NONCOVALENT SORPTION AND DESORPTION OF N-ALKYLBENZENES AT INFINITE DILUTION ON SINGLE- WALL CARBON NANOTUBES (SWCNT) BY EQUILIBRIUM HEADSPACE GAS CHROMATOGRAPHY

by

Corina Cooling A Thesis Submitted to the Graduate Faculty of George Mason University in Partial Fulfillment of The Requirements for the Degree of Master of Science Chemistry

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at George Mason University

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Dedication

This thesis is dedicated to Mariah Perez, Christian McClure, Gisele Diaz, Mia McClure and Carter Jackson McClure. May your dreams be big and you never feel limited.

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Abstract

NONCOVALENT SORPTION AND DESORPTION OF N-ALKYLBENZENES AT INFI-NITE DILUTION ON SINGLE-WALL CARBON NANOTUBES (SWCNT) BY EQUILIB-RIUM HEADPSPACE GAS CHROMOTOGRAPHY

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George Mason University, 2016

Thesis Director: Dr. Abul Hussam

Analysis of noncovalent sorption and desorption of complex samples is costly and time consuming. Efficiency of this analysis has been increased through the novel discontinuous vacuum extraction by equilibrium headspace gas chromatography technique (DVE-HSGC) that has been developed. This research quantified the simultaneous noncovalent sorption, desorption of 5 nalkylbenzenes: benzene, toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene, onto the surface of single walled carbon nanotubes (SWCNTs), in addition to calculating the surface area. Three different isotherm models were used to identify the best fit for the data and Spartan molecular modeling software was used to visualize the sorption mechanisms. The DVE-HSGC obtains data in the submonolayer region, effectively modeling infinite dilution. This research determined a correlation between the hydrophobicity of the sorbents and an increase in the affinity for the SWCNT and viability of the DVE-HSGC technique.

Chapter 1: Introduction

1.1 Introduction

Carbon nanotubes are fullerenes structurally related to Buckminsterfullerene or Bucky Balls, and graphene sheets comprised of benzene like motifs. They are known for their high conductivity, surface area, and chemical versatility [1] and since their discovery, research regarding carbon nanotubes, or CNTs, has exploded. According to PR Newswire, the worldwide carbon nanotube market is expected to reach 5.64 billion United States dollars by the year 2020. [2] A carbon nanotube coating on a given surface has very high strength and durability, [3] and various ligands can be attached to the surface of the carbon nanotube, [4] creating endless possibilities for novel or improved electronics, medical devices, batteries, composites and aerospace and defense applications. [2] As of yet, very little is known about the non-covalent association of environmentally harmful molecules of gasoline origin like n-alkylbenzenes (solute) at infinite dilution (or submonolayer coverage) on single walled carbon nanotubes (SWCNT). SWCNT are structurally defined materials with known dimensions which make them interesting compared to amorphous carbon and other non crystalline materials.

The primary goal of this research is to measure sorption, desorption, and association of these solutes so that reliable surface areas of SWCNT can be obtained. In this pursuit, different sorption models will be compared to determine which one most accurately describes the system. Also, a technique will be established that examines the interactions of several solutes on a given surface simultaneously using equilibrium headspace gas chromatography. Spartan will be used to illuminate possible sorption site mechanisms between solute and the SWCNT.

The solutes tested in this research are a mix of n-alkylbenzenes, specifically benzene, toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene. n-Alkylbenzenes naturally occur from petroleum and bituminous coal, but are synthesized and used in bulk in gasoline components and for industrial purposes. [5] Benzene is used as a basis for synthesizing functionalized aromatic compounds which are then used for a multitude of purposes such as use as a solvent, constructing polymers, or synthesizing other materials. [6] Toluene, methylated benzene, is commonly used as an industrial solvent but has various other uses such as, an ingredient in paints, glues, nail polish and hair dyes. [7] Toluene is also used to make the explosive trinitrotoluene or TNT. [8] Ethylbenzene, benzene with a saturated two carbon chain substituent, is also used as an industrial solvent and a key derivative in the commercial production of polystyrene, or Styrofoam, a household material. [9] Of the less used n-alkylbenzenes with propyl and butyl substituents, n-propylbenzene finds itself utilized in textile dying and printing [10] and n-butylbenzene is used in biochemical research to induce cell death in vitro. [11] These compounds are volatile, flammable, and hazardous to the nervous system upon prolonged exposure. [12] While n-alkylbenzenes readily degrade in nature [13] they are well studied and data obtained in this research is verifiable by a number of resources such as the CRC Handbook, the National Institute of Standards and Technology (NIST) Chemistry WebBook online database, and general organic chemistry textbooks as well.

Current analytical techniques to experimentally determine surface area vary, because in order to measure the amount of solute present on a surface, one must be able to measure the concentration of the solute. Specially designed instruments are sold that accomplish this such as the Micromeritics Gemini VII 2390 Series of surface area analyzer, which uses nitrogen gases as a solute. [14] By convention, the surface area of solids are typically obtained by using nitrogen gas adsorption and fitting it to a BrunauerEmmettTeller isotherm theory model. In this way, infinite dilution is not modeled and is not necessary for adequate measurement due to the inert properties of N_2 gas. This is effective, but it does not describe specific interactions of the solid with other solutes. This research will both obtain surface area values and illuminate specific n-alkylbenzene interactions with SWCNT.

Surface area values and specific interactions are important to obtain in the pursuit of catalysis design. When designing a catalyst for industrial or commercial processes, knowing the solute to solid ratio is a measure of efficiency and the interaction will define what can be achieved with the catalyst. We have developed a novel headspace gas chromatographic technique (HSGC) to measure the interactions of multiple compounds at low surface coverage and at infinite dilution on a given surface. In a single analysis, the surface area can be obtained along with specific interactions, making for a more efficient technique. The method is general as long as the solute remains volatile.

1.2 Singled Walled Carbon Nanotubes

A carbon nanotube, demonstrated in Figure 1.1, is a series of connected benzene like rings forming a nano-sized cylindrical structure with diameters ranging 0.7 to 10.0 nm. [1] SWCNT have a large, approximately $10^4 - 10^5$ length to diameter ratio. [1] Carbon nanotubes can be synthesized to have a single wall or multiple walls, both having their own properties and uses. [15] The multiwalled CNTs are easier to synthesize but have fewer innovative properties than their single walled counterparts. [16] Table 1.1 shows the advantages of SWCNT over other materials, specifically MWCNT, steel and carbon fibers.

Table 1.1: Table of single-walled carbon nanotube properties compared with multi-walled carbon nanotubes, steel and carbon fibers. [3]

Property	MWCNT	SWCNT	Steel	Carbon Fibers
Tensile Strength, GPa	300-600	300-1500	0.4	3-7
Elastic Modulus, GPa	500-1000	1000-1500	200	200-800
Specific Strength, GPa	200-300	150-750	0.05	2-4
Density, g/mL	2.6	1.4	7.8	1.5-2

The single walled nanotube structures are chiral or achiral, depending on type, and form either

metallic or semi-conducting entities. They are classified under three types, armchair and zigzag, which are achiral, and simply chiral carbon nanotubes. The names armchair and zigzag come from shape of the cross sectional ring. The length of the carbon nanotube, usually in hundreds of micrometers, can be used as an indication of the chirality. [1] Carbon nanotubes are a trending research subject because of their vast possibilities of applications. Due to the size of the structures and their properties, carbon nanotubes, or CNTs, can be used in medicine, in electrochemical power sources, as transparent conductive films, in tires and rubber, as polymer composites, or in metal alloys. [3] Antimicrobial coatings have been designed featuring single walled carbon nanotubes, [17] and body armor containing CNTs have displayed bullet protective properties. [18] Carbon nanotubes can be used as an electrochemical sensor [19] and recent research identified carbon nanotube viability as a smart fabric that can sense physiological response when worn on the body. [20] Single walled carbon nanotubes have a very high surface area and have both hydrophobic and hydrophilic properties due to the cylindrical conjugated carbon system as seen in Figure 1.2. [21]

Carbon nanotubes only occur in nature in trace amounts. CNTs can be synthesized naturally in a volcano from methane chemical vapor deposition with lava as a catalyst and substrate. [22] Rather than trying to harvest carbon nanotubes from volcanoes, much research is currently being performed on low cost, quick ways of synthesizing pure SWCNTs. With much attention placed on this, recently researchers at Rice University in Houston, TX were able to self-assemble carbon nanotubes using a Tesla coil. [23] While novel, the technique does not yield carefully designed CNTs, only SWCNT super structures. However, at the same time in Australia at Flinders University, a technique to reliably cut carbon nanotubes at a specific length was accomplished using inexpensive custom designed equipment. [24] Though carbon nanotubes have yet to find an exciting new niche in material science, there remains a lot of promise that carbon nanotubes will soon revolutionize modern industry given more research. [16]



Figure 1.1: Singled Walled Carbon Nanotube with a diameter of 11 nm from three different viewpoints, modeled in Spartan.



Figure 1.2: SWCNT electrostatic map modeled in Spartan. Orange coloration indicates a partial negative charge, red corresponds to a higher negative charge, and blue is a partial positive charge.

Chapter 2: Theory

This section explains the chemical theory behind the models used to analyze the data. It begins with noncovalent sorption and desorption interactions and the definitions used throughout the paper, then describes Langmuir, BET and ESW isotherm theories, explaining the mathematical derivations of the equations used in the data analysis.

2.1 Sorption and Desorption as Noncovalent Interactions

Sorption and desorption of solutes from solid or liquid surfaces are a universal phenomenon. Sorptions of neutral molecules are classified as physisorption where the interaction is weak and chemisorption is defined with strong covalent-like interaction. Sorption is a more generalized noncovalent interaction where adsorption suggests a stronger bind. However, most solute-substrate interact in non-covalent ways to form a monolayer and multilayer on the surface. Here, we describe some of the well-known theories of sorption and use them to calculate surface area of the substrate and the characteristic interaction energies. Because we are primarily interested in desorption of solutes in sub-monolayer region in presence of a mixture of molecules, the Langmuir isotherm should be the best model to fit the data. To gain further insight, we also used the Brunauer-Emmett-Teller (BET) and Excess Surface Work (ESW) Model. The ESW gives some insight into thermodynamic interaction parameters. All three models can predict the surface area of the substrate to a different degree of accuracy. These are discussed in the results and discussion section.

2.2 Langmuir Isotherm

The Langmuir isotherm theory, published in 1918 by Irving Langmuir, is a description of the monolayer coverage of gas on a given surface. [25] Langmuir based the theory on a kinetic basis,

deriving the semi-empirical model from statistical thermodynamics. This model is commonly used due to its relative simplicity, and despite the many assumptions made in the model, it is able to sufficiently model a variety of experimental sorption data up to monolayer coverage. But the assumptions made can place limitations on its applicability. The main assumptions are:

- All of the sites on the solid surface are two-dimensional and are energetically homogenous: With SWCNT, the outer surface can be considered energetically homogenous two-dimensional object because the thickness of the shell is of the atomic layer. Molecules like alkylbenzenes may sorb on the outer surface before it could enter into tube as permitted by steric factor. This could be confirmed by molecular mechanics calculation of energy minimization on optimized geometry.
- Only one molecule will adsorb per site: This can be achieved by controlling the number of molecules in the container, either by adding very low concentration or by extracting (desorption) the vapor phase to a very low partial pressure, $p/p_s < 0.01$. This was achieved by the vacuum extraction HSGC as discussed in the experimental section.
- Only a monolayer will form: The observed data generally show regions of sub-monolayer, monolayer, and multilayer sorption and desorption. With a mixture of solute we are interested in the sub-monolayer region where solute-solute interactions are negligible.
- There are no phase transitions: This cannot happen below the saturation pressure of the solute. Phase transition of the substrate should not happen.
- The adsorbates do not interact with each other: At low concentration and at infinite dilution this assumption is valid. Experimentally, desorption can be measured at very low partial pressure where this criteria is valid.

All of which rarely, if ever, take place at once in real experimental conditions unless the solute is at infinite dilution and only noncovalent interactions dominate. For example, gas adsorbing on glass can condense at or near saturation, the gas molecules are not exactly inert, even if they do not react. [25] However, depending on the complexity of the system, the Langmuir isotherm can be accurately used to model sorption and desorption on a surface. Langmuir put forward that the mechanism of adsorption as a noncovalent interaction that takes place as follows:

$$A + S \leftrightarrow AS \tag{2.1}$$

where A is a gas molecule and S is an adsorption site of the substrate. If k and k_{-1} are the sorption and desorption rate constants, and θ is defined as the fraction of adsorption sites occupied, then the equilibrium can be represented as:

$$K = \frac{k}{k_{-1}} = \frac{\theta}{(1-\theta)p} \tag{2.2}$$

Rearranged, the more common form of the Langmuir equation is written as:

$$\theta = \frac{Kp}{(1+Kp)} \tag{2.3}$$

where p is the partial pressure of the gas. Since, θ is difficult to measure directly; it can be represented in volumes at STP as:

$$\theta = \frac{V}{V_{mono}} \tag{2.4}$$

where V_{mono} is the volume of gas required to form a monolayer on the adsorbent (per gram of adsorbent). This equation can be rearranged into a linear form, which is then seen as:

$$\frac{p}{V} = \frac{p}{V_{mono}} + \frac{1}{KV_{mono}}$$
(2.5)

where the volume of the monolayer is easily determined once the amount on the surface, V, is quantified, and pressure is known. Equation above can also be written with equilibrium amount (mols) of sorbed, n_s , at pressure p and that of monolayer, n_m as follows:

$$(\frac{p}{p_s})(\frac{1}{n_s}) = (\frac{p}{p_s})(\frac{1}{n_m}) + \frac{1}{bp_s n_m}$$
(2.6)

where b is the coefficient of sorption or desorption, p_s is the saturation vapor pressure of the solute. The coefficient of sorption or desorption is dependent on temperature and specific to sorbent-solute pair. With HSGC, the peak area of solute is directly proportional to the partial pressure of the solute and the mols of solute retained (or sorbed), n_s can be obtained from difference between total mols of solute, n_t minus the mols of solute in the vapor phase, n_v . Therefore, a plot of $(p/p_s)(\frac{1}{n_s})vs.p/p_s$ should be a straight line with a slope $\frac{1}{n_m}$ and the intercept $\frac{1}{bp_s n_m}$, from which monolayer coverage and the interaction constants can be obtained. These values can be obtained without a monolayer coverage i.e., in the sub monolayer region.

2.3 Brunauer-Emmett-Teller Isotherm

The BET theory (defined originally in 1938) is an expansion of the Langmuir equation and uses more parameters, making it useful for post monolayer modeling.[26] Different regions of the isotherm indicate the level of surface saturation and while the surface area can be calculated using the monolayer saturation value, the most accurate data is achieved in the knee region of the curve which describes the submonolayer region. Here when the assumption is made that the solutes s on the surface do not interact with each other, it is most applicable. However, the assumptions used in the Langmuir model still apply with the additional ones:

- There is no limits of multilayer formation
- Adsorption and desorption will only occur from exposed locations

The BET equation can be rearranged and graphed linearly to find the BET constant, C, and the constant n_m , seen as:

$$\frac{p}{n(p_s - p)} = \frac{1}{Cn_m} + \frac{C - 1}{(Cn_m)(\frac{p}{p_s})}$$
(2.7)

where $\frac{p}{n(p_s-p)}$ is graphed on the y-axis and p/p_s is placed on the x-axis. One can get n_m and the BET interation constant, C, from the isotherm, generally at higher partial pressures than that of Langmuir isotherm. The knee region (A) is the submonolayer region in the BET isotherm as shown in Figure 2.1. The desorption experiments performed here are in the submonolayer region.



Figure 2.1: Plot of mmols of solute sorbed vs. solute partial pressure. Sorption of toluene on glass surface shows the small knee region (A), the flat portion (B) is monolayer region building-up to multilayer with sharp increase in the sorbate concentration until saturation. Experimental data were obtained from eHSGC chromatographic experiments as discussed in the text.

2.4 Excess Surface Work Model

The Excess Surface Work (ESW) isotherm model, published in 1996, describes sorption isotherm with a two-parameter function. [27] The excess surface work function, Φ , is defined as the product

of sorbed amount and the change in chemical potential:

$$\Phi = n_{ads} \times \Delta \mu \tag{2.8}$$

where n_{ads} is the amount of moles sorbed to the surface, and

$$\Delta \mu = RT ln \frac{p}{p_s} \tag{2.9}$$

where T is the solute temperature, $R = 8.314 \frac{J}{mol \times K}$, p is the vapor pressure of the solute (sorbate), and p_s is the saturation vapor pressure (similar to vapor pressure of pure solute). A plot of Φ vs n_s gives a curve with a minimum when monolayer is formed. The parameters in the minima: $n_m, \Phi_m, \Delta \mu_m$, are all properties of the first layer. A typical example is shown in Figure 2.2.



Figure 2.2: A plot of Φ vs n_s . Sorption of toluene on 0.2048 g Carbopack at 298.16 K. (This work). Plot shows minimum surface work at monolayer coverage.

The first derivative of Equation 2.8 becomes:

$$d\Phi = \Delta \mu dn_s + n_s d\Delta \mu \tag{2.10}$$

It can be shown that when $d\Phi$ vanishes at monolayer, by integration and linearization:

$$ln \mid \Delta \mu \mid = \frac{-n_s}{n_m} + ln \mid \Delta \mu_o \mid \tag{2.11}$$

Therefore, a plot of $ln | \Delta \mu |$ vs n_s should be linear with a slope $\frac{-1}{n_m}$ and the intercept $ln | \Delta \mu_o |$, where $| \Delta \mu_o |$ is a measure of initial change in chemical potential which is unique for the solutesorbent pair. Experimentally, $\Delta \mu$ is easily measured by HSGC peak areas, and the amount of solute sorbed, n_s , can be obtained from mass balance $(n_s = n_t - n_v)$. It appears ESW model uses fewer assumptions than the Langmuir and BET isotherms and explains sorption in terms of change in chemical potential. [27] [28]

Chapter 3: Experimental

This section details the experimental method and materials used in the research. It begins by explaining the eHSGC instrument and functionality. Then the physical properties of the single walled carbon nanotubes, Carbopack and n-alkylbenzene mix used in the sorption and desorption experiments are described. The glass sample cell used in the experiment is also discussed. The procedure begins with the gas chromatography program, and then explains the method of determining the volume injected into the cell by the autosyringe. The experimental procedure for the sorption and desorption of toluene on Carbopack is explained, including the data analysis. Finally, the procedure for the desorption of the n-alkylbenzene mix from the SWCNT and corresponding data analysis is detailed.

3.1 Apparatus

3.1.1 Equilibrium Headspace Gas Chromatography (eHSGC)

In order to determine sorption-desoprtion isotherms and thermodynamics of volatile solutes on carbon nanotubes, an equilibrium headspace gas chromatography (eHSGC) was used. The eHSGC is a custom made instrument that can measure the concentrations of many volatile compounds at equilibrium in a given system in a single sampling.[29] Figure's 3.1 and 3.2 show the schematic diagram and the picture of the home-built instrument and the components, respectively. The details are described elsewhere. [29] Figure 3.3 shows the computer interface and the parameters used to control the instrument. Briefly, the sampling valve assembly positioned on the top of the GC injector is programmed to control the gas sampling from a thermostated cell. The direct connection between the sampling valve and the column allows on-column injection without loss of sample.



Figure 3.1: Schematic diagram of eHSGC. Instrument components are marked as: PC, personal computer; IC, interface controller; WB, water bath; GC, gas chromatograph; I, integrator; MS, magnetic stirrer; C, cell; AB, autoburet; HVB, heated valve box; CT, cold trap; VP, vacuum pump; L, sampling loop; V1, six-port gas sampling valve; V2 and V3, four-port sample selection valves; and B, ballast. [29]



Figure 3.2: Picture of the Equilibrium Headspace Gas Chromatography instrument. The headspace sampling valve assembly is wrapped with insulation and aluminum coated mylar thermal blanket (shiny) to maintain the temperature.

The eHSGC has unique functionalities that make it ideal for this research. It has a low detection limit due to the use of flame ionization detector which, requires very little sample (ppb hydrocarbon equivalent) in order to complete the analysis. Since the peak area of the solute is directly proportional to partial pressure of the solute in equilibrium with the substrate, direct measurement of solute activity at infinite dilution is possible. Also, it requires only basic information, such as mass of solute, sorbent, and the volume of the headspace cell in order to calculate sorption-desorption isotherms and surface area. However, the most critical feature of the eHSGC is that it can analyze many different compounds at very low concentrations from a single sample with excellent separation amongst the peaks. This minimizes resources used in the analysis and time spent in the lab. This is in contrast to more convoluted methods which require expensive equipment with high maintenance routines and sample prep. The eHSGC methods that will be used in this research have been proven to work and yield reproducible data as described elsewhere [30] [31] [32] The eHSGC methodology that will be deployed is advantageous over standard gas chromatography techniques because the sample is analyzed at equilibrium conditions allowing fairly direct measurement of equilibrium constants and simplifications during the analysis of the data. [33] Both sorption and desorption can be measured by the eHSGC without dismantling the sample cell which decreases sources of error. Figure 3.3 shows the computer program interface and the instrument parameters that control the HSGC, allowing for experimental conditions to be tweaked and reproduced easily.

🐕 microAnalytics Interface by Dr. Hussam	×
pH-mV TEST SETUP	•
CV C Lumin PULSE HSGC	
HSGC CONTROLLER	
NORMAL SAMPLING	
Initial Delay, s <mark>5</mark>	
Sampling time, s 10	
Residence time,s 10	
Injection Time,s 100	
No PurgeRuns 0	
No Replicate Runs 1	
No of additions 0	
Prg-Equil Time, m 0	
Autoburt time, s 0	
Purge time, s 0	
GC STATUS	
RUN STOP HSGC	
Data display	
	▼ //

Figure 3.3: An example of the user interface of the eHSGC, displaying experimental control parameters such as equilibrium time, purging, sample injection, number of sample analysis, etc.

3.2 Materials

3.2.1 Single-Walled Carbon Nanotubes

The SWCNTs used the experiment are 1.5 nm (15 Å) average diameter TUBALL®Single Wall Carbon Nanotubes with 75% purity. About 17% inorganic impurity is said to be within the sample, mainly consisting of Fe, O, Ni, Si, Cr, Na, and S elements. [3] The total carbon is approximately 85% w/w, where 10% is carbon present in the sample not in the form of a carbon nanotube, and the density of the sample is about 1.71.9 g/mL. According to TUBALL, the SWCNT sample is insoluble in water and organic solvents. The SWCNT sample has a surface area of 400 m^2/g by nitrogen gas adsorption fitted to a BET theory model. The sample was not purified in any way and was used as received.

3.2.2 Carbopack

The Carbopack B 60/80 mesh, an amorphous carbon powder, used in this experiment is commonly found in gas chromatograph columns as a stationary phase or support because of its established properties as a sorbent/desorbent. It has a surface area of approximately 100 m^2/g and the surface interactions are solely London Dispersion forces as advertised by Sigma Aldrich. [34] The literature value for the density of the Carbopack B solid is 0.35 g/mL. [34] Due to its use in GC columns, the properties have been thoroughly researched and can be reliably utilized as a standard on which further sorption /desorption experiments can be compared. The sample was not purified in any way and was used as provided by the manufacturer.

3.2.3 n-Alkylbenzenes

Benzene is a commonly used solvent utilized in a multitude of industrial and laboratory processes. Consisting of only carbon and hydrogen bonds but possessing polar-like qualities due to its π electron resonance, benzene is a thoroughly studied compound with its properties being tabulated in many sources. [35] Toluene, the simplest alkylbenzene, consisting of benzene with a single methyl group attached, is also a popular industrial solvent. Experimentally, toluene can represent interactions with supercritical CO_2 due to similar chemical behavior, without the need for extra laboratory preparation. [36] Therefore, any data collected using toluene as an adsorbate can also be applied to processes using supercritical CO_2 .

In addition to this, increasing the length of alkyl chain by one carbon, decreases the polarity of the sorbate in a systematic and quantifiable way, demonstrating the change in interaction with the sorbent as molecular weight and hydrophobicity increases.[35] This measurably describes the interaction of the SWCNT with compounds of varying intermolecular forces.

Properties	Benzene	Toluene	Ethylbenzene	n-Propylbenzene	n-Butylbenzene
MW (g/mol)	78.12	92	106	120.2	143.22
$\begin{array}{ccc} { m g} & { m in} & { m mixture} \\ { m (stock)} \end{array}$	6.2829	4.9607	4.467	4.2536	3.8506
mols in stock	0.080426	0.053920	0.042141	0.035387	0.0286887
mol fraction	0.33432	0.22414	0.17517	0.14710	0.11925
$\gamma, UNIFAC1$	0.9712	0.9895	0.9998	0.9928	0.9761
g fraction	0.2638	0.2083	0.1876	0.1786	0.1617
density (g/mL)	0.87	0.89	0.92	1.10	1.30
molar volume	89.79	103.4	115.2	109.3	103.2
(mL/mol)					
vapor pressure, pure solute (atm) 2	0.1252	0.0374	0.0125	0.0045	0.0014
expt activity co- efficient in wa-	2480	9190	32700	136000	566000
ter, Yw $\left[29\right]$					
molecular sur- face area (\mathring{A}^2) (calc) 3	33.7	38.1	41.8	45.5	48.9

Table 3.1: Table shows amount of n-alkylbenzenes taken to prepare the stock standard and some of their properties.

Notes:

• 1. γ , the activity coefficients of solute in the mixture, were calculated by UNIFAC (UNIQUAC Functional-group Activity Coefficients). For an ideal mixture of homologs the activity coefficients should be unity. The values are close to unity, but the exact values can be used to calculate the pure vapor pressure and the corresponding pure peak area from the peak areas of individual compounds from the vapor phase mixture. UNIFAC is a semi-empirical method

for the calculation of non-electrolyte activity coefficients in non-ideal mixtures. UNIFAC uses group contributions of functional group in a linear free energy relation. Calculations were performed by the open source program: Please check UNIFAC - Wikipedia, the free encyclopedia for other details.

- 2. Vapor pressure of pure solute was obtained from literature value
- 3. Molecular surface area was calculated from the equation described elsewhere



Figure 3.4: Stick and ball models constructed in Spartan of benzene, toluene, ethylbenene, n-propylbenzene and n-butylbenzene respectively.

3.2.4 Glassware

It was necessary to measure the volume of the sample cell as accurately as possible. The volume of the cell was determined by filling it completely with deionized water at room temperature (22.3 °C) and weighed on an electronic balance three times and an average was determined. Using the density the volume was calculated. The thermostated cell volume was found to be 35.987 mL.

3.3 Procedure

3.3.1 Gas Chromatographic Method

A single GC temperature program was used throughout the experiments. This program began with an initial oven temperature of 60 °C for one minute. The oven temperature then increased 20 °C every minute until a final temperature of 170 °C was reached. The oven then stayed at 170 °C for three minutes. The injector and the detector temperatures were 250 °C.

3.3.2 Calibration of Auto-Syringe

The auto-syringe is a motor driven syringe controlled by a switching signal from the data acquisition system for a specified activation time. The amount of sample delivered after the activation time was measured in an analytical balance $(\pm 0.0001g)$ and plotted as a function of time. This calibration was used for the calculation of accurate delivery amount and converted to gram fraction, mole fraction, and volume fraction of solute added to the substrate under study (SWCNT or solution). The relative standard deviation of sample delivery by this procedure was less than 5%.



Figure 3.5: Calibration of autosyringe used to deliver solute in the glass cell.

3.3.3 Sorption and Desorption of Toluene on Carbopack Solid

The sorption of toluene on Carbopack solid began by prepping the sample cell. The 35.987 mL glass sample cell was prepared by cleaning with deionized water and small amounts of dish soap, then oven dried at 190 °C for approximately 30 minutes. The cell was cooled to room temperature and a Carbopack solid sample of 0.1008 g was placed inside the cell. The cell was installed in the eHSGC instrument, as viewed in Figure 3.6, and set to a 25 °C isothermal condition. A blank was run on the cell after at least 30 minutes was given for the system to equilibrate. Then 0.0023 g of toluene was injected into the sample cell via programmed auto syringe. After 30 minutes of equilibrium time, the eHSGC analyzed a sample of the headspace of the sample cell using a flame ionization detector. In total, 30 additions of toluene were made, given the same 30 minute equilibrium time between each addition. Immediately following the completion of 30 toluene additions, desorption of toluene from Carbopack was accomplished by vacuum-purging the sample cell for 200 seconds through the same valve assembly. After a programmed 15 minute equilibriation time, a headspace sample was analyzed by the GC. Fifty (50) purges and subsequent samples were obtained.



Figure 3.6: Carbopack B in glass sample cell assembled in the eHSGC instrument.

3.3.4 Procedure for Data Analysis

Tracking the n-alkylbenzenes on the surface of the solid was accomplished by a mass balance approach. During the sorption portion of the experiment, the total moles added was determined using the formula:

$$n_t = \frac{\chi \times V \times x}{m} \tag{3.1}$$

where n_t is the total number of mols, χ is the gram fraction of benzene, V is the grams added per 10 second injection, x is the addition number, and m is the molecular weight. Then the amount of moles in the vapor phase were determined using the peak areas given by the eHSGC chromatogram using the formula:

$$n_v = \frac{A_p \times P_o \times V_c}{1000 \times A} \tag{3.2}$$

Where n_v is mole in vapor phase, V_c is the volume of the cell, A is peak area, P_o is the pure vapor pressure of the solute (in this case toluene), and A_s is the peak area at surface saturation. Finally, the amount present on the surface was achieved using the simple mass balance equation:

$$n_s = n_t - n_v \tag{3.3}$$

Once the moles of toluene on the Carbopack surface was known, isotherm models were fitted. The Langmuir analysis was completed using the function: $(p/p_s)/n_s$ on the y-axis and p/p_s on the x-axis. A BET plot showing the interaction between Carbopack solid and toluene was made using the equation:

$$BET = \frac{p/p_s}{n_s \times (1 - p/p_s)} \tag{3.4}$$

where n_s is the surface excess mols, on the y-axis and p/p_s on the x-axis. The ESW isotherm was plotted with mmols/g on the x-axis and Equation 9 on the y-axis.

The surface area is calculated by determining the mols per gram of solute present in the monolayer on the surface. This is determined differently per each model. For the Langmuir isotherm, determining the mols/g is done through the equation:

$$m_g = \frac{intercept^{-1}}{s} \tag{3.5}$$

where the intercept is found using the Langmuir graph described above, and s is the grams of sorbent. In the BET model, the same value is found using the method:

$$m_g = \frac{1}{intercept \times C} \tag{3.6}$$
where the intercept is obtained through the BET graph previously mentioned and the constant, C, is algebraically determined from the BET graph as well. The ESW monolayer value is calculated as:

$$m_g = \frac{s}{-slope \times 1000} \tag{3.7}$$

where slope is the slope of the ESW graph and s is the grams of sorbent. Once the mols/g of the monolayer of solute on the surface is established, the surface area in angstrom squared is calculated through the equation:

$$A_{as} = m_g \times S_a \times N \tag{3.8}$$

where A_{as} is the surface area in \mathring{A}^2 , N is Avogadros number, m_g is monolayer mole per gram, and S_a is surface area of the solute. However, to convert it to conventional surface area units of m^2/g , the calculation:

$$A_s = \frac{A_{sa} \times (1 \times 10^{-20})}{s}$$
(3.9)

(where A_s is surface area, s is grams of sorbent, and A_{sa} is the surface area in \mathring{A}^2) can be used. This method is used for all of three of the models.

3.3.5 Surface Area of the Solute

In order to complete these calculations, the S_a , or surface area of the solute, must be calculated. This was accomplished by beginning with the molar volume, then dividing by Avogadros number, thus obtaining the area of a single solute molecule. The solute is then modeled as a sphere for ease of calculations. Using the equation for the volume of a sphere, the radius of the sphere is solved for. Given the radius, it is then inserted into the equation for the area of a circle to determine an area of the solute that will take up space when sorbed onto the surface. This method is applied to all of the solutes used: benzene, toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene.

3.3.6 Desorption Experiment of n-Alkylbenzene on SWCNT

The next step was similar to the Carbopack/toluene methodology. The 35.987 mL glass sample cell was prepared by rinsing with deionized water and cleaning with small added amounts of dish soap then oven dried at 180 °C for approximately 30 minutes. The cell was cooled to room temperature then 0.1136 g of TUBALL SWCNT solid sample was placed inside the cell. The SWCNT is a very light and fluffy material in appearance and tend to stick to the glass in clumps. The cell was installed in the eHSGC instrument, show in the figure below, and set to a 25 °C isothermal condition. Two blanks were measured on the cell after at least 30 minutes was given for the system to equilibrate. The blanks showed no measurable volatile species. Then 25 μ L of benzene to nbutylbenzene stock-mix was manually injected into the sample cell, saturating the surface of the SWCNT solid. After 30 minutes of equilibriation time, the eHSGC was performed. The peak area from this measurement is proportional to the initial concentration of the gas phase in equilibrium with the SWCNT. The cell was then purged for 200 s intervals using a drop in pressure provided by the vacuum pump and 15 minutes was given for the system to equilibrate. Then a measurement was taken by the eHSGC, obtaining a peak area for each solute. The purge-equilibrium-sample regime was repeated 50 times to extract the vapor phase and thus desorb solute from the SWCNT surface in precisely known quantities until the peak area represents solute concentration in the submonolayer region.

Experimental extraction slope and vapor phase concentration can be obtained from a separate experiment without SWCNT in the cell as explained elsewhere. [33] The amount extracted can be calculated using the equation:

$$n_e = \frac{(n_{vi} - n_{ve}) \times r \times (V_c + V_{lb})}{1000}$$
(3.10)

where n_{vi} is initial moles in vapor phase, n_{ve} is moles of volume extracted, r is response factor, V_c is cell volume, and V_{lb} volume of the loop and ballast. From this information, the moles of solute

sorbed can be calculated from the same mass balance approach simply using the equation:

$$n_s = n_t - n_v - n_e \tag{3.11}$$

after each extraction, where n_s is the mols of on the surface, n_t is the total mols, and n_e is mols extracted, and n_v is the mols in the vapor phase. In this way, the moles of solute left on the surface are determined.

The Langmuir, BET and ESW models can now be created once the amount of moles on the surface is established and the surface area can be calculated as discussed previously. Therefore, the surface area occupied by each n-alkylbenzene solute monolayer was calculated. Because five solutes are present at the same time on the surface at infinite dilution, the surface area values must be summed to get the total surface area. This is shown simply as:

$$A_{total} = A_{benzene} + A_{toluene} + A_{ethylbenzene} + A_{propylbenzene} + A_{butylbenzene}$$
(3.12)

where A_{total} is the total surface area and the subscripts refer to the corresponding fractional surface area.



Figure 3.7: Image of SWCNT in thermostated glass sample cell installed in eHSGC instrument.

Chapter 4: Results and Discussion

This section starts with the experiment to measure the surface area of the glass cell used for the all the experiments. This is followed by the measurement of isotherms and surface area of a known carbon sorbent- Carbopack with toluene as the solute. Here, we have tested Langmuir, BET, and ESW models for sorption and desorption isotherms and calculated the surface area. The computational process was then applied to the measurement of isotherms for SWCNT with nalkylbenzene as solutes. Finally, a computational molecular model (Spartan) was used to calculate the best geometric arrangement for sorption and interaction energies.

4.1 Sorption of n-Alkylbenzene in Glass Cell

All chemical species adsorb on a glass surface. It is, therefore, necessary to measure the sorption of n-alkylbenzenes on the surface of a glass sample cell to correct for any measurement with SWCNT or other solids. It was also determined by using the same eHSGC technique. The amount of leakage from the auto-syringe through the capillary fused silica tube connecting syringe to cell was measured at the same time. It was accomplished by filling the syringe with standard nalkylbenzene mixture (Table 3.1) placing the fused silica delivery tube in the sample cell through the Teflon lined septa without activating the autosyringe, and sampling the gas phase in the cell by eHSGC after 40 minutes of equilibration time. Any leakage of solute from the tip of the fused silica in the cell was measured as peak areas of solutes in gas phase.

For sorption study, the glass cell was washed with acetone, water, and dried in a GC oven at 140 °C The solute was added to the cell through a fused silica tubing connected to the autosyringe. The inlet and outlet of the cell have small Teflon backed silicone septa to reduce excess sorption. The amounts of n-alkylbenzenes sorbed on the glass surface was determined from the isotherm generated by injecting 0.0023 g of n-alkylbenzene mixture into the cell allowing the system to

reach equilibrium for 40 minutes before eHSGC analysis. The same procedure was repeated 30 times after each injection. A representative chromatogram and the integrator peak area are shown in Figure 4.1. Table 4.1 shows the peak area of every n-alkylbenzene at each addition in the empty 298.16 K thermostated glass sample cell. The zeroth addition has no peak area indication a completely empty cell. Figure 4.2 shows the plot of raw data obtained from Table 4.1 where gradual coverage of the cell is visualized. Table 4.1 shows the leakage is less than 0.05% of the total amount added after 30 additions. This amount is precisely known that can be included in the amount of solute added at each addition, yet very small to produce any significant systematic error.

1111					
	RUN# 224		NOV	23, 2015	17:50:29
	AREA%				
	RT	AREA	TYPE	WIDTH	AREA%
	3.163	1473	VB	.052	.02484
	3.385	3786517	PB	.045	63.85736
	4.204	684986	PB	.033	10.20138
	5.050	273316	PB	.027	4.60931
A CONTRACTOR OF A CONTRACTOR O	5,810	185	PP	.024	.00312
	5,885	499617	PB	.025	8.42575
	6.778	760203	PB	.025	12.82037
	6.863	980	BB	.019	.01653
	7,826	299	BB	.024	.00504
	7.646	2153	PB	.024	.03631
	TOTAL AREA	=5929648			
	MUL FACTOR	t=1.0000E	+00		
.E"					

Figure 4.1: A typical chromatogram shows the peaks from vapor phase sampling of n-alkylbenzenes in equilibrium with SWCNT after the desorption step is shown on the left. The integrator output of peaks and impurities are shown in the chromatogram and their peak areas on the right. Peak area down to 300 counts can be measured with baseline separation from other peaks.

Table 4.1: Data shows vapor phase peak area of n-alkylbenzenes in equilibrium with the empty
glass cell at 298.16 K. The total amount of solute mixture (in g) added to the cell is shown the
second column. The 0th entry shows no measureable peaks of any kind, thus showing a clean glass
cell.

Addition Solution Benzene		Toluene	Ethylbenzene	n-Propyl	n-Butyl			
	No.	Added				Denzene	Denzene	
_		(g)						
	0	0	0	0	0	0	0	
	1	0.0023	11500	4074	1967	770	-	
	2	0.0046	394053	249695	190443	155920	124800	
	3	0.0069	5929786	3993936	3001966	2207880	1322983	
	4	0.0092	11004944	6485712	4107445	2343437	1013283	
	5	0.0115	15394208	8064202	4470416	2245150	864327	
	6	0.0138	19048624	9065472	4609856	2153598	785090	
	7	0.0161	21934064	9678272	4641674	2087123	736344	
	8	0.0184	24157120	10065848	4627821	2033410	706928	
	9	0.0207	25957088	10322160	4612163	1992303	685053	
	10	0.023	27534256	10523928	4593354	1962822	667594	
	11	0.0253	28873536	10671768	4574563	1937389	657348	
	12	0.0276	30150752	10813952	4556624	1906667	642741	
	13	0.0299	31107280	10886304	4528074	1885067	630417	
	14	0.0322	31892000	10950584	4515024	1870542	625324	
	15	0.0345	32579664	11006912	4513504	1859666	620493	
	16	0.0368	33206528	11046800	4485603	1841137	613744	
	17	0.0391	33810656	11097712	4486589	1836590	610656	
	18	0.0414	34254208	11121360	4481120	1829670	606893	
	19	0.0437	34587040	11140512	4469459	1823464	604125	
	20	0.046	34916512	11162968	4470246	1822146	604164	
	21	0.0483	35254144	11177992	4472790	1818232	602411	
	22	0.0506	35612256	11199360	4458022	1813304	600432	

4	.0E+07]				•• B	ł	
Percei	nt leakage	e after 30 ad	lditions	0.0306	0.0361	0.0445	0.0432	0
30	0.069	37589280	11296792	4423	3520	1783540	59031	.8
29	0.0667	37348480	11280480	4417	718	1782676	58799	9
28	0.0644	37148672	11275832	4423	3261	1789777	58942	5
27	0.0621	36934624	11266928	4430)714	1795091	59156	57
26	0.0598	36696608	11243104	4429	9402	1793098	59226	5
25	0.0575	36524256	11254920	4441	379	1802433	59462	25
24	0.0552	36270496	11243976	4457	7130	1804333	59631	.3
23	0.0529	35942240	11225760	4459	9744	1815171	59979	07



Figure 4.2: Plot of peak area of n-alkylbenzenes vapor sample from the glass cell as a function of number of aliquot additions from the autosyringe. Figure shows gradual coverage of the glass surface until saturation coverage on the plateau.

4.2 Calculation of Surface Area of Glass Cell

For the measurement of glass surface area the sorption isotherm of toluene was used. The data for the isotherm is presented in Table 4.3. The isotherm is also shown in Figure 4.3 The monolayer coverage is shown by the flat plateau after the knee. The multilayer sorption is the rising portion of the plot. At monolayer coverage, 1.159×10^{-5} mols of toluene were sorbed on the glass cell. Given the surface area of toluene at 34.2 Å^2 the surface area of the glass cell was found to be 2.394 m^2 at 298.16 K. This is a reasonable number but much smaller than high surface area carbon or nanotubes (few hundred square meters per g) as found in this study.

Additic	on Total	Mols in	Surface	p/ps = A/As	mmols sorbed
No	Mols	Vapor	Excess		
	Added	Phase	Mols		
0	0	0	0	0	0
1	5.151e-6	4.405e-9	5.147e-6	3.606e-4	5.147 e-3
2	1.030e-5	2.700e-7	1.003e-5	2.210e-2	1.003e-2
3	1.545e-5	4.318e-6	1.113e-5	3.535e-1	1.113e-2
4	2.060e-5	7.012e-6	1.359e-5	5.741e-1	1.359e-2
5	2.575e-5	8.719e-6	1.704e-5	7.138e-1	1.704e-2
6	3.091e-5	9.802e-6	2.110e-5	8.025e-1	2.110e-2
7	3.606e-5	1.046e-5	2.5559e-5	8.567e-1	2.559e-2
8	4.121e-5	1.088e-5	3.032e-5	8.910e-1	3.032e-2
9	4.636e-5	1.116e-5	3.520e-5	9.137e-1	3.520e-2
10	5.151e-5	1.138e-5	4.013e-5	9.316e-1	4.013e-2
11	5.666e-5	1.154e-5	4.512e-5	9.4447e-1	4.512e-2
12	6.181e-5	1.169e-5	5.012e-5	9.573 e-1	5.012e-2
13	6.696e-5	1.177e-5	5.519e-5	9.637e-1	5.519e-2

Table 4.3: Data shows calculation of sorbed amount of toluene on glass cell from which the surface area of the cell was obtained.

14	7.211e-5	1.184e-5	6.027 e-5	9.694 e- 1	6.027 e-2
15	7.726e-5	1.190e-5	6.536e-5	9.743e-1	6.536e-2
16	8.242e-5	1.194e-5	7.047e-5	9.779e-1	7.047e-2
17	8.757e-5	1.200e-5	7.557e-5	9.824e-1	7.557e-2
18	9.272e-5	1.202e-5	8.069e-5	9.845e-1	8.069e-2
19	9.787e-5	1.205e-5	8.582e-5	9.862e-1	8.582e-2
20	1.030e-4	1.207e-5	9.095e-5	9.882e-1	9.095e-2
21	1.082e-4	1.209e-5	9.608e-5	9.895e-1	9.608e-2
22	1.133e-4	1.211e-5	1.012e-4	9.914e-1	1.012e-1
23	1.185e-4	1.214e-5	1.063e-4	9.937e-1	1.063e-1
24	1.236e-4	1.216e-5	1.115e-4	9.953e-1	1.115e-1
25	1.288e-4	1.217e-5	1.166e-4	9.963e-1	1.166e-1
26	1.339e-4	1.216e-5	1.218e-4	9.952e-1	1.218e-1
27	1.391e-4	1.218e-5	1.269e-4	9.974e-1	1.269e-1
28	1.442e-4	1.219e-5	1.320e-4	9.981e-1	1.320e-1
29	1.494e-4	1.220e-5	1.372e-4	9.986e-1	1.372e-1
30	1.545e-4	1.221e-5	1.423e-4	1.000	1.423e-1

Notes: Surface excess mols equals mols added subtracted by mols in the vapor phase. Surface excess is same as the mols sorbed.



Figure 4.3: Figure shows plot of mmols of toluene sorbed on the glass cell surface as a function of partial pressure. Surface area calculated from the flat portion showing monolayer coverage of 2.394 squared meters. The knee at low pressure probably shows filling the nanopores.

4.3 Sorption-Desorption of Toluene on Carbopack Solid from Gas Phase

Large surface area amorphous carbon is known to be a good sorbent for many organic compounds. Here we use Carbopack carbon solid with known N_2 BET surface area (ca. 100 m^2/g) to study the sorption desorption of toluene by eHSGC. The experiment involves adding 0.0023 g of toluene added to 0.2048 g of Carbopack solid in the glass cell and taking eHSGC measurement of the vapor phase in equilibrium with the solid phase. Thirty (30) such additions were made. Then 41 vacuum desorption HSGC was performed. Table 4.4 shows the peak area data for these runs. Figure 4.4 shows the corresponding plots for sorption-desorption peak areas and the respective isotherms. Clearly, the rise of peak area during addition and sorption and the fall in peak area after vacuum desorption are observed. The sorption isotherm shows surface begins with no toluene, as none is yet in the cell, then as toluene is progressively injected into the cell, the amount increases to cover the surface from submonolayer knee to monolayer plateau until multilayers of toluene are on the Carbopack surface as shown in the rising portion. It should be noted that more desorption steps are measurable and more data in the submonolayer regions are obtained compared to that in the sorption steps. The submonolayer region signifies negligible solute-solute interactions. This is considered as infinite dilution where solute obeys Henrys law for gas-solid interactions. The discontinuous vacuum extraction process in the desorption step allows very small vapor phase concentration measured by eHSGC is the novelty of the technique compared to most other techniques where such low concentrations cannot be measured.

Sorption		Desor	rption		
Run No.	A_i	Run No.	A_i	Run No.	A_i
1	6159	31	30982176	61	632205
2	19210	32	29457136	62	592096
3	20704	33	28075760	63	558051
4	19973	34	26686688	64	528658
5	51624	35	25050592	65	501798
6	233580	36	23077120	66	477275
7	1232951	37	20694272	67	454679
8	4339674	38	18018960	68	434115
9	8037562	39	15240288	69	415696
10	11289272	40	12521888	70	397232
11	14219872	41	10036584	71	382910
12	16669752	42	7905002	72	368375

Table 4.4: Peak area due to toluene left in the vapor phase after sorption (run no. 1-30) and desorption steps (run no. 31-82).

13	18537056	43	6170912	73	355567
14	20423248	44	4851818	74	343388
15	21723312	45	3870317	75	329263
16	22810944	46	3124886	76	321611
17	24001044	47	2585138	77	311207
18	25053792	48	2179429	78	301052
19	25868848	49	1859569	79	290061
20	26542272	50	1612746	80	285370
21	27156976	51	1415687	81	277484
22	27771792	52	1253425	82	270024
23	28740416	53	1124451		
24	29114944	54	1017126		
25	29308400	55	926737		
26	29672672	56	845014		
27	30282016	57	782874		
28	30624432	58	723039		
29	31069280	59	676460		
30	31247920	60	632205		



Figure 4.4: Sorption- desorption of toluene on Carbopack. Top: Peak area due to sorption followed by vacuum desorption as function of run numbers (equals number of sorption steps plus number of desorption steps). Bottom: Figure shows the sorption followed by desorption isotherms.

Figure 4.4 shows a nonideal process where the sorption-desorption is not completely reversible. The hysteresis of sorption and desorption of toluene on Carbopack shows a strong intermolecular attraction between toluene and Carbopack. Toluene strongly adsorbs and is not fully removed through the desorption phase of the experiment. Both compounds are fairly nonpolar but polarizable and have binding affinity. This is in sharp contrast with nitrogen-carbon interactions. Therefore, a direct comparison with N_2 based isotherms and N_2 based BET surface area is not applicable. Now that viability is established, the Langmuir, BET and ESW isotherm calculations can be performed. The surface area of the Carbopack solid was determined as mentioned previously, six different ways from the single experiment. Figures 4.5 and 4.6 show the data fit plots with Langmuir and BET equations for sorption desorption processes, respectively. It is clear that more data points are available for desorption segment and thus a better model correlation.



Figure 4.5: Langmuir plot for toluene on Carbopack surface showing sorption in blue and desorption in red. Desorption experiment shows more data at very low partial pressures with more data points compared to that of sorption experiment.



Figure 4.6: BET plot of toluene sorbed onto Carbopack solid surface. While viable, the sorption contains very few usable points in the submonolayer region whereas the desorption part with more data points shows excellent data fit even at low solute activity, $p/p_s < 0.1$.

The data fit to ESW model is shown in Figures 4.7 A,B,C. Plot in Figure 4.7A shows the excess surface work $\Phi = n_{ads}\Delta\mu$, where $\Delta\mu = RTln(p/p_s)$ as a function of mole of solute sorbed. The minimum in the surface energy is the energy required to form a monolayer which is about -3.82 kcal/mol (-32.1 kJ/mol). Therefore, monolayer formation is an exothermic process involving attractive molecular forces. Such information is not directly available from Langmuir and BET models. The exact monolayer surface concentrations were calculated from Figures 4.7 B and C for sorption and desorption steps, respectively. The results are tabulated in Table 4.5.



Figure 4.7: ESW graphs showing sorption and desorption of toluene gas phase solute on Carbopack surface. Sorption appears in blue and desorption in red. A shows the typical ESW plot where the minimum models the monolayer of toluene, B is the linearization of the sorption and B linearizes the desorbtion portion of the experiment.

	E	BET		Langmuir		ESW	
Parameters	Sorption	Desorption	Sorption	Desorption	Sorption	Desorption	
Slope	7614.6	4526.5	3883.6	4478.8	-4400.2	-7444.1	
Intercept	-190.3	6.02	43.53	5.693	7.1851	9.278	
Interaction, C or b	-39.01	752.6	2381	21002	-	-	
Monolayer, $n_m(\mu mols/g)$	0.135	0.221	0.257	0.223	0.227	0.134	
r^2	0.9950	0.9999	0.995	0.9999	0.9835	0.9737	
Surface Area (\mathring{A}^2)	2.76e21	4.53e21	5.28e21	4.58e21	4.67e21	2.75e21	
Surface Area (m^2/g)	135	221	258	223	227	134	

Table 4.5: Table of characteristic parameters from BET, Langmuir, and ESW models. For sorption and desorption of toluene on Carbopack surface. Surface area Carbopack was calculated from both sorption and desorption isotherms.

Table 4.5 shows fitting functions and the calculated parameters for the three models studied. The slope, intercept and the interaction parameters are model dependent. The comparable values are monolayer concentration, correlation coefficients, and surface area. The monolayer range is $0.134-0.257 \ \mu mols/g$ and corresponding surface area between 134 and 258 m^2/g . The most reliable (with $r^2 = 0.9999$) surface area was obtained from the Langmuir and BET desorption isotherms, where more data points were available. This average surface area may be reported as $222.5 \ m^2/g$ of Carbopack. This is in sharp contrast to the manufacturer value of $100 \ m^2/g$ obtained by nitrogen gas adsorption. The higher values is due to the stronger intermolecular forces with toluene compared to that of N_2 with Carbopack. The optimum geometry and intermolecular forces are further examined in the molecular modeling section with SWCNT as the sorbent.

4.4 Discontinuous Vacuum Extraction Headspace Gas Chromatography (DVE-HSGC) of n-Alkylbenzenes in Equilibrium with SWCNT

The process of DVE-HSGC is described earlier. The purpose of the technique is to obtain desorption isotherm of solute in equilibrium with a substrate at progressively reduced concentration to a very low vapor phase concentration which obeys Henrys law near infinite dilution. At infinite dilution both in gas and solid phases the solute-substrate interaction becomes dominant and there is no solute-solute interaction. For a solute-solid system this concentration is below the monolayer sorption i.e., the submonolayer region. The experimental methodology described here, however, could be used to desorb solutes from multilayer to monolayer to submonolayer. Thus a progressive desorption can be studied throughout the isotherm by DVE-HSGC. Generally, the experiment starts with a known amount of solute in the cell containing the substrate followed by vacuum extraction-desorption in steps until very low concentration of solute remains in vapor phase to the limit of detection. This way a large number of very precise desorption data could be obtained mostly in the submonolayer region. Our experiment was performed in this manner where 25 μL of n-alkylbenzene mix was injected in the sample cell, followed by 30 minutes of equilibriation time and fifty 200 second vacuum purges. Table 4.6 shows the basic parameters and some initial values used to calculate desorption isotherms, fractional surface area coverage by molecular species, and thermodynamic constants as described earlier.

A plot of the raw peak area data yielded by the eHSGC is shown in Figure 4.8 where the system was held in equilibrium at 298.16 K. 50 extractions and samplings were made at equilibrium, yielding the plot. Concentrations of each solute begin at a maximum and decrease as the cell is purged and solute is desorbed from the surface of the SWCNT. The data after first few points (10 points) appear to follow the known isotherms and obey Henrys law. An example of Henrys law plot for benzene on SWCNT is shown in Figure 4.9.



Figure 4.8: Plot shows peak area due to equilibrium vapor concentration after vacuum desorption steps.



Figure 4.9: Henrys Law plot of benzene on SWCNT surface shows that mmols on surface are directly proportional to partial pressure.

Table 4.6: List of parameters used for the calculation of desorption isotherms of n-alkylbenzenes from SWCNT. Other parameters: cell volume 35.987 mL, weight of sorbent (SWCNT) 0.1008 g, temperature 298.16 K, gas constant 8.314472 J/(mol-K). bExtraction slopes were obtained from a separate experiment with 25 μL mixture of n-alkylbenzenes vaporized in cell in absence of sorbent. Twenty (20) vacuum extractions were performed for 200 s each and HSGC were done after 15 minute equilibrium times in between.

List of Parame-	Unit	Benzene	Toluene	Ethylbenzene	n-Propyl	n-Butyl
ters					Denzene	benzene
Vapor pressure of pure solute, P_o	atm	0.12523	0.03746	0.0125	0.0045	0.00142
Pure vapor molar conc, M_p	m mols/L	0.005115	0.0015302	0.0005106	0.00018383	5.8009e-5
Area due to	area	118411111	36600420	14291060	6416170	3344182
pure vapor/pure liquid, A_o						
Calc. response factor for solute, R	(mols/L)/area	4.320e-11	4.181e-11	3.573e-11	2.865e-11	1.734e-11
Peak Area at	area	3786517	604906	273316	499617	760203
zero extraction, A_z						
Mols of solute	mols	7.125e-5	4.7773e-5	3.733e-5	3.1353e-5	2.5418e-5
in cell before ex-						
traction, n_t						
Density of so- lute, d	g/mL	0.87	0.89	0.92	1.1	1.3
Surface area of	\mathring{A}^2	33.8	34.3	41	45	48
solute, S_a						
Molecular	g/mol	78.12	92	106	120.2	134.22
weight of solute, MW						
Molar volume of	$\mathrm{mL/mol}$	89.7931	103.3708	115.2174	109.2727	103.2462
solute, V_{mi}						

Weight of so- lute before ex-	g	5.5667e-3	4.3953e-3	3.9578e-3	3.7687e-3	3.4116e-3
traction started						
Extraction	$\ln(area)$	-0.2070	-0.1142	-0.0708	-0.0606	-0.0517
slope, k	/extr					
	num					

Figure 4.10A shows the mmols of solute left on the surface after the vacuum extraction desorption step. The amount left on the SWCNT surface is equivalent to the amount sorbed under the same partial pressure of the solute. The calculation of the amount left on the surface is described in the experimental section. However, with a discontinuous desorption one needs the extraction slope for each solute. The extraction slope was found by a separate experiment where no sorbent was present and the DVE-HSGC was performed. The rate of change of peak area vs. number of extractions assumed to follow a first order process if the vacuum extraction is reproducible. The calculated slopes are shown in Table 4.6. Figure 4.10A shows that the larger n-alkylbenzene sorption amount changes slowly compared to that of smaller ones i.e., the smaller n-alkylbenzenes readily sorb and desorb. The difference in cohesive intermolecular forces makes the difference in affinity for SWCNT.



Figure 4.10: A. Plot of mmols of benzene, toluene, ethylbenzene, n-propylbenzene and nbutylbenzene remained on surface per g of SWCNT as a function of headspace partial pressures. B. The same for n-butylbenzene on SWCNT.

Figures 4.11, 4.12, and 4.13 show the Langmuir, BET, and the ESW plots for all five solutes over the entire pressure range. They show excellent agreement with the theories. The linearity is even better with a correlation coefficient $r^2 > 0.999$ at solute fugacity ($p/p_s < 0.006$ i.e, the submonolayer region). This is indicative of sorption of one type of site. A closer examination at higher fugacity (less than 0.006) shows another straight line with a possible second type of site on SWCNT. Though not very distinct, the two sorption sites can be speculated form the experiment. This could be resolved through the use of molecular modeling and a hypothesis can be reasonably made regarding the sites.



Figure 4.11: A. Except for benzene, all other solutes obeyed Langmuir sorption isotherm with excellent correlation $(r^2 > 0.9998)$ as seen by the Langmuir modeled n-alkylbenzenes on SWCNT solid. B. At low relative pressure (< 0.006) region all solutes show Langmuir isotherm behavior with excellent correlation



Figure 4.12: A. BET plots of n-alkylbenzene on SWCNT at relative pressure. B. BET plots of n-alkylbenzene on SWCNT at relative pressure <0.006.



Figure 4.13: A. ESW plot of benzene, toluene, ethylbenzene, n-propylbenzene, and n-butylbenzene solutes on SWCNT surface. Change in chemical potential is plotted versus mols on the surface. B. Individual ESW plot of n-butylbenzene on SWCNT shows a clearly defined slope on a smaller x-axis.

A major assumption of the models is that all sites on the surface have the same binding affinity. While easier for calculations, this assumption is not always accurate and it is important to note when it is not the case. Of the solutes, benzene is seen to deviate the most from the solutes trends. As it is the first member of the homolog series, this is not unexpected. Table 4.7 shows the slope, intercept, the interaction terms, the monolayer concentration (n_m) , and the fractional surface area of SWCNT for the solute.

Benzene							
ESW BET Langmuir							
Slope	-460.54	40629	40918				
Intercept	122.87	-0.1836	-0.7099				
Interaction, C	-2.300e53	-221289	-4.09e6				
Monolayer, n_m	2.189e-7	2.461e-5	2.425e-4				
r^2	0.9886	0.9916	1.0000				
Area, \mathring{A}^2	6.446e18	7.249e20	7.141e21				
Area, m^2/g	0.63952	71.916	71.408				

Table 4.7: The series of tables show the graphical linearization data from the plots viewed in Figures 4.11-4.13, featuring slope, intercept and r^2 values. In addition, the monolayer concentration, n_m , (mmols/g) and surface area in \mathring{A}^2 and m^2/g .

Toluene						
	ESW BET Langmu					
Slope	-3.464	21311	20749			
Intercept	10.849 17.464		19.212			
Interaction, C	-51482	1221.3	2906.1			
Monolayer, n_m	2.909e-5	4.689e-5	4.781e-4			
r^2	0.9889	0.9996	0.9992			
Area, \mathring{A}^2	6.011e20	9.686e20	9.878e21			
Area, m^2/g	59.637	96.092	98.776			

Ethylbenzene							
	ESW BET Langmuir						
Slope	-11.79	27313	26903				
Intercept	13.665	3.749	4.848				
Interaction, C	-860268	7286.99	216945				
Monolayer, n_m	8.549e-6	3.632e-4	3.688e-4				
r^2	0.9890	0.9916	1.0000				
Area, \mathring{A}^2	2.15e20	9.14e20	9.14e21				
Area, m^2/g	21	91	91				

n-Propylbenzene				
	ESW	BET	Langmuir	
Slope	-69.921 32518 3		32200	
Intercept	31.035	-0.0134	0.3929	
Interaction, C	-3.008e13	-2426715	1.836e6	
Monolayer, n_m	1.44e-6	3.075e-5	3.081e-4	
r^2	0.9985	0.9916	1.0000	
Area, \mathring{A}^2	3.9e19	8.4e20	8.4e21	
Area, m^2/g	4	83	84	

n-Butylbenzene				
	ESW	Langmuir		
Slope	-469.54	40629	40918	
Intercept	122.87	122.87 -0.1836 -0.7		
Interaction, C	-2.300e53	-221289	-2.425e-4	
Monolayer, n_m	2.189e-7	2.461e-5	2.425e-21	
r^2	0.9886	0.9916	1.0000	
Area, \mathring{A}^2	6.4e18	7.2e20	7.1e21	
Area, m^2/g	0.6	72	71	

As discussed earlier, at lower pressures, where the amount of solute is below the monolayer threshold, the assumptions made by the BET and Langmuir are most applicable. Here, infinite dilution is most closely modeled and the calculations show fewer deviations from linearity. The slope of the best fit lines increase as the solute size increases. The absolute value of the slope indicates the degree of affinity to the SWCNT surface where a higher value means a higher affinity. The same applies to the interaction constant, C, derived from the models. The monolayer concentration and the surface area calculated from this are very consistent with Langmuir and BET models for all solutes. The same calculated from ESW model is much lower in value and not consistent. The ESW plots the natural log of change in chemical potential as a function of mols on the surface, which is very different from the BET and Langmuir models. While not relying on assumptions of ideal conditions, like BET and Langmuir, the ESW model assumes that the lowest amount of change in chemical potential corresponds to the exact monolayer coverage on the surface. However, if no monolayer coverage is ever fully achieved by a solute, then the assumption condition is not satisfied and the model does not reflect true conditions in the sample cell. In this case, the minimum is simply the maximum change in excess surface work, which is less significant without the monolayer meaning. However, given linearity of the ESW model, it is viable and useful to extract free energies of sorption in the submonolayer region. It shows that n-butylbenzene has the highest affinity for the surface, consistent with the other models and data. Like the other models, the ESW model shows as the molecular weight increases, the affinity for the SWCNT surface increases.

The surface area of SWCNT occupied by each solute is shown in Table 4.7 and recompiled into Table 4.8 for clarity. It has been proven that surface concentrations are in the submonolayer region and obeyed Henrys law. Therefore, with 5 different solutes simultaneously binding to the surface without interacting with each, only the SWCNT surface, a complete monolayer of individual solutes is not likely to occur. Therefore, the surface area calculated from this study should be considered the fractional surface area occupied by the solutes. The sum of the fractional surface area, therefore, should be approximately equal to total surface area of SWCNT. The Langmuir and the BET models yield 456.2 m^2/g and 466.9 m^2/g , respectively. The reported BET- N_2 surface area is 400 m^2/g . In contrast the ESW gave a much lower surface area value 179.6 m^2/g , which indicates a weakness of the model. Deviations from the 400 m^2/g could be attributed to the sorption on impurities within the SWCNT sample as the solid is only 75% pure. In addition, the simplification of modeling the solutes as spheres is an introduction of error that could explain the inflated surface area value. The alkyl substituents on the benzenes do not yield a perfectly spherical global molecule and the longer the alkyl chain, the more deviation is introduced. This study shows that a meaningful surface area can be obtained from Langmuir and BET isotherms from the submonolayer sorption- desorption data. Experimentally, this is possible by DVE-HSGC. This is probably the most novel application of the technique.

Solute	ESW	BET	Langmuir	
Benzene	90.84	112.96	120.68	
Toluene	62.9	9 96.1 98.8		
Ethylbenzene	21 91		91	
n-Propylbenzene	4 84		84	
n-Butylbenzene	0.6	72	71	
Total	179	456	466	

Table 4.8: Table of fractional surface area measured in m^2/g with benzene, toluene, ethylbenzene, n-propylbenzene and n-butylbenzene sorption on SWCNT by using BET, Langmuir and ESW isotherm model.

Table 4.8 shows that as the molecular weight increases, the fractional surface coverage of SWCNT decreases. This is consistent with the sorption plot that shows a decreased presence of larger solutes. The fractional surface areas are seen to decrease as the length of the alkyl chain substituent increases. This is depicted in Figure 4.14, for BET and Langmuir models. The larger the n-alkylbenzene, the higher the affinity for the SWCNT is displayed. With the removal of benzene, the first in the homolog series, an even better linear correlation is observed. The slope and the intercept of the line give the fractional surface coverage by a $-CH_2$ group (ca. 20 m^2/g) and the benzene ring (ca. 115 m^2/g) on SWCNT.



Figure 4.14: Figure plotting the partial surface area value versus the length of alkyl substituent on the n-alkylbenzene solute. Lower amounts are present on the surface as the length of the alkyl chain increases.

4.5 Molecular Mechanics and Molecular Modeling of Non-Covalent Interactions Between n-Alkylbenzene and SWCNT

Molecular modeling and mechanics are a good way to understand the structural and thermodynamic information for any molecular interactions due to the limitations of observing single molecule interactions directly. Here, we examined the interaction of n-alkylbenzenes and a model SWCNT to understand the noncovalent interactions.

Spartan, a user friendly molecular modeling and chemical computational software program designed by Wavefunction, Inc., draws molecules, performs quantum and classical mechanical calculations and provide spectral, transition state, thermodynamic, and a variety of other information on a given compound or atom. Energy calculations of the n-alkylbenzene solutes used (benzene, toluene, ethylbenzene, n-propylbenzene, n-butylbenzene) were performed using Hartree-Fock 3-21G quantum mechanical parameters to characterize the solutes. The resulting data is listed in the table below where the weight is given in amus and based on the atomic composition of the compound. The volume and area of the solutes, measured in Å, are calculated from the space-filling model that includes both nucleus and electron cloud. The heat, expressed in KJ/mol, describes the heat of formation and is calculated based on the energy required for the individual atoms to form the molecule. The energy, in au, is the value of the Gibbs Free energy of the molecule. [37]

Table 4.9: Table of properties and thermodynamic data of benzene, toluene, ethylbenzene, n-propylbenzene and n-butylbenzene as computed by Spartan software using the Hartree-Fock 3-21 G basis set.

	Benzene	Toluene	Ethylbenzene	n-Propylbenzene	n-Butylbenzene
Weight, amu	78.114	92.141	106.168	120.195	134.222
Volume, \mathring{A}^3	99.17	117.37	135.70	154.01	172.33
Heat, KJ/mol	78.31	46.47	23.98	1.61	-19.62
Area, \mathring{A}^2	115.00	134.81	154.81	174.85	194.90
Energy, au	-229.419	-268.239	-307.057	-345.876	384.695
Dipole Moment, debye	0	0.33	0.30	0.32	0.36

Corresponding to the table, models and electrostatic potential maps of the solutes are given below, demonstrating the rings electron resonance and the alkyl group hydrophobicity. The electrostatic potential map created in Spartan is an electron density surface of a molecule where colors correspond to numerical values of electrostatic potential. Red indicates a high negative potential and blue signifies a strong positive potential. Neutral or hydrophobic behavior would be seen as green. [37] This provides qualitative details to characterize the interaction with the SWCNT.



Figure 4.15: Stick and ball and electrostatic potential maps of benzene, ethylbenzene, toluene, n-propylbenzene and n-butylbenzene; made in Spartan.

In addition, the dipole vectors of toluene and ethylbenzene are placed below, detailing further forces at play that could impact the alkylbenzene interactions. As a hydrophobic side chain is present, the benzene electron delocalization moves creating a small dipole. This parameter is used qualitatively to help understand the interaction.



Figure 4.16: A. Toluene dipole modeled in Spartan. B. Ethylbenzene dipole modeled in Spartan.

A 1.1 nm diameter single walled carbon nanotube was modeled in Spartan by forming a graphene sheet and connecting the ends through carbon-carbon sp hybridized bonds. The 11 \mathring{A} diameter SWCNT model corroborated the experimental results that binding affinity increases as the alkyl chain substituent of the aromatic ring increases through the use of the Energy Minimization function, seen in Table 4.10. The program function provided a sorption mechanism as well.

Spartans energy minimization function takes a molecule or system designed by the user and arranges it into a low energy preferred conformation within a few seconds. It is not computationally rigorous, based on classical mechanics and produces a low energy arrangement that may or may not be the total lowest energy state of that molecule or system. [38] Commonly, this function gives a local energy minima and not the global energy minimum, but a low energy state is presented. Calculations can be determined of the computed arrangement and quantified which is detailed below. Upon performance of the energy minimization function, all alkylbenzenes placed at the mouth of the CNT were pulled inside of the tube as shown in the screenshots of Spartan below.



Figure 4.17: Before (A) and after (B) screenshots of the performance of the energy minimization function in Spartan of ethylbenzene and the 1.1 nm SWCNT. The ethylbenzene placed at the mouth of the tube is pulled inside of the CNT.

The molecular mechanics basis set, or set of parameters used to complete the given computations, only uses classical mechanics in its calculations, making it less rigorous than quantum mechanical parameters based on the Schrodinger equation. Classical mechanics rigidly models atoms as balls and bonds as sticks or springs and calculates energies based on Newtonian physics and the electrostatics of the charged particles. This model has long been established as incomplete as it does not account for the subtleties that occur at the subatomic level. However, given the limitations of current technology, larger molecules and systems, more than a couple of atoms total, such as proteins or carbon nanotubes, are restricted to these types of basis sets. [39] Granted the complexity and size of such systems, this model has been demonstrated to be useful [37]
in computational models and is regularly utilized. The Gibbs free energy values found through molecular mechanics calculations in Spartan are recorded below, where the global energy decreased approximately 30 kJ/mol more when butylbenzene was inside the SWCNT versus benzene, that has comparatively very little hydrophobic behavior.

Table 4.10: A table created from Gibbs Free energy values of single alkylbenzene interactions with a 1.1 nm SWCNT obtain in Spartan. The energy decreases as the alkyl chain substituent increases.

Energy, KJ/mol	Net Energy Difference, KJ/mol
6623.16	2.28
6620.75	4.69
6608.93	16.51
6596.25	29.19
6590.72	34.72
	Energy, KJ/mol 6623.16 6620.75 6608.93 6596.25 6590.72

To visualize the computed Gibbs free energy results of the n-alkylbenzene interactions with the CNT, as listed above, a graph was constructed. A distinct linear relation is demonstrated as a saturated carbon group is added to the alkyl chain substituent. The energy decreased linearly as the alkyl chain substituent length increased. Qualitatively this is also observed experimentally that larger solute has higher affinity for the surface.

The experimental values are on the same level of magnitude as the corresponding computed ones. This is seen in the graph below.



Figure 4.18: Graph showing the desorption energy found experimentally (points in red) with that of computed desorption energies of solutes within the SWCNT (in blue).

Length of the CNT did not have a measureable effect on the Gibbs free energy values obtained computationally. This was confirmed by varying the length of the CNT while keeping the diameter constant, and obtaining the energy values. The standard deviation of the values was calculated to be 0.06 nm. To determine the interactions that occur when the alkylbenzene is placed in positions other than the mouth of the carbon nanotube. The alkylbenzenes were placed on top of the carbon nanotube in various conformations, such as the benzene ring perpendicular to the tube or parallel, and then energy minimized. Universally, the low energy conformations yielded the aromatic ring approximately 4 angstroms away from the CNT with the alkyl groups in various positions, an example is pictured below.



Figure 4.19: An image of ethylbenzene sorbing to the exterior of a 1.1 nm diameter SWCNT.

Some alkyl groups would curve with the circumference of the tube in a hugging fashion. Others would snake down the length of the tube, parallel, approximately 4 angstroms away. Reproducible and meaningful energy values were not obtained with n-alkylbenzene interactions on the exterior of the CNT, most likely due to lack of success reaching a global minimum. The n-alkylbenzenes likely arranged in local minimum conformations, not providing a clear description of n-alkylbenzenes external interactions with the SWCNT. This study shows that there are at least two major sorption sites, one inside the tube and other on the surface. Experimentally, this is consistent with Langmuir and BET isotherm plots having two straight line sections representing two distinct sites. Further studies using Spartan, this can easily be resolved, as the program is capable of obtaining the information.

To gain further insight into the nature of noncovalent interactions, the electrostatic potential map of the SWCNT was then obtained through the same molecular mechanics computational model basis set. The electrostatic potential values which are translated to colors, are derived from Coulombs Law. The electrostatic potential map demonstrates the distribution of charge and thus electron density inside and out of the 1.1 nm diameter SWCNT. Comprised of benzene-like rings, electron delocalization is expected and shown in the figure below.



Figure 4.20: Spartan created electrostatic potential map of 1.1 nm diameter SWCNT, where an uneven electron density distribution is seen inside and outside of the tube. The strongest negative charge is seen inside of the tube (colored red) rather than on the exterior.

Electrostatic potential maps were obtained of the same SWCNT pictured previously along with n-alkylbenzenes placed inside and on top. The distinct negative charges observed largely disappeared with any addition of an alkylbenzene. Screenshots of the Spartan models follow where the green color, signifying a neutral charge, dominates. The change in color from orange/yellow/red negative charge to a general green appearance and hydrophobic is fairly unexpected. However, the increase in hydrophobicity could explain the increased affinity for the more hydrophobic solute, further illuminating n-alkylbenzene interactions with the SWCNT.



Figure 4.21: Spartan electrostatic potential maps of 1.1 nm diameter CNT interacting with n-propylbenzene on the exterior. The green color indicates hydrophobicity.

Chapter 5: Conclusion and Future Research

5.1 Conclusion

Carbon nanotubes are a hot research topic and new applications are being discovered every day, such as use as a gene transfer biomedical device [40] to be utilized in gene therapy or a thermoelectric power generator designed by the Department of Energy that captures and uses waste heat. [41] Nanotechnology itself is an exploding field of study and more quantitative understanding about the specific mechanisms and thermodynamics of the materials in play is vital to field advancement. This experiment yielded a more efficient method to analyze volatile sorption and desorption on a solid surface given eHSGC instrumentation and application of an effective isotherm model in order to analyze the data. This end was successfully achieved. The preliminary toluene sorption and desorption on carbopack experiment demonstrated method viability which was then utilized to analyze n-alkylbenzenes on single walled carbon nanotubes. Specific analysis of five n-alkylbenzene solutes desorbed from TUBALL single-walled carbon nanotubes was accomplished and used to calculate the surface area of the SWCNT. Through the three isotherm methods, Langmuir was observed to give the most accurate experimental surface area value of 456.2 m^2/g , compared to the manufacturer given value of 400 m^2/g , determined by nitrogen gas adsorption plotted on a BET isotherm model. Of the solutes, n-butylbenzene was seen to have the highest affinity as only $0.0021 \ mmodel{mmodel} mmodel{mmodel} g$ were desorbed from the carbon nanotube. The volume desorbed from the surface increased as the saturated alkyl group substituent length decreased, where benzene was seen to desorb $0.3469 \ mmols/g$ from the surface. These experimental results were further verified using Spartan software which computationally determined, using classical mechanic modeling, a linear decrease in Gibbs Free Energy as the molecular weight and hydrophobicity of the solute increased. A mechanism for n-butylbenzene sorption inside of the SWCNT was also proposed by Spartan energy minimization functionality.

This study has provided a method to research single-walled carbon nanotube interactions with a variety of volatile solutes simultaneously that can quickly and quantitatively investigate SWCNT or a multitude of other adsorbates. With a fundamental understanding of promising new materials such as carbon nanotubes, more novel applications can be devised and technology, on a nano and macroscale, can be advanced.

5.2 Future Research

To obtain a better understanding of n-alkylbenzene interactions with single walled carbon nanotubes and confirm this thesis findings, rigorous quantum mechanical based computational molecular modeling can be completed as a secondary check to the interaction mechanism amongst the sorbate and sorbant found by Spartan. While it is possible that the n-alkylbenzenes sorb inside of the SWCNT, the mechanism and arrangement of the n-alkylbenzenes on the exterior of the CNT is still unknown. Powerful modeling software such as Gaussian or Visual Molecular Dynamics (VMD) and the use of computer clusters that provide a great deal of computing power, can model the system in a more complete way that can illuminate the interactions in question. Thermodynamic information would also be fully described by a more rigorous too. Further computational studies regarding other solutes can be investigated as well. In addition to computational studies, completing another experiment with a hydrocarbon mix of hexane to decane mix as solutes on the SWCNT surface would be ideal. In this experiment, the sorption and desorption occurring will only have London Dispersion Forces, thus detailing the weakest intermolecular force attractions of SWCNT.

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Biography

I am a robot.