

Zeta-Potential Measurements of Surfactant-Wrapped Individual Single-Walled Carbon Nanotubes

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A systematic study of the zeta (ζ)-potential distribution of surfactant-wrapped individual single-walled carbon nanotubes (SWNTs) dissolved in water is presented here. The surface charge on the SWNT micelles, as measured by the ζ -potential, has implications for the stability of the dispersions and for the electrophoretic and dielectrophoretic assembly and alignment of SWNTs. Very highly charged SWNTs are obtained by dispersing the nanotubes in high concentrations of anionic and cationic surfactants, whereas almost neutral SWNTs are obtained by using non-ionic surfactants. The ζ -potential of the dissolved SWNTs is tuned by adjusting the surfactant concentration, the alkyl chain length of the surfactant molecule, and the solution pH in different surfactant–SWNT systems.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have attracted much attention in recent years due to their unique electronic, mechanical, and structural properties.^{1,2} Despite the remarkable potential of these nanoscale building blocks for applications in various fields, a number of challenges still need to be resolved. One major problem is the lack of control over the synthesis of nanotubes. Most available synthetic methods produce a mixture of different diameters and chiralities, which is a serious obstacle since the SWNTs can have widely varying properties depending on the chiral axis vector. Moreover, SWNTs tend to aggregate into bundles held together by strong van der Waals interactions, estimated to be ~ 500 eV per micrometer of tube–tube contact.³ This bundling strongly affects the electronic structure of the nanotubes and impedes separating them according to their diameter and chirality. To overcome this problem, several different approaches have been used to exfoliate the bundles into single tubes. The individualization of nanotubes by solubilizing them with surfactants in water is a particularly useful approach, because it does not destroy the electronic structure of the tube, as does covalent functionalization.³

The availability of individual tubes in solution has also helped to elucidate the physical properties of these structures.^{4,5} For example, the band gap fluorescence of semiconducting SWNTs is quenched by any metallic tubes in the bundle, and the individualization of SWNTs allows for the observation of this band gap fluorescence, which provides accurate spectroscopic assignment of the nanotube species.^{3,6} Moreover, the availability of individual nanotubes has enabled the chemical reactivity of different nanotube species to be studied as a function of the diameter and chirality.^{4,7} A method for the on-chip separation of SWNTs by chirality involves the use of AC dielectrophoresis,

which relies on the different polarizabilities of metallic and semiconducting SWNTs relative to that of water.⁸

Anionic surfactants such as sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (NaDDBS) are able to disperse nanotubes in high concentrations in aqueous solution. The initial model for surfactant wrapping of the nanotubes invoked the formation of cylindrical micelles around the tubes with the hydrocarbon chains arranged along the nanotube sidewalls.³ However, recent small-angle neutron scattering (SANS) experiments⁹ and density functional theory (DFT) calculations¹⁰ suggest the random and disordered adsorption of surfactant molecules on nanotube surfaces, which enables the dissolution of SWNTs in aqueous solution. Figure 1a shows a schematic depiction of the adsorption of SDS on the nanotube sidewalls. Adsorption is strongly dependent on surfactant structure, so while some of the surfactants used in this study are similar to SDS (NaDDBS and CTAB), the polymers used here (PMAOVE, Triton-X100, and the Pluronics) are quite different, so it is difficult to predict how these surfactants will interact with the nanotube.

The anionic surfactants are expected to impart a negative charge to the dispersed nanotubes. This negative charge leads to electrostatic repulsion between the surfactant molecules, and this stabilizes the nanotube colloids. The surface charge of the nanotubes has implications for the stability of the colloidal nanotube dispersions, the layer-by-layer assembly of nanotubes,¹¹ and the alignment and placement of nanotubes in electric fields by (DC) electrophoretic and (AC) dielectrophoretic processes.^{12,13} As an example of the former process, bundles of SWNTs have been deposited onto substrates as films by electrophoretic deposition in the presence of ionic salts, where the ionic salts are used as “chargers”.¹⁴

The dielectrophoretic force experienced by a nanotube in an AC electric field is

$$F_{\text{DEP}} = \frac{\pi d^2 l}{8} \text{Re} \left(\frac{\epsilon_t^* - \epsilon_m^*}{\epsilon_m^* + (\epsilon_t^* - \epsilon_m^*)L} \right) \nabla E^2 \quad (1)$$

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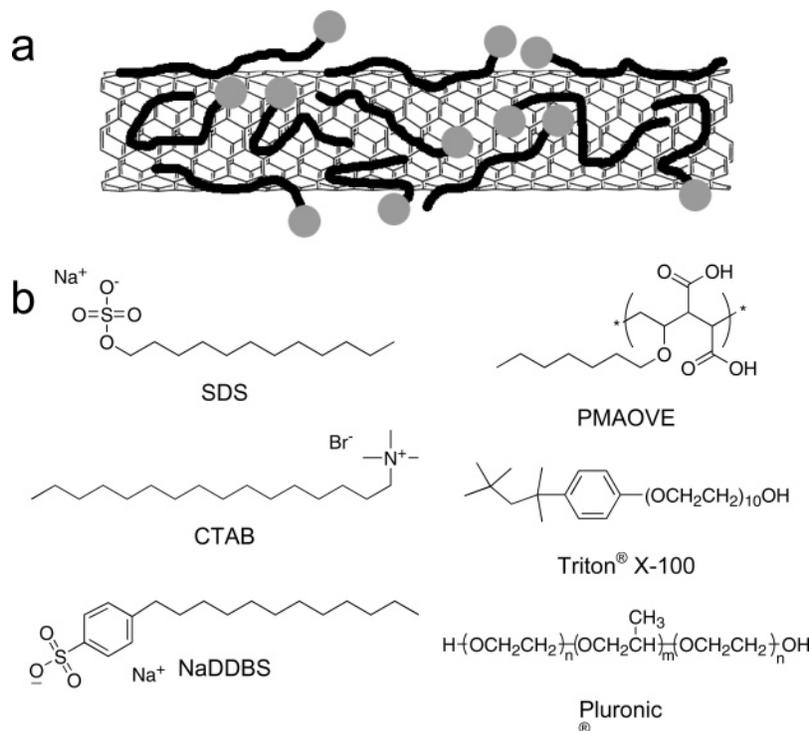


Figure 1. (a) Schematic depiction of the random and disordered adsorption of surfactant molecules onto the SWNT sidewalls. (b) Chemical structures of the surfactants and polymers used in this work.

where d and l are the diameter and length of the nanotube, L is the depolarization (geometric) factor, and ϵ_t^* and ϵ_m^* are the complex dielectric constants of the tube and medium, respectively, and can be written as

$$\epsilon_{t,m}^* = \epsilon_{t,m} - \frac{\sigma_{t,m}}{i\omega} \quad (2)$$

where ϵ_t and ϵ_m are the real dielectric constants of the tube and medium, respectively, and σ_t and σ_m are the conductivities of the tube and medium, respectively. If the nanotube micelle is approximated as a sphere, its conductivity, σ_p , is

$$\sigma_p = \sigma_{int} + \frac{2\lambda}{a} \quad (3)$$

where σ_{int} is the internal particle conductivity, λ is the surface conductance, and a is the diameter of the particle.¹⁵

The surface conductance term arises from the charged surfactants that form an electric double layer at the nanotube surfaces, which is similar to the phenomenon seen with latex beads and tobacco mosaic virus colloids.^{16,17} However, no direct measurements of the surface charge of surfactant-wrapped individual SWNTs have been reported so far. Here, we present a detailed study of the zeta (ζ)-potential of individual SWNTs solubilized by a variety of surfactants. We also show that the use of non-ionic surfactants, which solubilize SWNTs by steric stabilization rather than electrostatic repulsion, produces solutions of nearly neutral nanotubes. Better separation selectivity of metallic and semiconducting tubes is expected by dielectrophoresis for neutral SWNTs because the contribution from surface conductance is reduced. Consequently, separation is expected to be driven by the different real parts of the dielectric function, with $\epsilon_{\text{metallic-SWNTs}} \gg \epsilon_{\text{water}}$ and $\epsilon_{\text{semiconducting-SWNTs}} < \epsilon_{\text{water}}$.

In contrast, highly charged SWNTs are required for electrostatic assembly processes. Most electrostatic assembly tech-

niques make use of nitric acid-treated nanotubes, which have carboxylic acid groups on the ends and at defect sites of the SWNTs, leading to a negative surface charge. Mamedov et al. have used nitric acid-oxidized SWNTs with a ζ -potential of -80 mV to assemble a strong SWNT composite film via layer-by-layer assembly with polyelectrolytes.¹¹ Haddon and co-workers have found that the oxidation of SWNTs with nitric acid leads to the formation of amorphous carbon nanoparticulates. The nanoparticulates have a higher ζ -potential than the oxidized SWNTs at low pH values and thus form a more stable dispersion, enabling the purification of the SWNTs by centrifugation.¹⁸ The oxidized SWNT bundles had ζ -potentials ranging from -60 to -30 mV depending upon the pH. Noncovalent functionalization with surfactants, as used in this work, has the advantage of being less disruptive of the SWNT electronic structure, relative to covalent functionalization.

Oxidized multiwalled carbon nanotubes (MWNTs) have also been dispersed in aqueous solution using electrostatic charges induced by the formation of carboxylic acid groups.¹⁹ Other reports of dispersed MWNTs wrapped by polymers and surfactants indicate ζ -potential values of -40 to 10 mV for the dispersed nanotubes.²⁰ However, agglomeration is still observed among the MWNTs.

Here, we report a comprehensive study of the ζ -potential of individual SWNTs noncovalently wrapped by a variety of anionic, cationic, and non-ionic surfactants and polymers. Notably, we have obtained individual SWNTs with a ζ -potential as low as -97 mV, the most negative ζ -potential value observed for nanotubes,¹¹ as well as a stable SWNT solution with a ζ -potential of only -18 mV. It is worth noting that previous ζ -potential studies of nanotubes have focused on colloidal dispersions of bundled SWNTs,^{11,18,21} so the data presented here represent the first measurements of individual SWNT micelles.

2. Experimental Section

HiPCO SWNTs prepared by the high-pressure catalytic decomposition of CO were used for all the experiments.²²

Sodium dodecyl sulfate (SDS C-12) and Triton X-100 were obtained from Fluka, while sodium dodecylbenzene sulfonate (NaDDBS) was acquired from Aldrich. Hexadecyltrimethylammonium bromide (CTAB) and sodium tetradecyl sulfate (SDS C-14) were supplied by Eastman Kodak; sodium decyl sulfate (SDS C-10) was purchased from Acros; Dowfax 3B2, a proprietary disulfonate salt, was received from Dow; and various Pluronic surfactants with the structure (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)) were obtained from BASF and Aldrich. All surfactants were used as received except for SDS and NaDDBS, which were purified by recrystallization and washing with ethanol. (The purification procedure removed impurities, which give rise to a second peak in the SWNT ζ -potential curves.) The purity of SDS was confirmed by ^1H NMR spectroscopy. Poly(maleic acid/octyl vinyl ether) (PMAOVE) was provided by International Specialty Products, Inc., and it was hydrolyzed by a previously published procedure.²³ Figure 1b shows the chemical structures of the surfactants. In a typical noncovalent solubilization process, the SWNTs were dispersed in a 1 wt % aqueous solution of the surfactant by ultrasonication for 15 min using a Branson Sonifier sonicator. Deionized MilliQ water with a resistivity of $>18.2\text{ M}\Omega\text{-cm}$ was used to prepare all the solutions. The dispersion was then centrifuged at $100\,000g$ for 4.5 h to separate the bundles, amorphous carbon, and residual catalytic material from the single tubes. The supernatant was decanted and used for the optical and ζ -potential measurements. This supernatant was stable for several months, and the SWNTs remained individualized as determined by UV-vis-NIR and photoluminescence (PL) measurements.

Steady-state PL spectra were recorded on a Fluorolog-2 spectrometer (Jobin Yvon Inc.) using a near-IR-sensitive PMT detector (H9170-45; Hamamatsu). The excitation source was a diode laser (CQL784/D4; Philips; 22 mW; irradiation intensity, 35 mW/cm^2) emitting at 785.5 nm, powered by an LD1100 Constant Power Laser Driver (Thorlabs Inc.). Absorption spectra were recorded on a Cary 5000 UV-vis-NIR spectrophotometer. The pH of the solutions was tracked using an Accumet Basic AB15 pH meter. All the solutions were studied at their natural pH unless otherwise specified, in which case the pH was increased with NaOH.

ζ -Potential measurements were conducted on a Malvern Zetasizer NanoZS system with irradiation from a 632.8 nm He-Ne laser. The samples were filled in folded capillary cells and measured using a mixed mode method combining fast field reversal and slow field reversal, which eliminated electroosmotic effects. The ζ -potential was determined from the measured electrophoretic mobility, μ , using the Smoluchowski approximation:

$$\mu = \frac{\zeta\epsilon_m V}{4\pi\eta D} \quad (4)$$

where V is the applied voltage, η is the viscosity of the solution, ϵ_m is the dielectric constant of the medium, and D is the electrode separation. We have used the Smoluchowski equation even though it is rigorously valid only for spherical particles. The Smoluchowski approximation also assumes that the particle permittivity is much less than ϵ_m , which is true for semiconducting SWNTs but not for metallic SWNTs. O'Brien and Ward have extended this model to higher-aspect ratio structures taking into account the change in the ion densities induced by the applied electric field.²⁴ Depending on the magnitude of the ζ -potential, the spherical Smoluchowski approximation may overestimate the actual ζ -potential by up to 20%.

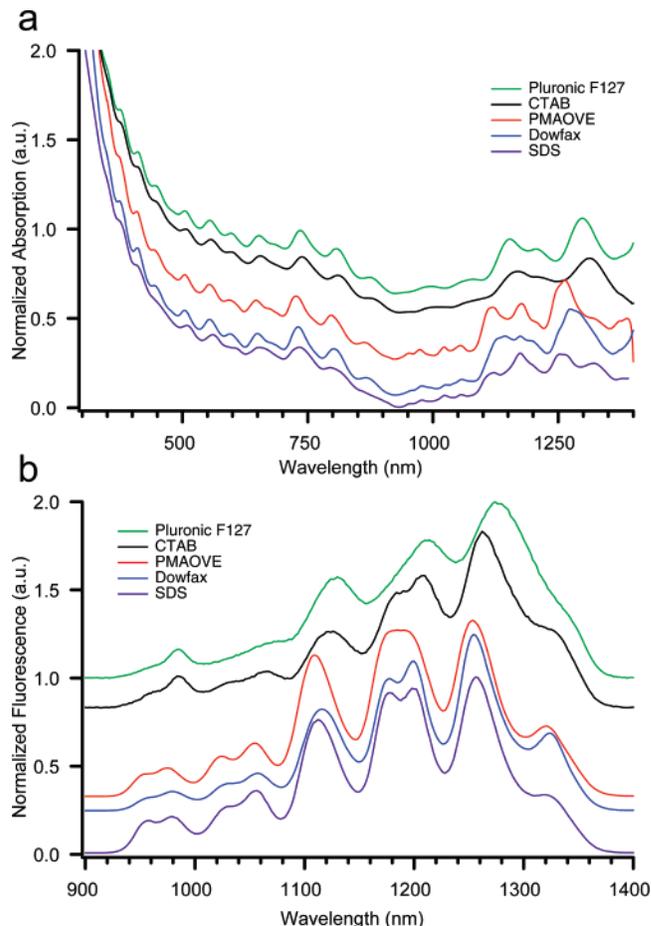


Figure 2. (a) UV-vis-NIR absorption spectra of SWNT solutions in F-127, CTAB, PMAOVE, Dowfax, and SDS. The surfactant concentration is 1 wt % in each case and used at the natural pH, except PMAOVE, which was increased to pH 5.0. The sharp features indicate the presence of individual SWNTs. (b) Corresponding PL spectra of the SWNT aqueous solutions, showing band gap fluorescence from individual semiconducting tubes.

3. Results and Discussion

Figure 2 shows the UV-vis-NIR absorption and PL spectra of the surfactant-wrapped tubes. The UV-vis-NIR spectra show sharp features corresponding to electronic transitions between the SWNT Van Hove singularities. The observation of pronounced spectral features suggests the presence of individual SWNTs in solution, since bundling would lead to a broadening of the absorption spectra.³ Additionally, the PL spectra of the SWNTs in Figure 2b further corroborate the presence of individual nanotubes in solution, because bundled SWNTs do not show band gap fluorescence due to quenching by metallic tubes.³ The sharp absorption features and the band gap fluorescence provide definitive evidence for the individualization of SWNTs by noncovalent functionalization.

Figure 3 and Table 1 show the ζ -potential distributions for SWNTs wrapped with different surfactants (1 wt % in all cases) at their natural pH. A combination of laser Doppler velocimetry and phase-analysis light scattering (PALS) allows the determination of the entire ζ -potential distribution for a given species. The SDS-, NaDDBS-, and Dowfax-wrapped SWNTs appear to be the most negatively charged. The SDS- and NaDDBS-wrapped tubes show relatively similar ζ -potential distributions, which is not surprising considering their closely related structures (Figure 1b). The ζ -potential values for SDS-, NaDDBS-, and Dowfax-wrapped nanotubes are among the highest observed

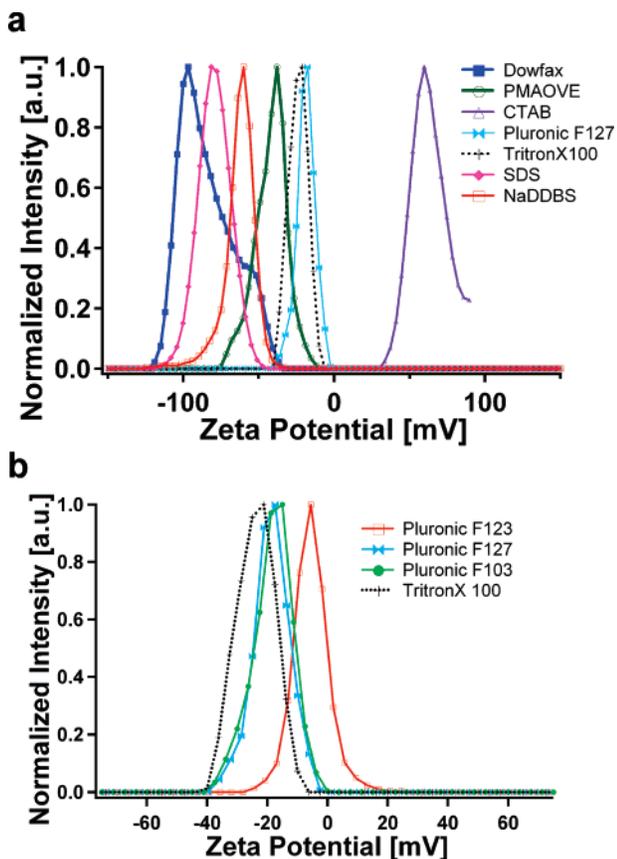


Figure 3. (a) The ζ -potential distribution curves for individualized SWNTs wrapped by anionic, non-ionic, and cationic surfactants. The surfactant concentration is 1 wt % in each case. (b) The ζ -potential distribution of individual SWNTs wrapped by non-ionic surfactants Triton X-100 and Pluronic F-127, P-123, and P-103.

TABLE 1: ζ -Potential Peak Maximum and fwhm of ζ -Potential Distribution for Aqueous Solutions of SWNTs in 1 wt % Surfactants. Gaussian Lineshapes Have Been Fitted to the Distribution Curves Shown in Figure 3

| surfactant | natural pH | concentration (value divided by CMC) | peak/s of ζ -potential distribution [mV] | fwhm of ζ -potential distribution [mV] |
|----------------|------------|--------------------------------------|--|--|
| CTAB | 4.1 | 30 ^a | +61.5 | 16.0 |
| Pluronic P-123 | 3.2 | 400 ^b | -5.8 | 6.7 |
| Pluronic P-103 | 6.4 | 14 ^b | -17.3 | 8.1 |
| Pluronic F-127 | 6.1 | 1.4 ^b | -18.4 | 7.6 |
| Triton X-100 | 5.8 | 67 ^b | -23.6 | 10.0 |
| PMAOVE | 3.1 | no CMC | -40.2 | 12.8 |
| SDS (C-12) | 6.3 | 4 ^a | -79.3 | 15.1 |
| SDS (C-10) | 7.4 | 1.3 ^a | -84.4 | 19.0 |
| SDS (C-14) | 5.5 | 15.5 ^a | -49.9 | 12.8 |
| NaDDBS | 7.4 | 100 ^a | -60.4 | 9.5 |
| Dowfax 3B2 | 5.9 | 83 ^b | -97.3 | 11.6 |
| | | | -75.9 | 36.0 |

^a CMC value from Pasupati et al.²⁹ ^b CMC value from Manufacturer.

for SWNTs. In addition to these anionic surfactants, the cationic surfactant CTAB was used, along with non-ionic surfactants, which are described below.

In all cases, the peaks exhibit broadening due to the presence of SWNTs with many diameters and chiralities in the solution, as well as the varying number of surfactant molecules on the surface of the tubes. All the measurements shown here were conducted at 25 °C. The magnitude of the electrophoretic mobility of the SDS–SWNT colloids increases monotonically

from 5 to 45 °C (see Supporting Information) due to a decrease in the viscosity of the solution. Temperature variation therefore can provide an additional degree of control over the electrophoretic mobility of the charged SWNT colloids.

The ζ -potential is often used as an index of the magnitude of electrostatic interaction between colloidal particles and is thus a measure of the colloidal stability of the solution. Particles with a ζ -potential less than -15 mV or more than 15 mV are expected to be stable from electrostatic considerations,²⁵ but particles with ζ -potentials between -15 and 15 mV can still be stable if they are stabilized sterically. Indeed, SDS and NaDDBS are among the most popular surfactants used for the nanotubes due to the high colloidal stability afforded by the high negative surface charge of these surfactants. The SDS, NaDDBS, and Dowfax dispersions of nanotubes are stable over several months without any flocculation of the tubes. A double-tailed biomimetic anionic surfactant, dioctyl sodium sulfosuccinate (AOT), also yields stable solutions of SWNTs in water. The AOT-wrapped SWNTs have a relatively broad ζ -potential distribution with a peak at -65.6 mV.²⁶ A cationic surfactant, CTAB, has also been used to disperse the SWNTs.¹⁵ SWNTs covered by CTAB display a ζ -potential of 61.5 mV, and they are stable for several months.

Figure 3, parts a and b, also shows the ζ -potential distributions of SWNTs wrapped by two types of non-ionic surfactants, Pluronic and Triton X-100. The non-ionic surfactants stabilize the nanotubes in solution primarily by steric and not electrostatic interactions. Pluronic is a type of block copolymer of poly(ethylene oxide) and poly(propylene oxide). Different domains of the polymer likely orient themselves in energy-minimized conformations around the nanotubes. The nanotube dispersions in Triton X-100 and Pluronic are also stable over several months. SWNTs wrapped by Pluronic F-127 show a ζ -potential of only -18 mV. (The other pluronics gave more neutral potentials, but led to lower concentrations of nanotubes in solution.) Previous attempts at obtaining neutral (or nearly neutral) SWNT micelles have involved mixing together negatively charged SDS-wrapped tubes and positively charged CTAB-wrapped tubes.¹⁵ It was proposed that the mixing of SDS and CTAB nanotube micelles would result in the formation of large-diameter vesicles and surfactant crystallites, as was previously observed for mixtures of CTAB and SDS in the absence of SWNTs.²⁷ These vesicles would encapsulate the nanotubes to provide stable solutions due to reduced electrostatic repulsion.¹⁵ This picture may not be entirely reasonable given that the SWNTs are not encapsulated in micelles but instead are dissolved by randomly adsorbed SDS and CTAB species.^{9,10} Furthermore, our ζ -potential experiments indicate that SWNTs wrapped in 1 wt % SDS or CTAB may not have identical charge magnitudes and thus complete neutralization of the charges is unlikely when they are mixed in a 1:1 ratio if adsorption of each were equally probable. Our experiments indicate that the SWNTs have a strong preference to bind SDS rather than CTAB; when SDS is added to a solution of CTAB-wrapped nanotubes, the nanotubes become negatively charged with ζ -potential values of -60 mV even for a SDS/CTAB ratio of 1:2. We note that our findings differ from those of Baik et al.,¹⁵ possibly because of differences in the preparation method. We followed the same preparation procedure here as in the other experiments reported (and did not centrifuge the sample after mixing, as in ref 15). In contrast, wrapping with non-ionic surfactants is seen to be an excellent approach for obtaining nearly neutral tubes.

We have also investigated the ζ -potential of two different surfactant–nanotube systems in more detail: SDS-wrapped

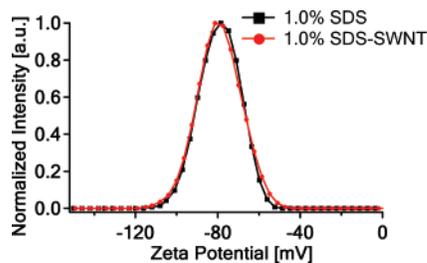


Figure 4. The ζ -potential distribution of SDS-wrapped SWNTs and SDS micelles by themselves without any SWNTs. The SDS concentration is 1 wt % in both cases.

SWNTs, because they are commonly used for spectroscopic characterization and dielectrophoresis,^{3,9} and PMAOVE-wrapped SWNTs, because they provide a stable dispersion over a wide range of pH and temperatures.²⁸

Upon addition of SWNTs to the SDS solution, there is a slight negative shift in the ζ -potential (Figure 4). The ζ -potential distributions are however quite similar with and without the addition of SWNTs. It is likely that at SDS concentrations far above the critical micelle concentration (CMC),²⁵ different shapes of micelles are present; this may lead to the relatively broad lineshapes observed. As mentioned before, the situation is far more complex for SWNTs solubilized by these surfactants since well-defined micelle structures are not formed on the surface of the nanotube. Table 1 shows the correlation of the surfactant concentrations used to the CMC for the different surfactants studied here.²⁹

By increasing the SDS concentration we can adjust the charge on the SWNTs to a desired negative value. Figure 5a shows the variation of the ζ -potential distribution of SDS-solubilized nanotubes with SDS concentration. With increasing amounts of SDS, more SDS is adsorbed onto the nanotube sidewalls, and therefore the nanotubes become more negative until a value of about -80.3 mV is reached at 1.5% SDS concentration. Note that at 0.1 wt % of SDS, there are no SDS micelles in solution because the concentration is below the CMC, and thus the observed signal arises solely from the scattering from SDS-wrapped SWNT colloids. Thus the ζ -potential distributions observed here are likely to arise primarily from the surfactant-wrapped nanotube species (as depicted in Figure 1a). Figure 5b plots the conductivity of the nanotube solution as a function of the SDS concentration. The conductivity monotonically increases with the surfactant concentration as would be expected from the increased presence of ionic species (both surfactant molecules and cut SWNTs). The 1.5 wt % SDS-wrapped SWNTs is the most negatively charged system studied in this sequence, with a ζ -potential as low as -80 mV.

To verify the generalizability of these results, we have also dispersed SWNTs in 0.1 wt % solutions of the surfactants depicted in Figure 3a (Figure 6). Notably, we are able to obtain stable solutions of individualized SWNTs even at these low surfactant concentrations. As observed for SDS, the magnitude of the ζ -potential of the surfactant-wrapped SWNTs tend to be slightly lower at these surfactant concentrations than for the 1% solutions (except for CTAB which shows a similar ζ -potential for both 0.1 and 1 wt % solutions). The general similarity of the results for the 0.1 and 1 wt % solutions suggests that, at most, a small part of the scattering signal used to determine the ζ -potentials comes from the surfactant micelles.

The ζ -potential distributions for high concentrations of SDS (C-12)-wrapped SWNTs and similarly for its C-10 and C-14 analogs are shown in Figure 7. A shorter alkyl chain leads to the adsorption of a greater number of molecules on the SWNTs,

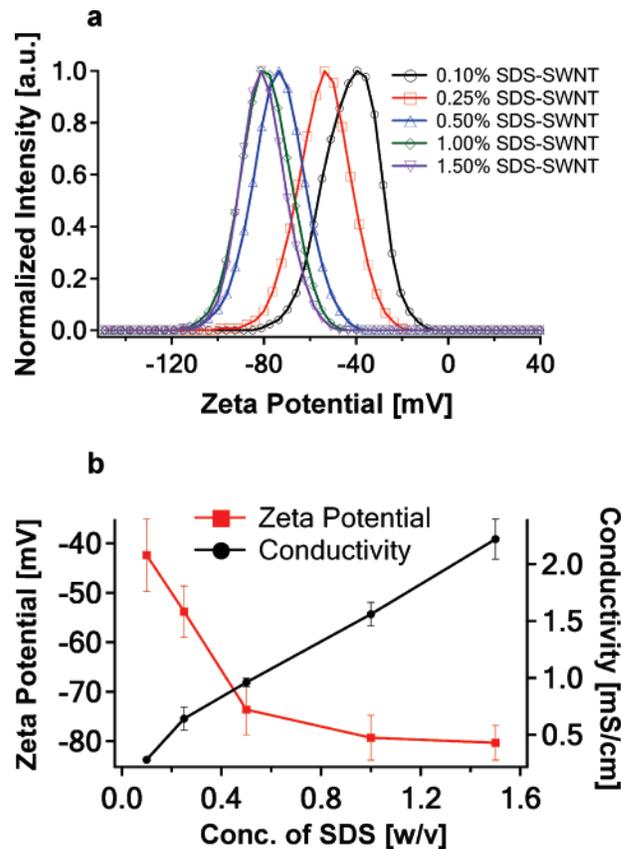


Figure 5. (a) The ζ -potential distribution of SDS-wrapped SWNTs for different SDS concentrations. (b) Plot of the peak maximum of the ζ -potential distribution and the conductivity of the surfactant-wrapped SWNT solutions versus the SDS concentration.

due to steric packing at high concentrations, which is reflected as a more negative ζ -potential. The C-18 analog was found to be too insoluble in water to be studied. The packing of the surfactants on the SWNT sidewalls and thus the net charge of the colloid can be tuned by varying the chain length of the alkyl chain.

Aqueous suspensions of PMAOVE-wrapped SWNTs are extremely robust and can withstand temperatures up to 97 °C and pH conditions ranging from 3 to 12 without any observed flocculation.²⁸ The structure of PMAOVE is shown in Figure 1b. The octyl side chains of the polymer form intramolecular hydrophobic domains, whereas the acid groups form an interface with water, thereby imparting water solubility.³⁰ As with conventional micelles, it is expected that the hydrophobic side chains associate with the SWNTs, whereas the acid group interacts with the bulk aqueous phase.²⁸ Figure 8a tracks the ζ -potential of the PMAOVE-dispersed SWNTs as a function of the pH. The ζ -potential becomes more negative with increasing pH until a neutral pH is reached and then starts to increase again. The increase in the magnitude of the ζ -potential with pH increasing from 2 to 7 can be explained by the ionization of the COOH groups on the PMAOVE. Fluorescence experiments using pyrene as a model for SWNTs indicate that at low pH the hydrophobic domains are tightly packed and the polymer is tightly coiled.²³ As depicted in Figure 8b, several polymer segments likely form clumps on the SWNTs; the pendant COOH groups at the interface with the aqueous phase help to solubilize the nanotubes. As the pH increases, the COOH groups start to ionize and thus the ζ -potential becomes more negative. However, the ionization of the COOH groups on the polymer backbone is also accompanied by the stretching and

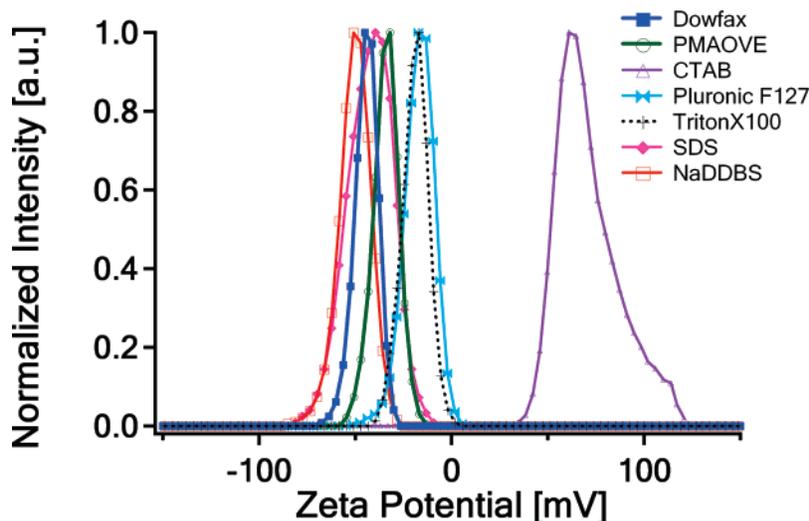


Figure 6. The ζ -potential distribution curves for individualized SWNTs wrapped by anionic, non-ionic, and cationic surfactants. The surfactant concentration is 0.1 wt % in each case.

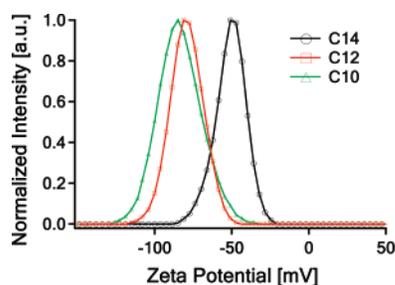


Figure 7. The ζ -potential distribution as a function of the chain length for sodium alkyl sulfates with 10, 12, and 14 carbon atoms in the hydrocarbon chain. The surfactant concentration is 1 wt % in each case.

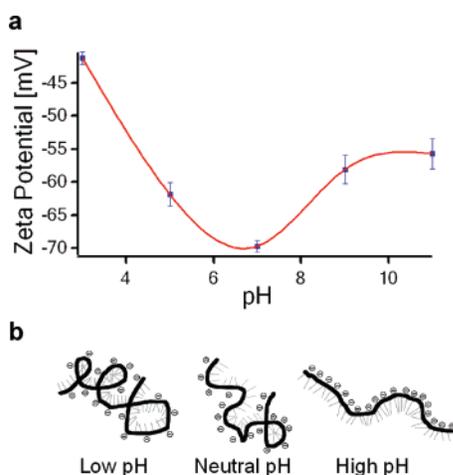


Figure 8. (a) Plot of the ζ -potential peak maximum of PMAOVE SWNTs as a function of the pH. (b) Schematic depiction of conformational changes in PMAOVE.

swelling of the nanodomains.²³ The uncoiling of the polymer eventually results in fewer polymer segments wrapping around the entire tube (at high pH), instead of numerous tightly packed clumps dotting the SWNT sidewalls (at low pH). As a result, the ζ -potential of the SWNTs shifts to less negative values since the absolute number of ionic groups present on the tubes decreases. A schematic is shown in Figure 8b, depicting the changes in the polymer conformation with pH. Thus the ζ -potential of these PMAOVE-wrapped nanotubes can be tuned to some extent by varying the pH.

4. Conclusions

We present here a systematic ζ -potential study of individual SWNTs wrapped by different surfactants. Noncovalent functionalization with surfactants and polymers is nondestructive and does not damage the electronic structure of the SWNTs, while providing stable dispersions of individual nanotubes in solution. The ζ -potential is a good measure of colloidal stability, and thus different ionic surfactants can be evaluated for their ability to stabilize SWNTs in solution. (Because some of the solutions studied here are not truly micellar solutions, we are currently studying the critical coagulation concentration (CCC) of these surfactant-wrapped SWNT solutions, which will provide a more quantitative estimate of the long-term stability of these systems.) Very highly charged tubes with ζ -potential values of roughly -95 mV are obtained by wrapping with high concentrations of anionic surfactants such as Dowfax. Positively charged SWNTs are obtained by wrapping with the cationic surfactant CTAB. SWNTs wrapped with SDS have been studied in some detail. The ζ -potential distribution can be tuned by changing the surfactant concentration and alkyl chain length of the anionic alkyl sulfate surfactants. These highly charged SWNTs may be useful for fabricating assemblies by electrostatic interactions and for the electrophoretic deposition of SWNT films.^{11,14} Nearly neutral tubes are also obtained by wrapping SWNTs with non-ionic surfactants such as Pluronic F-127 and Triton X-100. Such SWNTs may be useful for obtaining better selectivity between metallic and semiconducting SWNTs during the dielectrophoretic separation and alignment of individual SWNTs in electrode geometries.^{13,15} Studies of the separation of tubes by varying the surface conductance are currently underway. The robust PMAOVE-wrapped SWNT system has also been explored. The ζ -potential of these polymer-wrapped SWNTs can be tuned by simply varying the pH of the solution, which induces changes in the conformation of the polymer.

The data presented here are the first ζ -potential measurements of individualized SWNTs and will be useful in understanding the electric double layer effects at the SWNT–surfactant interface, which can be used as a handle to assemble the SWNTs in different hierarchical architectures.

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Supporting Information Available: Temperature dependence of the electrophoretic mobility. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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