Activated Complex Model and Surfactant Reorganization during SWCNT Separations on Hydrogels

Adam B. Phillips and Michael J. Heben^{*}

Wright Center for Photovoltaics Innovation and Commercialization, Department of Physics and Astronomy, School of Solar and Advanced Renewable Energy, University of Toledo, Toledo, Ohio 43606, USA

^{*}Corresponding author. Email: Michael.Heben@utoledo.edu

Abstract

Hydrogels can efficiently separate metallic and semiconducting single-wall carbon nanotube (SWCNT) species at high rates by selective adsorption in a column configuration, but mechanistic details remain unclear. We examined the temperature dependence of SWCNT adsorption in an operating column using a model that considers the formation of an activated complex. The enthalpy and entropy changes associated with formation of the activated complex were determined. Due to a high sensitivity to protonation doping, large diameter pulsed laser vaporization tubes provided an opportunity to probe details of the adsorption mechanism. In contrast to the prevailing view in the literature, we conclude that the surfactant environment surrounding the nanotube is substantially reorganized upon adsorption and that adsorption also occurs within gel pores. Our findings provide new mechanistic insights that should assist in the development of improved separation methods.

1. Introduction

The potential impact of carbon single-walled nanotubes (SWCNTs) in a variety of technologies depends on ready access to tubes of a single electronic structure. Unfortunately, SWCNT syntheses produce a mixture of semiconducting (s-SWCNT) and metallic species (m-SWCNTs) in a range of diameters and chiralities. Advances in synthesis are reducing the polydispersity of the as-produced materials,[1, 2] but there is still a great need for scalable methods that can efficiently produce large quantities of SWCNTs with specific (n,m) indices. Early separation efforts attempted to selectively destroy the metallic species.[3, 4] More recently, the use of polymeric wrappers has allowed s-SWCNTs to be quantitatively obtained[5, 6] at purities greater than 99.95%.[7] Polymer wrapped s-SWCNTs have been used to fabricate transistors[7, 8] and solar cells[9] with promising results, but organic solvents are required for the separations and the wrapping polymers are expensive and difficult to remove due to relatively strong binding. The latter is significant because any remaining polymer can adversely impact device performance.[10]

Processing in aqueous solutions with loosely bound, inexpensive surfactants can afford environmentally friendly, low-cost routes to chirality-pure, solid-state samples that are not contaminated with other species. The first widely successful approach for aqueous solutions, density gradient ultracentrifugation (DGU),[11] exploited differences in buoyancy between surfactant-suspended SWCNT species. The subtle differences in surfactant packing density and adsorption interactions depend on many parameters including the chemical structure of the surfactants and the surfactant ratios,[11] pH,[11] temperature,[12] and the ionic strength of the solution.[13] With careful optimization, s-SWCNT[14] and m-SWCNT[15] solutions with >99% purity can be obtained. DGU separated SWCNTs have been used in a wide variety of device and photophysical studies.[14, 16-18] Unfortunately, DGU is an inherently small-batch process.

Two aqueous phase separation methods that use relatively inexpensive components and have the potential to scale-up have recently been presented. In the aqueous two-phase (ATP) process,[19] SWCNTs are dispersed in sodium cholate (SC) and added to an aqueous mixture of dextran, polyethylene glycol (PEG), and sodium dodecyl sulfate (SDS). Once equilibrated, the solution separates into a high density phase comprised of PEG and s-SWCNTs and a lower density phase containing dextran and m-SWCNTs. This process can be repeated to improve the quality of separation, and >99.0% s-SWCNT purity has been obtained after two iterations.[19]

As with DGU, the interplay between relevant parameters affects the quality of the separations.[19-21] Though capable of producing high purity s-SWCNT solutions in larger quantities than is possible by DGU, the ATP method is also a batch process with limited throughput.

Column chromatography is a second aqueous separation method that is being extensively studied due to an excellent combination of high separation efficiency and high throughput. s-SWCNT purities >99.9% have been demonstrated,[22] as has chiral enrichment of specific (n,m) species.[23, 24] Importantly, the technique has the potential for continuous operation.[22] Separations are performed by introducing a solution of SDS-dispersed SWCNTs into a column filled with agarose beads or other similar hydrogel medium.[25, 26] As the mobile phase moves through the column, s-SWCNTs selectively interact and adsorb onto the stationary gel phase while the m-SWCNTs remain in solution and are collected in the first eluent (E1). A second solution containing a surfactant that has a greater affinity for s-SWCNTs, such as sodium deoxycholate (DOC), is then introduced into the column. The previously adsorbed tubes are resuspended by the DOC solution as it moves through the column. This fraction is collected as a second eluent (E2).

Though hydrogel-based separations are highly effective, there is considerable debate on the underlying mechanisms. For example, Flavel *et al.* concluded that the surfactants which organized around m-SWCNTs and larger diameter s-SWCNTs at reduced pH were converted to alcohols that inhibited interactions with the column.[24] In contrast, Hirano *et al.* suggested that O₂ absorption caused SWCNTs to remain in E1.[27] Clar *et al.* concluded that only the surfaces of the beads were accessible, and explored the potential role for van der Waals, ionic, hydrophobic, π - π , and ion-dipole interactions.[28] Studies have also been performed to evaluate the effects of gel[22, 29] and electrolyte concentrations,[30] and surfactant selection for transferring the s-SWCNTs into E2.[25] SDS concentration[31] and pH[24, 32] have also been investigated for separating relatively small diameter HiPco SWCNTs according to their (n,m) indices. Tvrdy *et al.* reported HiPco SWCNT adsorption on Sephacryl as a kinetically-driven selective adsorption process that was well-described by irreversible first-order site association kinetics with a single rate constant for each (n,m) species.[33] Larger diameter SWCNTs produced by pulsed laser vaporization (PLV) and arc discharge has been separated with column chromatography as well,[22, 26] but (n,m) separation has proven to be difficult[23] due to the

comparatively larger number of species per radius increment. Significant work remains to develop a more detail understanding of the mechanisms, especially if the goal is to develop improved approaches for larger diameter tubes that offer promise in photonics, electronics, and solar energy applications.[34, 35]

Experiments in which the separation temperature was varied have shown that the quality of separation can be enhanced. Lui et al. exploited the temperature variation in SDS coverage for differing C-C bond curvatures to obtain single-chirality separation of small diameter HiPco SWCNTs using a dextran-based column.[36] The separation efficiency was extremely sensitive to column temperature and surfactant concentration. More recently, Yahya et al. reported separation results for a large range of SWCNT diameters using temperature variation and an agarose column.[37] They attributed the ability to separate SWCNTs by electronic type to differences in SDS orientation around the SWCNT species, and also concluded that separation occurs at the surfaces of the agarose beads.

Underlying the results and interpretation to date are the thermodynamics associated with the interactions between the surfactant-suspended SWCNTs in solution and the stationary hydrogel column material. Very few reports have directly addressed this topic and, to our knowledge, none have addressed these issues in an operating column or with PLV SWCNTs. Hirano et al. incubated SDS-suspended HiPco SWCNTs with two different hydrogels, agarose and Sephacryl, over long periods of time and measured the adsorption equilibria as a function of temperature.[38] Under the assumption of Langmuir adsorption, a van't Hoff plot was constructed from which the standard Gibbs free energy for adsorption was evaluated for both m- and s-SWCNTs. Surprisingly, the selective adsorption of s-SWCNTs onto the hydrogel was determined to be an entropy-driven process, which suggests a complex interaction between the SWCNTs, surfactant, and hydrogel in the system.

In this contribution, we analyze the temperature dependence of the adsorption process in an operating column using large diameter PLV tubes and agarose as a separation medium. Our analysis is done from a new perspective and includes thermodynamic and kinetic aspects of the separation process by postulating that adsorption occurs via the formation of an activated complex. Like other studies, our methods cannot completely discriminate between the specific types of interactions that are possible when SDS stabilized SWCNTs adsorb on the stationary hydrogel (*vide supra*), but the approach allows the role of surfactant reorganization and

desorption to be evaluated. Consequently, the results shed new light on the fundamental mechanisms that control the column separation process.

2. Methods and Materials

PLV SWCNTs were synthesized using a modified laser vaporization process[39] and purified by refluxing in 4 M nitric acid for 24 hours, collecting the solids by filtration, and heating the resulting paper at 900 °C in slowly flowing CO₂. Four milligrams of the purified SWCNT were probe sonicated in 40 mL of 1% (0.01 g/mL, or 35 mM) SDS (>99.0%, P212121, Inc.) using a ¼” probe tip at 15-25% power (100% amplitude, Fisher 550 Sonic Dismembrator) for 10 minutes. The sonicated solution was spun at 141,000 g for 4 hours to remove bundles from the solution. The average SWCNT length was taken to be ~800 nm based on previous experience with materials that were synthesized and processed identically.[40] The top 80% of the spun solution was decanted and used for separation experiments.

Sepharose 2B (GE Healthcare, Sigma Aldrich), shipped in ethanol, was used as the column material for all studies. Columns were prepared by filling a 10 mL disposable syringe (14 mm inner diameter) with 10 mL of the as-received sepharose solution. The ethanol was removed by rinsing with at least 20 mL of D₂O or H₂O. Experiments were performed with a 4 mL aliquot of 1% SDS/SWCNT solution that was introduced and rinsed through the column with 10 mL of 1% SDS. The first eluent (E1) was collected and analyzed by linear absorption spectroscopy (*vide infra*). The SWCNTs bound to the stationary gel phase were subsequently freed from the column by introducing 10 mL of 2% sodium deoxycholate solution (DOC; BioUltra, Sigma Aldrich). This second eluent (E2) was also collected and analyzed. A cotton plug in the tip of the syringe produced a column elution rate of approximately 0.1 mL/min.

The column temperature was controlled between 18.9 and 50 °C using a customized wine chiller (Wine Enthusiast, 12 bottle model). Temperatures above ambient (22 to 50 °C) were obtained by reversing the polarity of the voltage applied to the thermoelectric cooler. The temperature was controlled with an Omega CN7800 temperature controller. Absorption spectra were obtained between 1850 and 350 nm using a Perkin Elmer 1050 spectrophotometer and 10 mm quartz cuvettes.

3. Results and Discussion

To quantify the separation efficiency at each temperature, we determined the change in the concentration of s- and m-SWCNTs relative to their natural concentrations in unseparated samples. The above baseline area for the second optical transitions for the s-SWCNTs (S2) and the first optical transitions for the m-SWCNTs (M1) was assessed from absorption spectroscopy measurements (see Supplementary Material) following the well-accepted approach of Itkis et al.[41] A full accounting of all nanotubes during column separation was achieved by assessing the total mass of SWCNTs in the column. The total mass for the s- and m-SWCNT species was determined by summing the above baseline S2 and M1 areas after multiplying by the published extinction coefficients.[41] With knowledge of the total amount of SWCNTs and the m/s ratio in each sample, the mass balance for SWCNTs introduced to the column could be expressed as:

$$i\text{-SWCNT}_{\text{tot}} = i\text{-SWCNT}_{\text{free}} + i\text{-SWCNT}_{\text{ads}} + i\text{-SWCNT}_{\text{irr}} \text{ (for } i = m \text{ or } s) \quad (1)$$

Here, $i\text{-SWCNT}_{\text{tot}}$ is the total amount of m- or s-SWCNT introduced into the column ($i = m$ or s), $i\text{-SWCNT}_{\text{free}}$ is the amount of m- or s-SWCNTs collected in E1, $i\text{-SWCNT}_{\text{ads}}$ is the amount of m- or s-SWCNTs collected in E2, and $i\text{-SWCNT}_{\text{irr}}$ is the mass of introduced m- or s-SWCNTs that are irreversibly adsorbed and retained on the column after passage of both E1 and E2.

Figure 1 shows the SWCNT accounting data for experiments performed at six different temperatures (See Supplementary Material for the absorption spectra). The ratio of m- to s-SWCNTs in both the E1 and E2 eluents is shown in separate bars at each temperature. The dark line in each bar at 33% of the bar height marks the natural m-SWCNT content for PLV SWCNTs, and the difference between the red/blue boundary and this line indicates the effectiveness of the separation at the specific temperature. The sum of the total SWCNT mass in both E1 and E2 fractions is the amount of SWCNTs recovered during the separation, and is shown as a red horizontal line for each temperature. The difference between this value and 100% is the fraction of introduced SWCNT mass that is irreversibly retained by the column (i.e. $m\text{-SWCNT}_{\text{irr}} + s\text{-SWCNT}_{\text{irr}}$).

