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# Thermodynamic and Kinetic Characterization of Porous Graphitic Carbon in Reversed-Phase Liquid Chromatography

By

Yuening Zhang

A THESIS

Submitted to Michigan State University In partial fulfillment of the requirements For the degree of

MASTER OF SCIENCE

Department of Chemistry

### Abstract

### THERMODYNAMIC AND KINETIC CHARACTERIZATION OF POROUS GRAPHITIC CARBON IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

By

### Yuening Zhang

In this dissertation, the thermodynamics and kinetics of solute transfer for alkylbenzenes and methylbenzenes on porous graphitic carbon were studied.

In the thermodynamic studies, the retention factor increases with an increase in the number of methylene or methyl groups. The data indicate that increases in the number of methylene or methyl groups result in more negative changes in molar enthalpy ( $\Delta H_{sm}$ ). Hence, the transition from mobile to stationary phase is a more energetically favorable exothermic process with each methylene or methyl group added. The data also show that the change in molar volume ( $\Delta V_{sm}$ ) is close to zero, which indicates that the solute molecules adsorb on the surface of porous graphitic carbon during retention.

In the kinetic studies, the rate of solute transfer increases with increasing number of methylene and methyl groups. The activation enthalpy from the stationary phase to transition state ( $\Delta H_{\pm s}$ ) was found to increase with increasing number of methylene and methyl groups. But the activation enthalpy from the mobile phase to transition state ( $\Delta H_{\pm m}$ ) was much smaller than  $\Delta H_{\pm s}$ . The volume barriers  $\Delta V_{\pm s}$  and  $\Delta V_{\pm m}$  again are very close to zero.

These results provide a thorough and detailed characterization of the retention mechanism for porous graphitic carbon, which is based on adsorption.

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# **Chapter 1: Introduction and Background**

High-performance liquid chromatography (HPLC) is one of the most widely used techniques in the analytical sciences. By relying on the subtle interplay of solute interactions with mobile and stationary phases, HPLC is capable of separating a variety of complex mixtures, including neutrals, charged species, enantiomers, and biological materials. However, to separate a wide range of sample types, different stationary phases are often required. During the past few years, there has been an intense search for new adsorbents because of the rapid proliferation of HPLC and the realization of the disadvantages of most commonly used silica-based materials.

Porous graphitic carbon (PGC) is a two-dimensional graphite with a unique sponge-like structure, which gives it good mechanical strength while maintaining an adequate surface area (around 150 m<sup>2</sup>/g) and porosity (around 80%) [1]. Porous graphitic carbon has unique chromatographic properties, being the only truly hydrophobic adsorbent. It shows strong retention of non-polar, polar, and ionic organic compounds as well as novel stereoselectivity. It gives chromatograms of high efficiency.

This chapter presents a description of the PGC stationary phase that was used in this study, as well as the relevant thermodynamic and kinetic theory.

# **1.1 Porous Graphitic Carbon (PGC)**

#### **1.1.1 Structure and Method of Preparation**

There are, in fact, three distinct forms of carbon to which the term "graphitic" can reasonably be applied and which have well-defined crystal

structures. Two of these forms are shown in Figures 1.1 and 1.2. The Bernal structure of perfect three-dimensional graphite consists of layers of carbon atoms, organized in a hexagonal array and ordered ABABAB.... This form of graphite is termed hexagonal graphite. A second, rarer form of three-dimensional graphite, the Lipson and Stokes form, also exists, but here the layers are ordered ABCABC.... This is termed rhombohedral graphite. In both crystalline forms, the layer spacing is 3.354 Å and the atomic spacing within the layer is 1.42 Å.

Most synthetic carbons, when heated to about 3000 °C, assume the second structure shown in Figure 1.2. This is two-dimensional graphite in which graphitic sheets are randomly oriented relative to one another. In two-dimensional graphites, the layer spacing is slightly greater than in three-dimensional graphites at 3.40-3.43 Å, and the atomic spacing within the layers is slightly less.

The template required for the production of PGC should be a well-bonded silica gel of high porosity. The spherical silica is specially prepared and has a pore volume of 1.4 cm<sup>3</sup>/g with a specific surface area of 50 m<sup>2</sup>/g. The mean particle size diameter is 7  $\mu$ m. This template is impregnated with a melt of phenol and hexylamine in a 6:1 weight ratio. The impregnated material is heated gradually to 150 °C to form phenol-formaldehyde resin within the pores of the silica gel.



Figure 1.1: Atomic structure of graphite: Bernal structure of perfect three-

dimensional graphite with ABAB... layer registration [1]



**Figure 1.2:** Atomic structure of graphite: Warren structure of two-dimensional turbostratic graphite with no layer registration [1]

This silica-polymer is then heated slowly to 900 °C in a stream of oxygenfree nitrogen in a specially designed rotary furnace. Approximately 50% of the weight of the polymer is thereby lost, and the density of what remains is increased to about 2 g/cm<sup>3</sup>. The silica-carbon particles are then treated with hot aqueous potassium hydroxide to dissolve the silica template. The remaining porous glassy carbon has a BET (Brunauer-Emmet-Teller) surface area of 450-600 m<sup>2</sup>/g and a pore volume of 2.0 cm<sup>3</sup>/g, corresponding to a particle porosity of about 80%. This carbon is then heated to 2500 °C in oxygen-free argon. The final carbon has a surface area of about 150 m<sup>2</sup>/g and a pore volume similar to that of the carbon before high-temperature treatment. The carbon retains the spherical form and the particle size of the original silica template [1].

#### **1.1.2** Physical and Chemical Properties

The structure of the porous carbon has been studied in detail by X-ray diffraction, electron diffraction, scanning electron microscopy, and high-resolution electron microscopy. These techniques provide a self-consistent picture.

The scanning electron micrograph in Figure 1.3 clearly shows the spherical shape of the particles and their sponge-like structure [1]. The strong sponge-like structure is capable of withstanding considerable shearing forces, such as those met with in high-performance liquid chromatography. Figure 1.4 is the high magnification of the surface [1]. The porous two-dimensional graphite (PGC) consists of 3-10  $\mu$ m spherical particles.

Figure 1.5 is the transmission electron micrograph of a spherical particle of PGC. Figure 1.6 shows the high-resolution electron micrograph (HREM) of PGC



Figure 1.3: Scanning electron micrograph: Spherical particle of PGC

(black band represents 2 µm) [1]



Figure 1.4: Scanning electron micrograph: High magnification of surface

(white horizontal line represents 400 nm) [1]



Figure 1.5: Transmission electron micrograph: Spherical particle of PGC





after heating to 2500 °C [1]. Particularly notable are the straight, parallel lines, indicating ordered graphitic sheets. Also seen are a number of rounded corners and several groups of curved or bent sheets. There is also some evidence of surface defects.

The high-resolution electron micrograph (HREM) indicates that PGC consists of intertwined ribbons of carbon, where each ribbon consists of some 30 discrete layers or sheets about 3.4 Å apart. It is this ribbon form that accounts for the high mechanical strength of PGC. The crystallites comprise tens of layers of graphitic sheets, thus giving stack heights of 30-60 Å, in agreement with the X-ray evidence.

Carbon in the form of graphite is one of the most attractive packing materials for HPLC, as it should be free from the disadvantages peculiar to silica gels, such as the limited pH of the mobile phase and the strongly adsorptive silanol groups. The reason is the following. Pure graphite is a crystalline material made up of sheets containing hexagonally arranged carbon atoms linked by the same conjugated 1.5-order bonds that are present in any large polynuclear aromatic hydrocarbon. There are, in principle, no adventitious functional groups on the surface because the aromatic carbon atoms have all valencies satisfied within the graphitic sheets. Perfect graphite is therefore an intrinsically reproducible material with a completely uniform surface, free from any functional groups.

Furthermore, graphite is one of the most unreactive substances known and can withstand any mobile phase that will not attack the HPLC equipment itself.

Problems, however, may arise when a material of high specific surface area is required. Surface defects must therefore be present at the edges of such crystallites and the ideality of bulk graphite is lost to some extent. However, it is still possible to provide high-surface-area graphites with minimal adventitious surface groups. As an example, a square array of graphitic carbon atoms with a side of 10 nm will contain 40,000 C atoms, of which 160 will be at the edge of the sheet. The edge atoms will thus comprise about 0.4% of the total C atoms.

In fact, characterization using X-ray photoelectronic spectroscopy (XPS) of the graphitic carbon spheres detected only the C(1s) band, pointing to a surface devoid of any appreciable oxygen-containing functionalities (estimated detection limit, 0.2 atomic %) [2]. If these oxyen-containing functionalities are present, they will produce much stronger retention for the solutes than graphitic carbon.

#### **1.1.3 Applications of PGC in Separations**

There are several main factors that influence retention by graphite in HPLC [3].

#### 1. Mobile phase-solute attraction

These attractive interactions include dispersion, dipole-dipole, dipole-induced dipole, ion-ion, ion-dipole, ion-induced dipole, and hydrogen bonding forces. These interactions discourage retention by keeping the solute in the mobile phase.

#### 2. Mobile phase-solute repulsion

These repulsive interactions arise from disruption of the structure of the hydrogen-bonded mobile phase by non-hydrogen-bonding solutes. These

hydrophobic interactions occur between an aqueous or aqueous-organic mobile phase and any nonpolar segments of the solute. These interactions encourage retention by expelling the solute from the mobile phase.

#### 3. Stationary phase-solute interaction

These interactions arise from dispersion forces of the London type between the graphite surface and the solute. These interactions are balanced to a greater or lesser extent by similar interactions between the graphite surface and the mobile phase. The net effect may either encourage or discourage retention, but may have an important effect on selectivity.

In addition, charge-induced interactions between the stationary phase and solute can promote the retention of polar compounds. These charge-induced interactions are strongest when the polar groups of the solute are forced into direct contact with the graphite surface by the stereochemistry of the solute molecule. In such cases, the additional interactions resulting from a polar group can be so strong that they more than compensate for the increased solute-mobile phase interactions. When stereochemistry does not force direct contact of the solute surface, the effect is less strong but still significant.

The overall effect of these competing interactions is that an increase in the hydrophobicity of the solute, say by adding alkyl groups, always increases retention, as expected in a typical reversed-phase mode. However, an increase in the polarity of the solute by adding groups that can either donate or accept electrons or can polarize the graphite surface may also increase retention,

particularly if these groups are constrained to be in close contact with the graphite surface.

Porous graphitic carbon shows separations of nonpolar organic compounds [4], highly polar organic compounds [5], geometric isomers [6], and ionized organic compounds [7]. Porous graphitic carbon has proven to have a number of unsuspected properties that have substantially enlarged its area of applications and opened up entirely new possibilities.

### **1.2 Thermodynamic and Kinetic Theory**

In order to characterize the solutes undergoing adsorption on the PGC stationary phase, it is necessary to utilize a mathematical system by which they can be compared. The relationships of chemical thermodynamics and kinetics provide such a system. For this purpose, traditional thermodynamic and transition state theories need to be synthesized first.

In Figure 1.7, the retention behavior is depicted by using an energy coordinate diagram when the solute moves from mobile (X<sub>m</sub>) to stationary phase (X<sub>s</sub>). The thermodynamic changes in molar enthalpy ( $\Delta H_{sm}$ ) and molar volume ( $\Delta V_{sm}$ ) represent the difference between the final and initial states. If the molar enthalpy ( $\Delta H_{sm}$ ) is positive, it means the solute gains enthalpy when it transfers from mobile to stationary phase. The chromatographic process is thus unfavorable. Conversely, if the molar enthalpy is negative, the chromatographic process is energetically favorable. If the change in molar volume ( $\Delta V_{sm}$ ) is positive, it implies the solute occupies a larger volume when it is adsorbed on the stationary phase than in the mobile phase. The reverse is true too.



**Figure 1.7**: Energy coordinate diagram depicting the transfer of solute from mobile phase  $(X_m)$  to stationary phase  $(X_s)$  via a high-energy transition state  $(X_{\ddagger})$ . Other thermodynamic and kinetic parameters as described in the text.

The kinetic aspects of the retention behavior are characterized by a fast equilibrium between the mobile phase (X<sub>m</sub>) and transition state (X<sub>t</sub>) with equilibrium constant K<sub>tm</sub>, followed by a rate-limiting step between the transition state and the stationary phase with rate constant k<sub>sm</sub>. The corresponding changes in activation enthalpy and activation volume are represented by  $\Delta H_{tm}$  and  $\Delta V_{tm}$ , respectively.

A similar diagram can be drawn to illustrate the transition from stationary to mobile phase, in which the rate constant  $k_{ms}$ , activation enthalpy  $\Delta H_{\ddagger s}$ , and activation volume  $\Delta V_{\ddagger s}$  are used.

#### **1.2.1 Thermodynamics**

The equilibrium distribution of the solute (X) between mobile (m) and stationary phases (s) can be characterized by

$$X_m \leftrightarrow X_s$$

This process can be mathematically defined by using the equilibrium constant expression

$$K = \frac{a_s}{a_m} \approx \frac{[X]_s}{[X]_m} \quad (1.1)$$

where  $a_m$  and  $a_s$  are the activities, and  $[X]_m$  and  $[X]_s$  are the molar concentrations of the solute in the mobile and stationary phases, respectively.

The physical characteristics of the system in which molecules enter equilibrium is characterized by the phase ratio ( $\beta$ ), which is the ratio of the surface area of the stationary phase ( $A_s$ ) and volume of the mobile phase ( $V_m$ ):

$$\beta = \frac{A_s}{V_m} (1.2)$$

The equilibrium constant and phase ratio are important because they are utilized in the calculation of thermodynamic parameters that characterize solutes as they undergo adsorption.

The retention factor (k) is a function of the retention times of a solute  $(t_r)$  as well as an unretained compound  $(t_0)$ :

$$k = \frac{t_r - t_0}{t_0} \quad (1.3)$$
$$k = \frac{K}{\beta} \quad (1.4)$$

The change in Gibbs free energy ( $\Delta G$ ) can describe whether or not an equilibrium transfer is spontaneous. When applied to the chromatographic process, the Gibbs free energy is an indicator of how favorable is a transition from the mobile to the stationary phase. Traditionally defined as

$$G = H - TS$$
 (1.5)

this equation describes the inherent energy of a molecule in some defined state where H is the enthalpy, T the absolute temperature, and S the entropy. Given that a single molecule in a chromatographic system can exist in one of two mutually exclusive phases, it is necessary to define each phase with its own energy ( $G_m$  or  $G_s$ ). As the molecule equilibrates between these two states, the change in energy ( $\Delta G_{sm}$ ) can be measured. This change is defined by

$$\Delta G_{sm} = \Delta H_{sm} - \Delta (TS)_{sm} (1.6)$$

This energy can be directly related to the equilibrium constant described in Equation 1.1 through the van't Hoff equation:

$$\ln K = \frac{-\Delta G_{sm}}{RT} \quad (1.7)$$

The importance of this equation is that it directly links the equilibrium constant to the Gibbs free energy, thus correlating a molecule's affinity for a given phase to a thermodynamic value that describes how energetically favorable is a transition into that phase.

Instead of K,  $\Delta H_{sm}$  is used as a quantitative measure of the equilibrium event. A relationship between the retention factor (k) and phase ratio ( $\beta$ ) allows for the calculation of  $\Delta H_{sm}$ . By substituting Equation 1.4 into Equations 1.6 and 1.7, the resulting equation is

$$\ln k = \frac{-\Delta H_{sm}}{RT} + \frac{\Delta S_{sm}}{R} - \ln\beta (1.8)$$

Equation 1.8 allows for the calculation of  $\Delta H_{sm}$  from the slope of a graph of ln k vs. 1/T at constant pressure. The assumption within this calculation is that neither  $\Delta H_{sm}$  nor  $\Delta S_{sm}$  are temperature dependent. The intercept contains information about the change in molar entropy as well as the phase ratio. Because it is not known how the phase ratio  $\beta$  changes with temperature and pressure, the change in molar entropy  $\Delta S_{sm}$  cannot be reliably calculated.

In addition to the energetic parameters that describe a system, the change in molar volume ( $\Delta V_{sm}$ ) can also be calculated. When applied to the chromatographic system,  $\Delta V_{sm}$  is the physical change a molecule undergoes as it tranfers from mobile to stationary phase. This transition can be described through a model of solvation. In the mobile phase, a solute molecule is surrounded by a given number of solvent molecules. As the solute transfers into the stationary phase, these solvent molecules may be stripped away. When the transition is complete, the molecule is solvated by the stationary phase molecules if it has partitioned, or has lost some of its hydration shell if adsorbed. As a result,  $\Delta V_{sm}$  is an indicator of physical change as the molecule moves between the mobile and stationary phases.

In order for  $\Delta V_{sm}$  to be calculated, enthalpy must be further defined as a function of the internal energy ( $\Delta E$ ), pressure (P), and volume (V). When using these three fundamental variables of a system, the change in enthalpy ( $\Delta H_{sm}$ ) is defined as

$$\Delta H_{sm} = \Delta E_{sm} + \Delta (PV)_{sm} \quad (1.9)$$

By substituting Equation (1.9) into Equations (1.6) and (1.7), under constant temperature, the retention factor k can be related to the pressure:

$$\ln k = \frac{\left(-\Delta E_{sm} + T\Delta S_{sm} - P\Delta V_{sm}\right)}{RT} - \ln\beta (1.10)$$

Equation (1.10) allows for the change in molar volume to be extracted from the slope of a graph of ln k vs. P at constant temperature by assuming that neither  $\Delta E_{sm}$  nor  $\Delta S_{sm}$  are pressure dependent. Using these graphical methods of analysis, it is possible to quantify the physical change of a solute as it transfers between phases.

Thermodynamics provide a simple method by which physical and energetic properties can be calculated. While the parameters defined above allow for the comparison of solutes, they do not provide insight into the rate at which a given transition may occur. As a result, transitions that may be energetically favorable (i.e. large negative  $\Delta G_{sm}$ ) may be either slow or fast. Since thermodynamics is incapable of describing the rate at which a transfer between mobile and stationary phases will occur, kinetic studies need to be conducted.

#### **1.2.2 Kinetics**

Kinetic theory requires an initial definition of the transitions a molecule undergoes, where  $k_{ms}$  is the rate constant for transfer from stationary to mobile phase and  $k_{sm}$  is the rate constant from mobile to stationary phase. The first step in elucidating kinetic data is the determination of the rate constants. By using the retention factor (Equation 1.3), the rate constants are defined by

$$k_{ms} = \frac{2kt_0}{\tau^2}$$
 (1.11) .  $k_{sm} = kk_{ms} = \frac{2k^2t_0}{\tau^2}$  (1.12)

where  $\tau$  is the exponential component. These rate constants quantitatively define the transfer, thereby allowing for comparison between solutes, mobile phases, and stationary phases. However, a more in depth treatment of kinetics using transition state theory allows for other rate parameters to be calculated.

Transition state theory is an expansion on the kinetic process shown above. The crux of the theory is based upon the existence of a transition state: a short-lived, high-energy state on the reaction coordinate diagram (Figure 1.7), where  $K_{\pm m}$  is an equilibrium constant for the solute from mobile phase to transition state reaction,  $k_{\pm m}$  is a rate constant, and  $X_{\pm}$  is the transition state. This conformation can be defined more clearly by relating the rate constants  $k_{ms}$  and  $k_{sm}$  to transition state energy ( $\Delta E_{\pm m}$ ,  $\Delta E_{\pm s}$ ), enthalpy ( $\Delta H_{\pm m}$ ,  $\Delta H_{\pm s}$ ), and volume  $(\Delta V_{\ddaggerm}, \Delta V_{\ddaggers})$ . To demonstrate the mathematical relationships,  $k_{sm}$  will be used as an example.

In order to calculate the three kinetic parameters, the Arrhenius equation is first used. Defined by the form

$$k_{sm} = A_{tm} exp(-\Delta E_{tm} / RT) (1.13)$$

this equation relates the rate constant to the internal energy necessary to cross the barrier on the reaction coordinate, where  $A_{\pm m}$  is the pre-exponential factor and  $\Delta E_{\pm m}$  is the activation energy. By algebraic rearrangement, the Arrhenius equation becomes

$$lnk_{sm} = lnA_{tm} - \frac{\Delta E_{tm}}{RT} \quad (1.14)$$

Thus,  $\Delta E_{\ddagger m}$  can be calculated from the slope of a plot of ln k<sub>sm</sub> vs. 1/T at constant pressure under the assumption that A<sub> $\ddagger m$ </sub> and  $\Delta E_{\ddagger m}$  are temperature independent.

In order for activation enthalpy to be calculated, a relationship between the energy and the enthalpy must be defined. Given the form

$$\Delta E_{\pm m} = \Delta H_{\pm m} + RT - \Delta (PV_{\pm m})$$
(1.15)

Equation (1.15) directly relates the activation energy to the activation enthalpy at a given temperature and pressure. As illustrated, though, the change in activation volume ( $\Delta V_{\ddaggerm}$ ) as a molecule moves between the mobile phase and the transition state must first be calculated.

Using a similar method to the thermodynamic equations,

$$lnk_{sm} = \frac{\left(-\Delta E_{\ddagger m} + T\Delta S_{\ddagger m} - P\Delta V_{\ddagger m}\right)}{RT} (1.16)$$

 $\Delta V_{\ddagger m}$  is calculated from the slope of a plot of ln k<sub>sm</sub> vs. P at constant temperature. Once again an implicit assumption is that  $\Delta E_{\ddagger m}$  and  $\Delta S_{\ddagger m}$  are pressure independent. As a result, it is possible to calculate the activation enthalpy ( $\Delta H_{\ddagger m}$ ) by using the activation volume and activation energy by means of Equation 1.15.

By using the above method, the thermodynamic and kinetic parameters that characterize the adsorption events in reversed-phase liquid chromatography can be determined in the following chapter.

### **1.3 Previous Investigations of Thermodynamics and Kinetics**

# in Reversed-Phase High-Performance Liquid Chromatography

A number of very unusual separations can be successfully performed with PGC as stationary phase. These separations are difficult or impossible with more conventional reversed-phase materials, such as octadecylsilica (ODS) or polymeric materials. Porous graphitic carbon is thus a totally unique chromatographic material which will, no doubt, be the subject of much further research. At this stage, the retention mechanism on PGC is not well understood. A detailed thermodynamic and kinetic study of the solutes on PGC will help to understand the retention better. Before this, a brief summary of thermodynamic and kinetic studies on conventional reversed-phase materials will be summarized for comparison with PGC.

#### 1.3.1 Thermodynamics

A number of homologous series have been used to study the effect of repeating structural units on chromatographic retention behavior. Such series

have included fatty acids, alkylbenzenes, and polycyclic aromatic hydrocarbons (PAHs). These series can offer a simple relationship between the retention factor (k) and the number of units, such as the methylene ( $CH_2$ ) groups. Early studies showed that an increase in methylene unit number results in a logarithmic increase in the retention factor [8].

The effect of stationary phase chain length was studied by Berendsen and de Galan for a number of solutes with varying methylene unit numbers [9]. The data from their study indicated that there is a critical chain length, beyond which retention does not change. According to the authors, the limiting chain length lies between 6 and 14 carbons for the alkylsilica materials. The critical chain length is independent of mobile phase composition, but increases with increasing length of the solute alkyl chain.

Similarly, Tchapla et al. investigated seven series of alkyl-substituted solutes including alkylbenzenes, alkylchlorides, and carboxylic acids on different stationary phases. They concluded that the solute alkyl chains intercalate into the alkylsilica stationary phase [10].

In addition to studies of retention, the molar enthalpy and molar entropy have also been studied for homologous series. Issaq and Jaroniec calculated the molar enthalpy using Equation 1.8 for alkylbenzenes using binary mobile phases and alkylsilica stationary phases ( $C_1$ ,  $C_4$ ,  $C_8$ ,  $C_{18}$ ) [11]. They concluded that the change in molar enthalpy and molar entropy depend linearly on the number of methylene units in the alkyl chains of the homologous series, not the bonded stationary phases. McGuffin and Chen studied the retention of a series of even-

numbered fatty acids (C<sub>10</sub> through C<sub>22</sub>) not only as a function of temperature, but also pressure [12]. From their experiments, they quantitated the changes in molar enthalpy ( $\Delta\Delta$ H) and molar volume ( $\Delta\Delta$ V) of -3.5 kcal/mol and -14.1 mL/mol, respectively, for methylene units.

In addition to the studies of retention as a function of methylene unit number, series containing phenyl units have also been investigated. Most notably, PAHs have been used since they have repeating phenyl units in different configurations. Whereas alkylated solutes can be characterized as a function of the number of methylene units, PAHs have been studied as a function of ring number, annelation structure (i.e. degree of ring fusion), and planarity [13-16]. Studies have shown that an increase in the ring number leads to a logarithmic increase in the retention factor. An increase in temperature results in a decrease in the retention of PAHs. By contrast, the effect of pressure is much smaller.

McGuffin and Howerton studied the thermodynamics of solute transfer for a series of PAHs as a function of ring number, annelation structure, planarity, temperature, pressure, and bonding density using octadecylsilica (ODS) [17,18]. The data from their study indicated that an increase in ring number results in more negative changes in molar enthalpy ( $\Delta H_{sm}$ ) and molar volume ( $\Delta V_{sm}$ ). For a series of isomers, solutes with condensed annelation structure exhibited less negative changes in molar enthalpy and molar volume than the more linear solutes. Nonplanar solutes demonstrated changes in molar enthalpy and molar volume that are less negative than would be expected based upon ring number alone. These data indicated that the condensed PAHs, as well as the nonplanar PAHs, interacted with the first few carbons near the distal terminus of the ODS phase. But the more linear solutes as well as those with more rings interacted with the more ordered regions of the ODS closer to the proximal terminus.

#### 1.3.2 Kinetics

Although the thermodynamics of retention have been extensively probed, less work has been conducted into the kinetics of retention. Work on kinetics has generally fallen into two classes based on the techniques employed: nonchromatographic and chromatographic.

Nonchromatographic experiments have utilized pressure, temperature, and dipole jump methods [19-24], as well as fluorescence correlation spectroscopy [25,26] to investigate chromatographic materials. However, the inherent difference between these systems and a packed chromatography bed provide limited information about the kinetics of an actual separation. A greater problem is that the temperature or pressure jump actually changes the kinetics of the system, according to Equations 1.14 and 1.16.

To circumvent these difficulties, several chromatographic techniques have been used, including frontal analysis and pulse methods [27-29]. Frontal analysis involves injecting a large concentration of the solute onto the chromatography column, and then analyzing the resultant curve. Also know as a breakthrough curve, this curve provides information about the kinetics of sorption. However, it does not represent the most common type of chromatography, which involves injecting smaller concentrations of material onto the column.

Pulse methods better approximate a typical chromatographic separation since they involve the injection of smaller volumes/concentrations. However, the current method to elucidate the kinetics is also questionable. Thus the current chromatographic methods are not ideal for characterizing the kinetics of retention since these methods rely upon a number of assumptions and approximations.

Using the exponentially modified Gaussian model (EMG), McGuffin and Howerton have studied the kinetics of PAHs in ODS [17,18]. The rate constants decreased with increasing ring number and less condensed annelation structure. The enthalpic and volume barriers were found to be very large. These barriers increased as a function of ring number, but decreased with more condensed annelation structure.

### **1.4 Conclusions**

Although significant efforts have been invested in the applications of PGC in both chromatography and extraction, the retention mechanism is far from being understood. Limitations in both theory and experimental design have hindered definitive quantitative analysis.

In this dissertation, the thermodynamic and kinetic contributions to retention of two series of aromatic compounds on PGC will be explored using the EMG model. These studies will help to understand the retention mechanism on PGC.

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# Chapter 2: Retention of Aromatic Hydrocarbons on Porous Graphitic Carbon

### **2.1 Introduction**

As depicted in Figures 2.1 and 2.2, eighteen aromatic hydrocarbons have been chosen to investigate the effect of length of alkyl chain and number of methyl substituents on the thermodynamics and kinetics of retention on porous graphitic carbon (PGC). Alkyl-substituted benzenes were chosen as the solutes for two reasons. First, they make a good homologous series in establishing retention trends. Second, for environmental and toxicity concerns, BTEX levels in oil are a very important parameter. BTEX is the collective name of benzene, toluene, ethylbenzene, and the xylene isomers ( $o_{-}$ ,  $m_{-}$ , and  $p_{-}$ -xylenes). BTEX compounds are the most common aromatic compounds in petroleum, comprising up to a few percent of the total weight for some crude oils. BTEX constitutes the most soluble, most mobile fraction of crude oil and many petroleum products. BTEX compounds have many chemical applications and are widely used in the manufacture of paints, synthetic rubber, agricultural chemicals, and chemical intermediates. The concentration of BTEX in petroleum can directly affect the physical and chemical properties of petroleum such as density, viscosity, flash points, dispersibility, emulsion stability, solubility, and weathering processes. On the other hand, BTEX compounds frequently enter soil, sediments, and groundwater because of accidental oil spill, leakage of gasoline and other petroleum fuels from underground storage tanks and pipelines, and improper waste disposal practices.



Figure 2.1: Structure of alkylbenzenes used to study retention on

porous graphitic carbon.


Figure 2.2: Structure of methylbenzenes used to study retention on porous graphitic carbon.

In these cases, BTEX compounds can also be used as markers in identifying the presence and determining the composition of these weathered fuels originating from leaking underground fuel tanks or pipelines. BTEX are hazardous carcinogenic and neurotoxic compounds and are classified as priority pollutants regulated by the U.S. Environment Protection Agency (EPA) [1], especially benzene, which has a very low tolerance standard in drinking water of  $5 \mu g/L$ .

# **2.2 Experimental Methods**

## 2.2.1 Solutes

The alkylbenzenes (Figure 2.1) were chosen as a homologous series to study the effects of methylene addition on retention. Benzene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene and hexylbenzene were obtained from Aldrich.

The methylbenzenes (Figure 2.2) were chosen as a homologous series to study the effects of methyl substituent addition on retention. Toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene 1,3,5-trimethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene were obtained from Aldrich. Mixed standard solutions were prepared around  $10^{-3}$  M in high-purity methanol (Burdick and Jackson, Baxter Healthcare) such that there was no overlap of solute zones at any temperature and pressure. A nonretained marker, acetonitrile, was added to each solution at a concentration of 1 M.

## 2.2.2 Chromatographic System

The chromatographic system is shown schematically in Figure 2.3. It includes a single-piston reciprocating pump (Model 114 M, Beckman Instruments) operating in constant pressure mode ( $\pm$  15 psi) over the range of 6.90 × 10<sup>6</sup> Pa (1000 psi) to 3.45 × 10<sup>7</sup> Pa (5000 psi). The pump allows for the mobile phase to be supplied continuously without the need for depressurization during the refill cycle. At all pressures, the flowrate was maintained at approximately 1 mL/min at room temperature.

Samples are introduced via a manual injection valve (20  $\mu$ L, Model 7125, