29] This structure is especially dominant for small diameter SWCNTs, such as the (6,6) nanotube. The formation of this orientation was due to the high energetic penalty required to bend the SDS molecules around the nanotube. Therefore, the SDS head groups are surprisingly very close to the surface of SWCNTs. Another important result from these

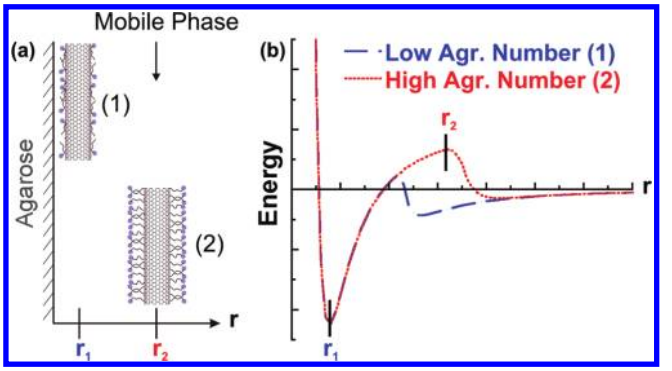

Figure 4. Effect of surfactant structure on the interaction potential between the SWCNT and the agarose substrate. (a) Those SWCNTs with a low aggregation number of surfactant molecules on the SWCNT will adsorb onto the surface while those SWCNTs with a high aggregation number will remain in the mobile phase. (b) Diagram illustrating how the aggregation number of surfactant will change the interaction energy as the SWCNTs approach the agarose substrate.

calculations was that the surface of small SWCNTs is partially covered by the SDS molecules.

Any differences in surfactant structure will affect the interactions between the SWCNTs and agarose. Figure 4 shows how the surfactant morphology could dictate the interactions of the SWCNT with the agarose matrix. Regardless of the nature of the repulsive force (e.g., electrostatic or steric), a thick brush-like surfactant structure (a state of high aggregation number) would provide more repulsion, likely preventing a nanotube from adsorbing onto the surface because of the repulsive barrier that overcomes the van der Waals interactions. On the other hand, a low aggregation number of surfactant can significantly alter the interaction energy, allowing the nanotube to be adsorbed onto the surface.

Experimental[25,26,30,31] and theoretical investigations[28,29] have shown that surfactant molecules can have different orientations around SWCNTs and that parts of the nanotube may be highly exposed to the surrounding media. Therefore, the orientation of surfactants or lack of coverage on SWCNTs could influence the retention characteristics. Understanding the factors that control the adsorption process may lead to improvements in the separation efficiency of this technique. The surfactant shell of an initial SDS−SWCNT suspension is modified by electrolyte tuning[30,31] and swelling with organic solvents to investigate its

Table 1. Summary of SWCNT Suspensions Studied and the Effect That the Modifiers Had on PL Intensity and Retention Behavior[a]

sample	effect on PL intensity	SWCNT coverage	peak 1 (%)	peak 2 (%)
initial SDS−SWCNTs	−	−	38 ± 3	62 ± 3
0.1 wt % GA	increased	increased	70	30
60 mM NaCl	increased	increased	70	30
ODCB-swelled	greatly reduced	decreased	76	24
p-xylene-swelled	greatly reduced	decreased	76	24
CCl_4-swelled	increased	increased	53	47
benzene-swelled	increased	increased	52	48
ODCB-evaporated	similar	similar	50	50
CCl_4-evaporated	increased	increased	50	50
DNA−SWCNTs	greatly reduced	decreased	70	30

[a] The changes are described in reference to the SDS−SWCNTs suspension.

role.[26] The effects that these processes have on the surfactant assembly have been explained in previous publications and will be the starting point of the discussion presented below. Table 1 summarizes the effect of the modified surfactant structures on SWCNT PL and their surface coverage as well as their subsequent elution characteristics.

Changes to Retention Characteristics by Altering the Surfactant Structure through Electrolyte Tuning. The first method used to alter the surfactant structure was the addition of NaCl to the SDS−SWCNT suspension. Previously, Doorn and co-workers showed that SDS-suspended SWCNTs experience intensity changes and blue shifts in the fluorescence spectra when salt is added.[31] Figure S6 in Supporting Information confirms that larger SWCNTs are more sensitive to the increase in NaCl concentration.[30] The differences in intensity and emission energy indicate that the immediate environment surrounding SWCNTs has changed. Alterations in the buoyant density of the surfactant−SWCNT complexes also reflect changes in the immediate environment surrounding SWCNTs. The changes are more dramatic for m-SWCNTs, which migrate to density points lower than that for s-SWNTs and form a distinct red band in the centrifugation tube (see Figure S6).

The difference in PL emission energy and intensity along with the decrease in buoyant density indicates changes to the conformation and aggregation number of SDS molecules on the SWCNT surface.[31] Doorn and co-workers also postulated that the partial screening of the charge on the headgroup of the surfactant not only allows a higher packing density on the SWCNTs but also reorients the molecules, causing the head groups to move further away from the sidewall of the nanotube. A recent study by the same group shows that these changes are not abrupt and take place incrementally as NaCl is added.[32]

The changes in the retention characteristics are seen by comparing the results for NaCl-modified SWCNT suspensions in Figure 5a to the initial SWCNT suspensions in Figure 1. Although there are still two peaks in the elution curve, it is clear that the retention has been significantly affected by modifying the surfactant structure with 60 mM NaCl. While the initial (as-prepared) suspensions had approximately 62% of all SWCNTs reversibly retained in the column, the salt-modified SWCNT suspensions in Figure 5a had approximately 30% retention. In addition, a

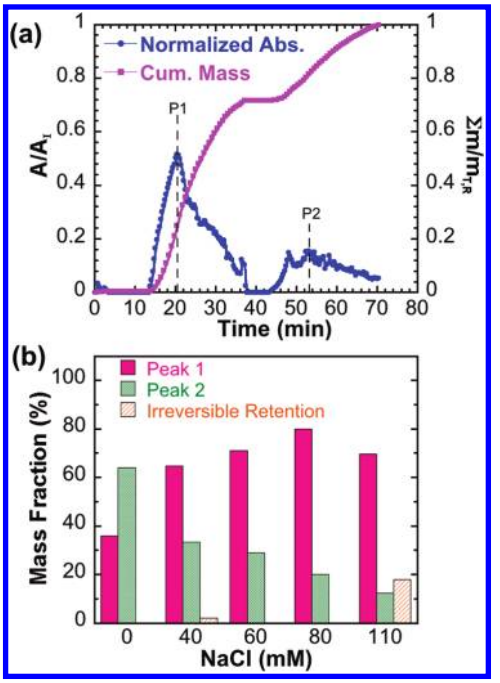

Figure 5. Retention behavior of salt-modified SWCNT suspensions. (a) Elution and cumulative mass curves for 1 wt % SDS−SWCNTs modified with 60 mM NaCl. The elution curves as well as absorbance spectra at other NaCl concentrations are shown in Figure S3. (b) Mass fraction of SWCNTs that are eluted in Peak 1 (P1) and Peak 2 (P2) as well as those that are irreversibly retained within the column.

shoulder now appears on the first peak. This shoulder becomes larger as the salt concentration increases up to 80 mM (see Figure S7 in Supporting Information). The changes in the retention behavior induced by increasing the NaCl concentration are better observed in Figure 5b. The amount of SWCNTs retained in the column (second peak) steadily falls from 62% to 20% as the salt concentration increases from to 0 to 80 mM NaCl. At the high NaCl concentration of 110 mM, aggregation is already significant for larger SWCNTs. As a consequence, approximately 20% of SWCNTs are irreversibly retained at the top of the column. In order to rule out charge screening on the agarose matrix as a possible cause for the reduced retention, elution of SWCNTs was attempted with a SDS−NaCl solution gradient. The SDS concentration was 1 wt % and the NaCl concentration was slowly increased from 0 to 80 mM over 6 CV (see Figure S8 in Supporting Information). It was observed that only a small fraction of SWCNTs are eluted with this method. Hence, the events that induce changes to the retention behavior occurred prior to the SWCNT interaction with the agarose matrix. Finally, the lack of peaks in the absorption spectra between 400 and 600 nm shown in Figure S7 confirm that the s- rather than m-SWCNTs are those retained in the column.

Because the surfactant structure is altered without changes to the aggregation state, these results again confirm that selective adsorption is responsible for the selective retention of s-SWCNTs. The smooth changes in the retention behavior of SWCNTs also reflect the incremental changes in the surfactant structure that take place as NaCl is added. The surfactant makes a gradual transition from a structure with low aggregation number to one with higher packing density as salt is added. The elution profiles show that the transition in aggregation number greatly affects the

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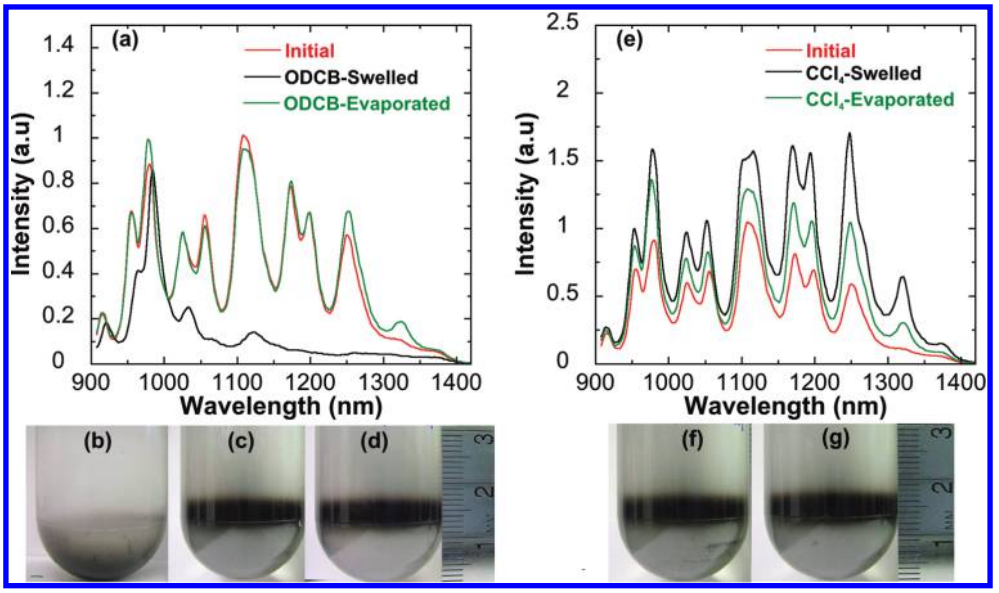

Figure 6. Altering the surfactant structure around SWCNTs with ODCB and CCl_4. (a) PL spectra for SWCNTs treated with ODCB. Images of the centrifugation tubes for the (b) initial, (c) ODCB-swelled, and (d) ODCB-evaporated SWCNT suspensions in a density gradient medium. (e) PL spectra for SWCNTs treated with CCl_4. Images of the centrifugation tubes for the (f) CCl_4-swelled and (g) CCl_4-evaporated SWCNT suspensions in a density gradient medium.

interaction of the nanotubes with the agarose matrix. As shown in Figure 4, these differences will affect the interaction potential between the SWCNTs and the agarose, altering the retention characteristics.

Changes to Retention Characteristics by Altering Surfactant Structure through Solvent Swelling. The next method used to modify the as-prepared SWCNT suspension was to swell the surfactant structure surrounding SWCNTs with immiscible organic solvents, such as carbon tetrachloride, benzene, *o*-dichlorobenzene (ODCB), and *p*-xylene (see Figure S9 in Supporting Information).[26,27] The intention was to probe the retention behavior with solvents that induce significant changes to the PL spectra of SWCNTs during swelling. It was previously observed that the PL intensity of most SWCNT types falls dramatically when SDS−SWCNTs are swelled with ODCB (see Figure 6a) and *p*-xylene (data not shown). In addition, large red-shifts are detected for those nanotubes whose PL intensity is not quenched. These observations indicate that dramatic changes in the immediate environment surrounding SWCNTs have taken place. After solvent evaporation, the PL intensity of the initial suspension in Figure 6a is recovered for the smallest diameter SWCNTs while the larger nanotubes (longer wavelength) show small PL intensity increases. Hence, swelling does not change the aggregation state of SWCNTs. In addition, the presence of the solvent alters the nature of the surfactant−SWCNT interface both before and after evaporation, resulting in changes to the buoyant density of SWCNTs (see Figure 6b−d). The quenching of PL intensity indicates that during swelling with ODCB the SWCNT surface is greatly exposed to the medium.[26] It is probable that small random surfactant domains form on the SWCNT surface where the orientation of SDS molecules changes while their packing density increases, resulting in a lower buoyant density for the SDS−SWCNTs.

Figure 7b shows the changes to retention behavior caused by swelling SDS−SWCNTs with ODCB. Note that the low amount of solvent in the SWCNT suspension upon swelling will not poison the agarose matrix. It is observed that the presence of ODCB greatly reduces the retention of SWCNTs by the agarose beads. The second peak of Figure 7b is decreased while the first peak is larger and sharper than the peak in Figure 7a. In this case, the retained SWCNTs in the second peak account for approximately 25% of all the nanotubes that are initially injected into the column. These values are substantially lower than the 62% retained in the control sample. According to the absorbance measurements, the nanotubes injected into the column are completely recovered. Once again, the absorbance spectra show that the nature of the nanotubes eluted in the second peak has not changed (see Figure S10 in Supporting Information). As shown in Table 1, suspensions modified with *p*-xylene not only have similar spectral changes to ODCB but identical retention characteristics as well. Similar to the results for salt-modified suspensions, a change in the surfactant structure of SWCNT by addition of either ODCB or *p*-xylene results in reduced retention on the agarose matrix. This result is striking because, despite *p*-xylene- and ODCB-swelled SWCNTs having their surface largely exposed, their retention is much lower than the initial suspension. This suggests that exposed sidewalls from a lack of surfactant are not the active adsorption sites. If these exposed regions constituted the active adsorption sites, increasing their amount would have increased retention.

Interestingly, SDS−SWCNT suspensions swelled with CCl_4 or benzene (data only shown in Table 1) show PL behavior different from that of *p*-xylene- and ODCB-swelled SWCNTs. Figure 6e shows the PL spectra from SWCNTs treated with CCl_4. Increases in intensity as well as blue-shifts in emission energy are observed for most SWCNT species. Once again, these changes indicate that the local environment around SWCNTs has been modified. While the spectra for ODCB-swelled SWCNTs largely returned to the initial spectra after evaporation of the solvent, the PL spectra for CCl_4-swelled SWCNTs remain more intense. The buoyant density of all CCl_4-modified

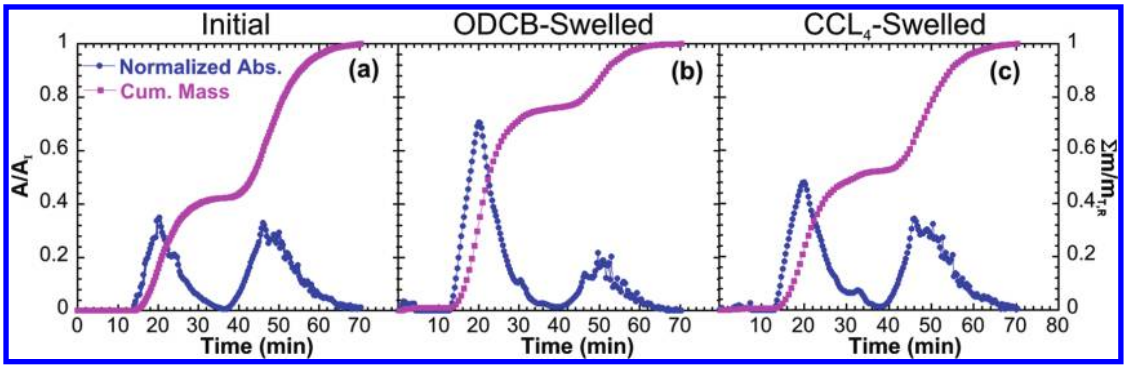

Figure 7. Retention behavior of ODCB- and CCl_4-modified SWCNT suspensions. Elution and cumulative mass curves for the (a) initial, (b) ODCB-swelled, and (c) CCl_4-swelled SWCNT suspensions.

SWCNTs decreases (see Figure 6f,g), confirming that the solvent alters the nature of the surfactant−SWCNT interface. It was previously speculated that the SDS molecules and solvents benzene and CCl_4 uniformly cover the SWCNT surface during swelling.[26] Contrary to the results with ODCB and *p*-xylene, the presence of CCl_4 or benzene only slightly reduces the extent of SWCNT retention on the agarose beads. Figure 7c shows the differences in the retention behavior. The elution and cumulative mass curves of CCl_4-swelled SWCNTs are similar to those of the 1 wt % SDS-suspended SWCNTs. However, as the first peak decays, there is a distinct peak around 30 min that does not appear in the control sample. The appearance of this peak is probably due to the elution of some nanotubes whose binding strength has been reduced and that otherwise would come out in the second peak. Therefore, the percentage of nanotubes coming out in the second peak is reduced from 60% to approximately 50% by swelling the hydrophobic core with either CCl_4 or benzene. The absorbance spectra from the CCl_4-swelled SWCNTs at different elution times shows that the selectivity has not been affected and the spectra look very similar to that of the control sample (see Figure S11 in Supporting Information).

Effect of Exposed Nanotube Surface on Retention Characteristics. The selective interaction and, consequently, the selective adsorption of SWCNTs onto the agarose matrix must be due to different surfactant morphologies on the surface of each SWCNT type. Although altering the surfactant structure through charge screening shows that the aggregation number affects retention, it does not eliminate the potential role that exposed sidewalls from a lack of surfactant may have in adsorption. As stated above, despite the significant amount of exposed nanotube surface, Figure 7b shows that the retention for ODCB-swelled suspensions is substantially lower than that for the pristine SDS−SWCNTs (approximately 24% vs 62%). Therefore, it can be argued that exposed regions on the nanotubes are not responsible for the strong interaction of SDS−SWCNT with the agarose matrix. To investigate this wissue further, column experiments were conducted with DNA-suspended SWCNTs. DNA-suspended SWCNTs are a good probe since it is known that the DNA assembly on SWCNTs leaves significant portions of the nanotube surface exposed to the medium. It is important to note that although the dispersion quality of DNA-suspended SWCNTs is high, their PL intensity is very low due to their considerable exposure to the suspending medium and, consequently, PL quenchers (see Figure S12 in Supporting Information).[5,33−35]

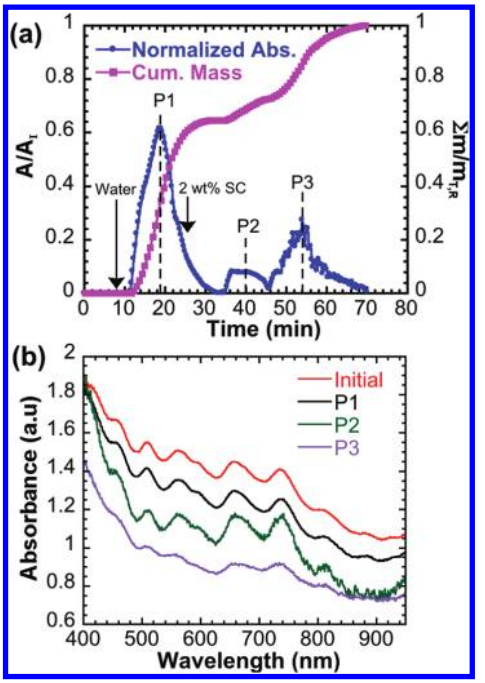

Figure 8. Retention behavior of SWCNTs suspended with DNA. (a) Elution and cumulative mass curves. (b) Absorbance spectra from the initial sample and the effluent at the first (P1), second (P2), and third (P3) peaks of the elution curve, which are shown as dashed lines in part (a). The SWCNT suspension is injected at time zero. The plot also shows the times at which the eluents, water, and 1 wt % SC, are injected.

The concentration of SWCNTs in this suspension was adjusted to match the absorbance of the SDS−SWCNT suspensions at 763 nm. Figure 8a shows the elution curve of the DNA-suspended SWCNTs. The absorbance spectra in Figure 8b shows that the retention of DNA-suspended SWCNTs is not selective since the peaks are similar. This result is not surprising since the DNA used in this work does not assemble differently on m- and s-SWCNTs. Most importantly, the retention in the column is lower for DNA-SWCNTs (approximately 30% vs 62% for SDS suspensions). The reduced retention indicates that the orientation of the surfactant rather than an exposed nanotube sidewall must be the dominant feature of adsorption. The lack of significant retention for either the ODCB-swelled or DNA-suspended SWCNTs as well as the effect of ionic strength on retention behavior

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strongly suggests that the orientation of the surfactant is the most critical parameter that determines selective adsorption.

Summarizing the Effect of Surfactant Structure on the Selective Interaction of s-SWCNTs with Agarose. By disrupting the retention process with GA, it has been demonstrated that selective adsorption is responsible for the selective retention of SWCNTs on the agarose matrix. The gradual transition from a structure with low aggregation number to one with higher packing density and the concomitant surfactant reorientation as NaCl is added to the initial SWCNT suspension suggests that surfactant orientation is the dominant factor in the adsorption process. In addition, modifying the surfactant structure around the SWCNTs by swelling with ODCB or *p*-xylene shows that the exposed regions on the surface of nanotubes are not the active adsorption sites. Performing experiments with DNA-coated SWCNTs, which have a highly exposed surface to the medium, further support this conclusion. The behavior of ODCB- and *p*-xylene-modified SWCNTs was contrasted with that of CCl_4- and benzene-swelled SWCNTs. These latter swelled systems, which form a uniform solvent—surfactant shell, show similar behavior to the initial SWCNT suspension.

Kataura et al. have correctly attributed the cause of separation to the selective interaction of s-SWCNTs with agarose.[11,12,36] However, they argued that the surface of s-SWCNT is partially covered by the SDS molecules, which in turn causes their stronger interaction with agarose due to electrostatic interactions or van der Waals forces.[11] In a more detailed study, Li et al. used thionine (dye) to track changes to the SDS molecules on the SWCNT surface. They concluded that during electrophoresis, s-SWCNTs are stripped of SDS molecules and consequently interact strongly with agarose through hydrophobic interactions. However, these results should not be extended to the case of elution chromatography due to the absence of electric fields.

On the basis of the experimental results shown above, we propose that the orientation of the surfactant is responsible for the selective adsorption of s-SWCNTs. This mechanism requires that differences in surfactant orientation are present in the initial as-prepared suspension. Although the theoretical surfactant concentrations used in prior simulations[28,29,37] cannot be directly translated to experimental concentrations, Xu et al. predicted that SDS molecules transition from lying flat on the SWCNT surface to lying perpendicular when their surface density changes from low to high.[29] On the basis of the differences in surfactant coverage between m- and s-SWCNTs described previously by Doorn et al.,[32] the m-SWCNTs are likely surrounded by a larger number of surfactant molecules. Therefore, extending the argument of Doorn and co-workers, we propose that s-SWCNTs in the initial suspension have a surfactant structure with the molecules lying flat on the sidewall of the SWCNTs while m-SWCNTs have the surfactant oriented away from the nanotube surface. Consequently, m- and s-SWCNTs will have weaker and stronger interactions with the agarose matrix, respectively, as depicted by the high and low aggregation number states in Figure 4. The weaker interactions for m-SWCNTs allow them to pass through the column while the s-SWCNTs are adsorbed. Once the eluent is changed to an SC solution, the SDS configuration on the SWCNTs is disrupted, altering the interaction between the SWCNTs and the agarose matrix. The SC molecules might also adsorb strongly to agarose and displace the adsorbed nanotubes.

CONCLUSIONS

It has been shown that selective adsorption rather than size-exclusion is responsible for the selective retention of SWCNTs on agarose beads. Moreover, the systematic modification of the surfactant shell enabled a study of the factors that determine adsorption of SWCNTs on the agarose matrix. For future work, it will be interesting to take a closer look at the forces that drive the adsorption of SWCNTs on the agarose matrix and to investigate the nature of the selectivity further. It should be noted that the observations presented above are not limited to agarose-based media. Recent work has shown that Sephacryl (cross-linked copolymer of allyl dextran and *N*,*N*′-methylene bisacrylamide) also provide selective adsorption of s-SWCNTs.[14,38] The insights provided in this article could potentially help to select chromatographic media different from agarose-based materials to improve the separation performance, operability, and overall cost.

ASSOCIATED CONTENT

Supporting Information. Experimental setup, calculation of cumulative mass curves, elution characteristics, and corresponding spectra for NaCl-, ODCB-, CCl_4-, and GA-modified SWCNT suspensions, elution curves for NaCl gradients, PL and absorbance spectra for SWCNT suspensions at different aggregation states, DNA-suspended SWCNTs and NaCl-modified SWCNTs, and images of centrifugation tubes after DGU for NaCl-modified SWCNTs. This information is available free of charge via the Internet at http://pubs.acs.org.

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