Figure 1. Fractions of SWCNTs in E1 and E2 as a function of temperature. The blue and red parts of each bar represent the m-SWCNT and s-SWCNT fractions, respectively. The thick black line within each bar is at the as-synthesized ratio of m- and s-SWCNTs (1:2). The distance between the blue/red boundary and the line marking the as-synthesized ratio indicates the effectiveness of the separation. The thick red lines for each temperature at the top of the figure indicate the total fraction of SWCNTs that were collected in E1 + E2. The difference between this line and 100% represents the amount of SWCNTs that were irreversibly retained by the column.

With the data presented in this way, we can examine the temperature dependence of the separation process. At 18.9 °C, for example, nearly all the tubes introduced to the column are collected in either E1 or E2, with a roughly equal amount found in each eluent. At this temperature, E1 contains most of m-SWCNTs that were introduced. The m-SWCNT purity in E1 was fairly low at ~60%, but was significantly enhanced over the as-synthesized m-SWCNT concentration of ~33%. In contrast, E2 is comprised of ~95% s-SWCNTs.

With increasing temperature, the total mass of SWCNTs in E1 decreases while the total mass in E2 and the irreversibly retained mass increase. Thus, the amount of SWCNTs transferred from the mobile, E1, phase to the adsorbed, E2, phase increases with temperature. At 39.8 °C, very few tubes pass through the column and are collected in E1, ~95% of the collected SWCNTs are in E2, and a large fraction of the total SWCNTs introduced (~30%) are trapped in the column. The increase in the mass of SWCNTs in E2 at the higher temperatures is also

accompanied by a reduction in the separation efficiency. The ratio between s- and m-SWCNTs at 39.8 C in both E1 and E2 approaches that of as-synthesized materials. Note that the composition of the irreversibly bound m- and s-SWCNTs must also approach 1:2, indicating that widespread bundling becomes dominant and thwarts separation as the temperature is increased. Interestingly, the fraction of irrecoverable SWCNTs begins to grow at the temperature at which the m-SWCNT purity in E1 peaks.

The increase in SWCNT adsorption on the column with increasing temperature indicates that at least one of the mechanistic steps is thermally activated. Previous measurements of the temperature dependence of photoluminescence (PL) quenching in SDS stabilized SWCNT dispersions indicated that surfactant desorption was the rate-limiting step in bundle formation.[42] In that work, surfactant stabilized solutions were diluted to reduce the surfactant concentration below a critical value and the PL was quenched in a first order process. Measurements as a function of temperature allowed the activation energies for desorption to be determined by an Arrhenius analysis. Due to similarities in the temperature dependence observed for uptake of s-SWCNTs by the column, it is reasonable to consider that SDS desorption also plays a role in SWCNT adsorption on agarose.

To develop a deeper understanding of the process, we constructed a simple reaction model for SWCNT/gel interactions with steps as shown in Figure 2. The model assumes separate, non-interacting equilibria for both s- and m-SWCNTs as the 1% SWCNT/SDS solution moves through the column. Thus, in contrast to studies that assumed that the SDS surfactant sheath remains essentially intact,[27, 30, 37] our model specifically considers that the surfactant sheath is altered to allow specific SWCNTs to intimately interact with and adsorb on the column material. Consequently, partial surfactant desorption is explicitly considered as an elementary step (Step 1, Figure 2). Once the surfactant is sufficiently desorbed/reorganized, a second elementary step is the localization/adsorption of the SWCNT onto unoccupied adsorption sites on the agarose gel (Step 2, Figure 2). Note that we are not considering that SWCNTs are actually devoid of surfactant and still stable in solution. Instead, the “activated” SWCNT shown on the right side of Step 1 and left side of Step 2 schematically represents the existence of a transient, reactive intermediate, i.e., an activated complex, that involves a SWCNT species that may transition into an adsorbed state. Combining Steps 1 and 2 yields the overall process for adsorption on the column, Reaction 1, where separate reactions are considered for m- and s-

SWCNTs. Not shown is an additional step that could occur in the system; the bundling and precipitation of such activated species. This step was explored previously for SWCNT dispersions in bulk solution,[42] and begins to dominate at the higher temperatures. In the presence of the hydrogel column, however, activated SWCNTs may be selectively adsorbed prior to bundling.

Figure 2. Schematic diagram of the overall reaction associated with the SWCNT adsorption on the column (Reaction 1). Reaction 1 is comprised of two steps. Step 1 shows surfactant desorption from SWCNTs. Step 2 shows SWCNT adsorption on available agarose sites. The unsheathed SWCNT on the product side of Step 1 and reactant side of Step 2 is considered to be the activated complex.

The activated complex is considered to be the surfactant-depleted SWCNT species that may interact with energy preferred adsorption sites on the agarose gel via some unspecified binding mechanism. Note that one need not discriminate between possible binding mechanisms[28] in order to take this step in the analysis. As for any reaction that requires reorganization of species to form an activated complex, we can assume the existence of a potential energy barrier. If the barrier is not surmounted, the activated complex will relax back to the reactant side of the process, as expected for a dynamic equilibrium.

The equilibrium constant for Reaction 1 may be written as:

$$K_i = [i\text{-SWCNT}_{\text{ads}}] [i\text{-SDS}] / [i\text{-SWCNT}_{\text{free}}] [i\text{-OSites}] \quad (2)$$

Here, K_i is the equilibrium constant for either m- or s-SWCNTs, for $i = m$ or s , respectively, $[i\text{-SDS}]$ is the concentration of SDS liberated by the reaction, $[i\text{-OSites}]$ is the concentration of open (i.e. unoccupied) sites for i -SWCNT adsorption on the agarose gel, and $[i\text{-SWCNT}]_{\text{free}}$ and

$[i\text{-SWCNT}]_{\text{ads}}$ are as described previously. Unfortunately, Eqn. 2 cannot be directly evaluated due to the lack of information regarding the site density and the energetic landscape of the adsorbing surfaces.

Since $K_i = K_{1,i}K_{2,i}$, we can employ an alternate approach and attempt to separately evaluate $K_{1,i}$ and $K_{2,i}$, the equilibrium constants for Steps 1 and 2, respectively:

$$K_{1,i} = [i\text{-SWCNT}^*][i\text{-SDS}]/[i\text{-SWCNT}_{\text{free}}] \quad (3)$$

$$K_{2,i} = [i\text{-SWCNT}_{\text{ads}}]/[i\text{-SWCNT}^*][i\text{-OSites}] \quad (4)$$

Here, the concentration of the activated complex, $[i\text{-SWCNT}^*]$, is explicitly expressed, and the difficulty in evaluating $[i\text{-OSites}]$ is confined to the evaluation of $K_{2,i}$. Despite being unable to evaluate $K_{2,i}$ directly, we can intuitively expect $K_{2,i}$ to be large, at least for s-SWCNTs, as evidenced by the column's strong affinity for binding s-SWCNTs from the SDS dispersions. Therefore, we can consider Step 1 to be rate-determining.

To proceed with evaluating $K_{1,i}$, the equilibrium constant for formation of the activated complex, we first consider the possible changes in $[i\text{-SDS}]$ with the reaction. We estimate that the change in SDS concentration associated with complete surfactant desorption during formation of the activated complex is very small in comparison to the background 35 mM SDS concentration ($\ll 1\%$, Supplementary Material). Therefore, we can neglect $[i\text{-SDS}]$ in Equation 3 and consider the conversion of $i\text{-SWCNT}_{\text{free}}$ into $i\text{-SWCNT}^*$ to be a thermally activated unimolecular process.

To proceed we utilize the fact that $[i\text{-SWCNT}_{\text{ads}}]$ is a measurable quantity that can be related to $[i\text{-SWCNT}^*]$ via a factor, k_{trans} , that expresses the probability that the activated complex will move toward the products side of Reaction 1 and become an adsorbed species. Thus, we rewrite $K_{1,i}$ as follows:

$$K_{1,i} = k_{\text{trans}}[i\text{-SWCNT}_{\text{ads}}]/[i\text{-SWCNT}_{\text{free}}] \quad (5)$$

This expression can be evaluated by simply comparing the difference in the area above baseline of m- and s-SWCNT envelopes in the E1 and E2 fractions.

With a method for evaluating $K_{1,i}$ in hand, we can now consider that the temperature dependence of $K_{1,i}$ is related to the free energy, enthalpy, and entropy of formation of the activated complex as follows:

$$\Delta G_i^* = -RT \ln K_{1,i} = \Delta H_i^* - T\Delta S_i^* \quad (6)$$

$$\ln K_{1,i} = -\Delta H_i^*/RT + \Delta S_i^*/R \quad (7)$$

Figure 3 shows plots of $\ln K_{1,i}$ versus $1/RT$ for the m-SWCNTs and s-SWCNTs. Each set of data points can be fit by a straight line where the slope and intercept provide a measurement of the change in enthalpy (ΔH^*) and entropy (ΔS^*), respectively, associated with the formation of the activated complex. Note that the choice of k_{trans} has no effect on the slope of the plot and, therefore, does not change ΔH^* . Furthermore, the choice of k_{trans} has only a minimal effect on ΔS^* (Supplementary Material).

Figure 3. Natural log of the equilibrium constant for the formation of the activated complex for both m- (blue) and s-SWCNTs (red) plotted versus inverse temperature. Linear regression fits to the data points are also presented with k_{trans} values of 0.1, 0.5, 0.9 for the probability of decomposition of the activated complex.

The fact that a straight line produces a reasonable fit for both the m- and s-SWCNTs suggests that all of the significant temperature dependences associated with SWCNT adsorption have been captured in the analysis. One may be concerned, however, that temperature dependent changes that are expected for surfactant configuration on the SWCNT, i.e. the reactant in Step 1, have been ignored. Based upon microcalorimetric investigations of a similar surfactant on graphite,[43] however, we can expect that the last surfactants to desorb would be the innermost species, and that these innermost species would have a constant and relatively high heat of formation. Consequently, we can conclude that the *relevant* SWCNT reactant configuration to

consider in Step 1 has a monolayer of strongly bound surfactant, and that this species has a temperature-independent configuration.

Tube Type	PLV		HiPco	
	ΔH^* (kJ/mol)	ΔS^* (J/mol-K)	ΔH° (kJ/mol)	$\Delta S'^\circ$ (J/mol-K)
s-SWCNTs	42.2 +/- 23.4	151 +/- 80	-4.9 +/- 3.5	36.6 +/- 11.6
m-SWCNTs	182 +/- 5.9	597 +/- 20	64.0 +/- 12	251.5 +/- 37.4

Table 1: Value for the enthalpy and entropy change associated with the formation of the activated complex (ΔH^* and ΔS^* , respectively) as determined via analysis of the data of Figure 3 ($k_{\text{trans}} = 0.5$). Also presented for comparison are the standard enthalpy (ΔH°) of Reaction 1, as well as $\Delta S'^\circ$, a parameter which is related to, but less than, the standard entropy change, as determined by Hirano et al. in Ref. 38.

Table 1 shows the ΔH^* and ΔS^* values for the s- and m-SWCNTs species in samples produced by PLV. The dramatically different slopes for m- and s-SWCNTs in Fig. 3 lead to a ΔH^* value for SDS desorption from m-SWCNTs that is more than 4x greater than the value for s-SWCNTs, indicating that SDS is much more strongly bound to the m-SWCNTs. Surprisingly, there is very little experimental or theoretical data regarding the difference in SDS binding strength between m- and s-SWCNTs. Molecular dynamics simulations have commented on surfactant packing and dynamics as a function of surfactant concentration and SWCNT diameter, but these calculations are currently unable to account for difference due to metallicity.[44-49] Naively, one might expect a lower van der Waals (vdW) stabilization energy for the hydrophobic tails of SDS on m- as compared to s-SWCNT walls, but a recent application of the Lifshitz theory to vdW interactions between SWCNTs suggests that dispersion forces should in fact be greater for s-SWCNTs.[50] Duque et al.[51] noted in a DGU-based experimental study that, as surfactant concentration was increased, SDS adsorbed on m-SWCNTs became limited in its ability to reorganize before SDS adsorbed on s-SWCNTs, suggesting a stronger binding energy for SDS/m-SWCNT interactions. We suggest that differences in the concentrations of charged

surface groups may lead to more stable packing for SDS on m- as compared to s-SWCNTs when water species are considered.

It is important to recall, that our model consists of two elementary steps, and that Step 1 is assumed to be rate limiting for both s- or m-SWCNT species. This assumption is based on the observation that s-SWCNTs rapidly adsorb onto the column. However, it is not clear that this assumption applies to m-SWCNTs. In fact, the experimental data suggests otherwise. Certainly, we do not expect $K_{2,m}$ to be pulled to the right when there is a large concentration of m-SWCNT* because m-SWCNTs clearly prefer to remain in E1, especially at the lower temperatures. Therefore, the very large value of ΔH^* for m-SWCNTs may be indicative of a lack of suitable binding sites for m-SWCNTs on the agarose gel.

Consistent with our findings, previously published ΔH^0 data for the overall reaction[38] under true equilibrium conditions indicate that the adsorption of s-SWCNTs is exothermic while the adsorption of m-SWCNTs is strongly endothermic (Table 1). Though the results of Hirano et al. do not directly comment on the properties of the activated complex, their data argues against Step 1 being rate determining for m-SWCNTs. Considered together, the ΔH^0 and the ΔH^* data suggest that the column discriminates against adsorption of m-SWCNTs due to a combination of strong SDS binding *and* the lack of suitable sites, especially at the lower temperatures. At the higher temperatures, m-SWCNTs appear significantly in E2 when bundling begins to dominate due to surfactant desorption for both m- and s-SWCNTs (Figure 1). Under these conditions, bundles with more s-SWCNTs on the exteriors might be more strongly bound by the column, while those with m-SWCNTs on the exteriors may be more likely to remain in E1. Some of the largest bundles may be unable to move through the porous structure and become trapped (*vide supra*).

The picture that emerges from consideration of enthalpy data for the activated complex and the overall reaction is that individualized m-SWCNTs do not interact appreciably with the column at the lower temperatures at which separation is most efficient. For s-SWCNTs, on the other hand, we can conclude that adsorption of s-SWCNTs is energetically favorable due to both a lower activation enthalpy and a more favorable enthalpy of reaction. If the two data sets are considered together, despite the different types of SWCNTs that were employed, we can construct a diagram for the enthalpy changes along the reaction coordinate, as shown in Figure 4.

Figure 4. Reaction coordinate schematic showing a surfactant-suspended SWCNT as a reactant (at left), an activated complex comprised of a partially or fully-unsheathed SWCNT (upper right, SWCNT with an asterisk), and, as a product, a SWCNT adsorbed at a preferred site on the hydrogel (lower right). The magnitudes of the ΔH^* and ΔH° values are to scale and taken from the s-SWCNT values presented in Table 1.

Consideration of the entropy changes yields information about the reorganization of the system components. The entropy change associated with formation of the activated complex, ΔS^* , is large and positive for both m- and s-SWCNTs, indicating an increase in disorder (Table 1). This contrasts with the decomposition of spherical micelles, in which the entropy is nearly always reduced due to the formation of ordered, clathrate-like water cages that solubilize the hydrophobic tails of the freed surfactant.[52, 53] With a lower entropy for surfactant suspended SWCNTs, we can conclude that SDS/SWCNT micelle formation is driven more by enthalpic, rather than by entropic, considerations.

The very large values of ΔS^* for the formation of the activated complex are a reflection of the large cooperative unit involved in the reaction. Thus, it is difficult to compare the absolute values of our enthalpy and entropy determinations to well-known values of, e.g., SDS micellization due to lack of knowledge regarding the size of the cooperative unit involved in the reaction. The length distributions of the m- and s-SWCNTs are expected to be comparable, so the entropy change observed for formation of m-SWCNT* as compared to s-SWCNT* (Table 1) is simply a restatement of the larger enthalpy of stabilization for SDS on m-SWCNTs. Also, we

can compare the ΔS^* values for PLV tubes to the ΔS° values for HiPco tubes under the assumption that the cooperative unit is similar in both instances. With the overall entropy of the adsorption reaction (ΔS°) being of the same sign but lower in magnitude than ΔS^* for both m- and s-SWCNTs we can conclude that the unit adsorbed on the column is more ordered than the activated complexes, but less ordered than the SDS-suspended complexes.

The change in entropy of the cooperative unit during progression along the reaction coordinate challenges current models for SWCNT adsorption on hydrogels. Although first reports using the gel-squeezing method considered that s-SWCNTs were substantially devoid of surfactant while m-SWCNTs remained well-sheathed,[54] more recent reports have concluded that the surfactant sheath on s-SWCNTs is not strongly perturbed upon adsorption and that the surfactant species themselves somehow mediate or participate in the adsorption process.[30] As pointed out previously,[38] this view disagrees with the measured increase in ΔS° . In fact, it is difficult to intuitively rationalize an adsorption process that involves an increase in entropy without substantial surfactant reorganization. However, the complexity of entropy considerations for even simple spherical micelles in solution highlights the difficulty of making quantitative statements on these matters. Our premise that a substantial disturbance of the SDS sheathing must occur with adsorption, i.e. the supposition that an activated complex exists, is validated by the measurement of a large and positive ΔS^* . As opposed to a model of a surfactant-clad SWCNT adsorbing onto the agarose via progression along a barrier-less adsorption potential, the conceptual view is now the large scale reorganization of the SDS/SWCNT micelle components into an overall lower energy configuration once adsorbed on the gel. The balance between entropy and enthalpy will be controlled by several factors including reorganization, incorporation, and binding of ancillary species such as water molecules and counter ions, as well as possible types of interactions between the SWCNT walls, surfactants, the ancillary species, and the functional groups that are presented at the surfaces of the agarose separation medium.

To gain a better understanding of the change in structure of the cooperative unit upon adsorption we performed *in situ* optical absorption spectroscopy of SWCNTs interacting with the agarose gel. Measurements were performed on an agarose gel column that was prepared between two glass slides that were epoxied together with a gap of ~0.5 mm. After the column was rinsed with D₂O, a reference spectrum was obtained. One milliliter of SWCNTs in 1%

SDS/D₂O was then introduced to the column and the absorption spectrum of the top 2 mm of the column was measured. The measured absorption spectrum (Figure 5) shows contributions from both adsorbed species and any free species that were not washed through the probed region. For comparison, the spectrum for the solution prior to introduction is also shown. We first note that spectrum of the SWCNTs interacting with the column shows an M1 absorption that is reduced in comparison to the solution spectrum even though E1 was not fully washed through the probed region. Thus, the separation is immediately evident. Most surprisingly, the S1 envelope is readily observed for the adsorbed SWCNT sample while the feature is missing in the solution spectrum. It is well known that the S1 absorption of PLV tubes is not observed due to p-type doping caused by protonation of chemisorbed oxygen species on the nanotube sidewalls.[55, 56] This effect is not observed for small diameter HiPco SWCNTs in SDS until the pH is reduced below 2.5,[55] but larger diameter PLV SWCNTs are readily doped by water at neutral pH.[57, 58] The fact that the S1 transitions are clearly evident when SWCNTs are interacting with adsorption sites on the column indicates that the adsorbed environment is very different from the free solution environment, and that the minimum energy configurations for adsorbed SWCNTs preclude arrangements that result in doping.

After rinsing with 2 mL of D₂O containing 1 wt% SDS, the E1 fraction is moved farther down the column and swept outside of the 2 mm band probed by optical absorption spectroscopy. Consequently, the spectral background due to the m-SWCNTs at the shorter wavelengths is reduced and the ratio of the S1 to S2 features is increased (Figure 5). After introducing a DOC containing solution, the absorption spectrum in the probed region is nearly featureless, as expected for removal of all adsorbed SWCNTs.

The strong intensity of the S1 envelope for the adsorbed SWCNTs indicates that the tubes are nearly completely deprotonated and likely adsorbed within the micropores of the hydrogel. If adsorbed SWCNTs were localized only on the exterior of the gel beads, perhaps within grooves or channels presented by the large area surfaces, complete deprotonation would not be expected since only a portion of the total SWCNT surface would be influenced by interactions with the agarose. Consequently, the data suggests that the SWCNTs are fully surrounded by the agarose environment, as would be expected if the SWCNTs were adsorbed within small internal pores.

Figure 5. Absorption spectra of a thin agarose filled column after introduction of SWCNTs (blue), rinsing with 1% SDS in D₂O (green), and rinsing with 2% DOC (red). Also included for reference is a spectrum of the SWCNTs dispersed in 1% SDS solution prior to introduction to the column (black). That data is normalized to the S2 peak of the SWCNT solution in the column. Note that when the SWCNTs are in solution with SDS, the S1 feature is quenched.

The possible physical and chemical interactions that could stabilize SWCNTs in the internal pores of agarose are a function of the chemical functionalities that comprise the pore walls. The pore walls are known to be quite heterogeneous and populated by at least three different types of hydroxyl groups as well as sulfonates, ester sulfates, ketal pyruvates, and carboxyl groups.[59] Thus, a variety of different types of interactions is possible with the surfactant-depleted SWCNT surfaces as has been discussed in detail elsewhere.[28]

It is known that SWCNTs, water, and SDS can readily access the internal pores,[60] so all of the same species that participate in SDS/SWCNT micelle formation in bulk water are present in the internal agarose environment. The inner landscape presented by the charges associated with the surface terminations can affect the shape, aggregation number, and diffusivity of SDS micelles.[61] Musnicki et al. attributed hindered diffusion of water in pores to a tendency for protons to be directed toward the surface hydroxyl groups.[61] It is likely that such interactions are also operative when SWCNTs are present in the hydrogel. The redirection of protons away from the chemisorbed oxygen species on SWCNT sidewalls would result in deprotonation and reappearance of the S1 band, as observed. Alternatively, one may consider

that the chemisorbed oxygen species are removed from the SWCNT sidewalls during the process of adsorption, which would preclude protonation altogether. However, it is difficult to imagine a mechanism for this process considering the thermal stability of the species when in equilibrium with laboratory air.[58]

4. Conclusions

Columns packed with agarose and other hydrogel materials offer the potential for separation of SWCNTs by conductivity type with both high throughput and high efficiency. Because the separation efficiency is not optimized for both s- and m- species at a single temperature, it is not yet possible to achieve quantitative separation in one pass. A more detailed understanding of the interactions between surfactant stabilized SWCNTs and hydrogels may allow for the design of more effective column materials in the future. In this contribution, we showed that an activated complex model offers a good description of the adsorption of s-SWCNTs on hydrogels. We report values for the enthalpy and entropy changes associated with formation of the activated complex for both s- and m-SWCNTs. The model assumes that surfactant must reorganize substantially for adsorption to occur, and this assumption was validated by *in situ* spectrophotometry examinations. The results are discussed with an emphasis on the reorganization of the system components during adsorption.

Acknowledgements

This material is based in part upon work supported by the Department of Energy under Award Number DE-SC0006349. We would to thank Dr. Jeffrey Blackburn of the National Renewable Energy Laboratory who kindly provided software for analysis of absorption spectra data.

- [1] Loebick CZ, Podila R, Reppert J, Chudow J, Ren F, Haller GL, et al. Selective Synthesis of Subnanometer Diameter Semiconducting Single-Walled Carbon Nanotubes. *J Am Chem Soc.* 2010;132(32):11125-31.
- [2] Ding L, Tselev A, Wang JY, Yuan DN, Chu HB, McNicholas TP, et al. Selective Growth of Well-Aligned Semiconducting Single-Walled Carbon Nanotubes. *Nano Lett.* 2009;9(2):800-5.
- [3] Collins PC, Arnold MS, Avouris P. Engineering carbon nanotubes and nanotube circuits using electrical breakdown. *Science.* 2001;292(5517):706-9.
- [4] Zhang GY, Qi PF, Wang XR, Lu YR, Li XL, Tu R, et al. Selective etching of metallic carbon nanotubes by gas-phase reaction. *Science.* 2006;314(5801):974-7.
- [5] Nish A, Hwang JY, Doig J, Nicholas RJ. Highly selective dispersion of singlewalled carbon nanotubes using aromatic polymers. *Nat Nanotechnol.* 2007;2(10):640-6.
- [6] Mistry KS, Larsen BA, Blackburn JL. High-Yield Dispersions of Large-Diameter Semiconducting Single-Walled Carbon Nanotubes with Tunable Narrow Chirality Distributions. *ACS Nano.* 2013;7(3):2231-9.
- [7] Brady GJ, Joo Y, Singha Roy S, Gopalan P, Arnold MS. High performance transistors via aligned polyfluorene-sorted carbon nanotubes. *Appl Phys Lett.* 2014;104(8):-.
- [8] Vijayaraghavan A, Hennrich F, Sturzl N, Engel M, Ganzhorn M, Oron-Carl M, et al. Toward Single-Chirality Carbon Nanotube Device Arrays. *ACS Nano.* 2010;4(5):2748-54.
- [9] Shea MJ, Arnold MS. 1% solar cells derived from ultrathin carbon nanotube photoabsorbing films. *Appl Phys Lett.* 2013;102:243101.
- [10] Bindl DJ, Shea MJ, Arnold MS. Enhancing extraction of photogenerated excitons from semiconducting carbon nanotube films as photocurrent. *Chemical Physics.* 2013;413:29-34.
- [11] Arnold MS, Green AA, Hulvat JF, Stupp SI, Hersam MC. Sorting carbon nanotubes by electronic structure using density differentiation. *Nat Nanotechnol.* 2006;1(1):60-5.
- [12] Niyogi S, Densmore CG, Doorn SK. Electrolyte Tuning of Surfactant Interfacial Behavior for Enhanced Density-Based Separations of Single-Walled Carbon Nanotubes. *J Am Chem Soc.* 2009;131(3):1144-53.
- [13] Niyogi S, Boukhalfa S, Chikkannanavar SB, McDonald TJ, Heben MJ, Doorn SK. Selective aggregation of single-walled carbon nanotubes via salt addition. *J Am Chem Soc.* 2007;129(7):1898-9.
- [14] Engel M, Small JP, Steiner M, Freitag M, Green AA, Hersam MC, et al. Thin Film Nanotube Transistors Based on Self-Assembled, Aligned, Semiconducting Carbon Nanotube Arrays. *ACS Nano.* 2008;2(12):2445-52.
- [15] Green AA, Hersam MC. Colored semitransparent conductive coatings consisting of monodisperse metallic single-walled carbon nanotubes. *Nano Lett.* 2008;8(5):1417-22.
- [16] Nougaret L, Happy H, Dambrine G, Derycke V, Bourgoin JP, Green AA, et al. 80 GHz field-effect transistors produced using high purity semiconducting single-walled carbon nanotubes. *Appl Phys Lett.* 2009;94(24):3.
- [17] Bindl DJ, Arnold MS. Semiconducting Carbon Nanotube Photovoltaic Photodetectors. *International Journal of High Speed Electronics and Systems.* 2011;20(3):687-95.
- [18] Green AA, Duch MC, Hersam MC. Isolation of Single-Walled Carbon Nanotube Enantiomers by Density Differentiation. *Nano Res.* 2009;2(1):69-77.
- [19] Khripin CY, Fagan JA, Zheng M. Spontaneous partition of carbon nanotubes in polymer-modified aqueous phases. *J Am Chem Soc.* 2013;135(18):6822-5.
- [20] Khripin CY, Tu XM, Heddleston JM, Silvera-Batista C, Walker ARH, Fagan J, et al. High-Resolution Length Fractionation of Surfactant-Dispersed Carbon Nanotubes. *Anal Chem.* 2013;85(3):1382-8.
- [21] Subbaiyan NK, Cambré S, Parra-Vasquez ANG, Hároz EH, Doorn SK, Duque JG. Role of Surfactants and Salt in Aqueous Two-Phase Separation of Carbon Nanotubes toward Simple Chirality Isolation. *ACS Nano.* 2014;8(2):1619-28.

- [22] Tulevski GS, Franklin AD, Afzali A. High Purity Isolation and Quantification of Semiconducting Carbon Nanotubes via Column Chromatography. *ACS Nano*. 2013;7(4):2971-6.
- [23] Liu H, Nishide D, Tanaka T, Kataura H. Large-scale single-chirality separation of single-wall carbon nanotubes by simple gel chromatography. *Nat Commun*. 2011;2:309.
- [24] Flavel BS, Kappes MM, Krupke R, Hennrich F. Separation of Single-Walled Carbon Nanotubes by 1-Dodecanol-Mediated Size-Exclusion Chromatography. *ACS Nano*. 2013;7(4):3557-64.
- [25] Tanaka T, Urabe Y, Nishide D, Kataura H. Continuous Separation of Metallic and Semiconducting Carbon Nanotubes Using Agarose Gel. *Appl Phys Express*. 2009;2(12):3.
- [26] Moshhammer K, Hennrich F, Kappes MM. Selective Suspension in Aqueous Sodium Dodecyl Sulfate According to Electronic Structure Type Allows Simple Separation of Metallic from Semiconducting Single-Walled Carbon Nanotubes. *Nano Res*. 2009;2(8):599-606.
- [27] Hirano A, Tanaka T, Urabe Y, Kataura H. pH- and Solute-Dependent Adsorption of Single-Wall Carbon Nanotubes onto Hydrogels: Mechanistic Insights into the Metal/Semiconductor Separation. *ACS Nano*. 2013;7(11):10285-95.
- [28] Clar JG, Batista CAS, Youn S, Bonzongo JCJ, Ziegler KJ. Interactive Forces between Sodium Dodecyl Sulfate-Suspended Single-Walled Carbon Nanotubes and Agarose Gels. *J Am Chem Soc*. 2013;135(47):17758-67.
- [29] Hirano A, Tanaka T, Kataura H. Adsorbability of Single-Wall Carbon Nanotubes onto Agarose Gels Affects the Quality of the Metal/Semiconductor Separation. *J Phys Chem C*. 2011;115(44):21723-9.
- [30] Silvera-Batista CA, Wang RK, Weinberg P, Ziegler KJ. Solvatochromic shifts of single-walled carbon nanotubes in nonpolar microenvironments. *Phys Chem Chem Phys*. 2010;12(26):6990-8.
- [31] Blanch AJ, Quinton JS, Shapter JG. The role of sodium dodecyl sulfate concentration in the separation of carbon nanotubes using gel chromatography. *Carbon*. 2013;60:471-80.
- [32] Flavel BS, Moore KE, Pfohl M, Kappes MM, Hennrich F. Separation of Single-Walled Carbon Nanotubes with a Gel Permeation Chromatography System. *ACS Nano*. 2014;8(2):1817-26.
- [33] Tvrdy K, Jain RM, Han R, Hilmer AJ, McNicholas TP, Strano MS. A Kinetic Model for the Deterministic Prediction of Gel-Based Single-Chirality Single-Walled Carbon Nanotube Separation. *ACS Nano*. 2013;7(2):1779-89.
- [34] Chen ZH, Appenzeller J, Knoch J, Lin YM, Avouris P. The role of metal-nanotube contact in the performance of carbon nanotube field-effect transistors. *Nano Lett*. 2005;5(7):1497-502.
- [35] Wang SJ, Khafizov M, Tu XM, Zheng M, Krauss TD. Multiple Exciton Generation in Single-Walled Carbon Nanotubes. *Nano Lett*. 2010;10(7):2381-6.
- [36] Liu HP, Tanaka T, Urabe Y, Kataura H. High-Efficiency Single-Chirality Separation of Carbon Nanotubes Using Temperature-Controlled Gel Chromatography. *Nano Lett*. 2013;13(5):1996-2003.
- [37] Yahya I, Bonaccorso F, Clowes SK, Ferrari AC, Silva SRP. Temperature dependent separation of metallic and semiconducting carbon nanotubes using gel agarose chromatography. *Carbon*. 2015;93(0):574-94.
- [38] Hirano A, Tanaka T, Kataura H. Thermodynamic Determination of the Metal/Semiconductor Separation of Carbon Nanotubes Using Hydrogels. *ACS Nano*. 2012;6(11):10195-205.
- [39] Dillon AC, Gennett T, Jones KM, Alleman JL, Parilla PA, Heben MJ. A simple and complete purification of single-walled carbon nanotube materials. *Adv Mater*. 1999;11(16):1354-8.
- [40] Tenent RC, Barnes TM, Bergeson JD, Ferguson AJ, To B, Gedvilas LM, et al. Ultrasoft, Large-Area, High-Uniformity, Conductive Transparent Single-Walled-Carbon-Nanotube Films for Photovoltaics Produced by Ultrasonic Spraying. *Adv Mater*. 2009;21(31):3210-6.
- [41] Itkis ME, Perea DE, Niyogi S, Rickard SM, Hamon MA, Zhao B, et al. Purity evaluation of as-prepared single-walled carbon nanotube soot by use of solution-phase near-IR spectroscopy. *Nano Lett*. 2003;3(3):309-14.

- [42] McDonald TJ, Engtrakul C, Jones M, Rumbles G, Heben MJ. Kinetics of PL quenching during single-walled carbon nanotube rebundling and diameter-dependent surfactant interactions. *J Phys Chem B*. 2006;110(50):25339-46.
- [43] Kiraly Z, Findenegg GH, Klumpp E, Schlimper H, Dekany I. Adsorption calorimetric study of the organization of sodium n-decyl sulfate at the graphite/solution interface. *Langmuir*. 2001;17(8):2420-5.
- [44] Wallace EJ, Sansom MSP. Carbon nanotube/detergent interactions via coarse-grained molecular dynamics. *Nano Lett*. 2007;7(7):1923-8.
- [45] Calvaresi M, Dallavalle M, Zerbetto F. Wrapping Nanotubes with Micelles, Hemimicelles, and Cylindrical Micelles. *Small*. 2009;5(19):2191-8.
- [46] Tummala NR, Striolo A. SDS Surfactants on Carbon Nanotubes: Aggregate Morphology. *ACS Nano*. 2009;3(3):595-602.
- [47] Tummala NR, Striolo A. Curvature effects on the adsorption of aqueous sodium-dodecyl-sulfate surfactants on carbonaceous substrates: Structural features and counterion dynamics. *Phys Rev E*. 2009;80(2):10.
- [48] Angelikopoulos P, Gromov A, Leen A, Nerushev O, Bock H, Campbell EEB. Dispersing Individual Single-Wall Carbon Nanotubes in Aqueous Surfactant Solutions below the cmc. *J Phys Chem C*. 2010;114(1):2-9.
- [49] Xu ZJ, Yang XN, Yang Z. A Molecular Simulation Probing of Structure and Interaction for Supramolecular Sodium Dodecyl Sulfate/Single-Wall Carbon Nanotube Assemblies. *Nano Lett*. 2010;10(3):985-91.
- [50] Hobbie EK, Ihle T, Harris JM, Semler MR. Empirical evaluation of attractive van der Waals potentials for type-purified single-walled carbon nanotubes. *Phys Rev B*. 2012;85(24):9.
- [51] Duque JG, Densmore CG, Doorn SK. Saturation of Surfactant Structure at the Single-Walled Carbon Nanotube Surface. *J Am Chem Soc*. 2010;132(45):16165-75.
- [52] Jolicoeur C, Philip PR. Enthalpy–Entropy Compensation for Micellization and Other Hydrophobic Interactions in Aqueous Solutions. *Canadian Journal of Chemistry*. 1974;52(10):1834-9.
- [53] Frank HS, Evans MW. Free Volume and Entropy in Condensed Systems III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes. *The Journal of Chemical Physics*. 1945;13(11):507-32.
- [54] Tanaka T, Jin H, Miyata Y, Fujii S, Suga H, Naitoh Y, et al. Simple and Scalable Gel-Based Separation of Metallic and Semiconducting Carbon Nanotubes. *Nano Lett*. 2009;9(4):1497-500.
- [55] Strano MS, Huffman CB, Moore VC, O'Connell MJ, Haroz EH, Hubbard J, et al. Reversible, band-gap-selective protonation of single-walled carbon nanotubes in solution. *J Phys Chem B*. 2003;107(29):6979-85.
- [56] Dukovic G, White BE, Zhou ZY, Wang F, Jockusch S, Steigerwald ML, et al. Reversible surface oxidation and efficient luminescence quenching in semiconductor single-wall carbon nanotubes. *J Am Chem Soc*. 2004;126(46):15269-76.
- [57] Engtrakul C, Davis MF, Gennett T, Dillon AC, Jones KM, Heben MJ. Protonation of carbon single-walled nanotubes studied using C-13 and H-1-C-13 cross polarization nuclear magnetic resonance and Raman spectroscopies. *J Am Chem Soc*. 2005;127(49):17548-55.
- [58] Haugen NO, Phillips AB, Dykstra TE, Waththage S, Heben MJ, Ellingson RJ. Intraexciton Transitions Observed in High Stability Doped Single-Wall Carbon Nanotube Films and Solutions. *The Journal of Physical Chemistry C*. 2014;118(43):25253-60.
- [59] Dumitriu S. *Polysaccharides: Structural Diversity and Functional Versatility*, Second Edition: Taylor & Francis; 2004.
- [60] Fakhri N, MacKintosh FC, Lounis B, Cognet L, Pasquali M. Brownian Motion of Stiff Filaments in a Crowded Environment. *Science*. 2010;330(6012):1804-7.

[61] Musnicki WJ, Lloyd NW, Phillips RJ, Dungan SR. Diffusion of sodium dodecyl sulfate micelles in agarose gels. *J Colloid Interface Sci.* 2011;356(1):165-75.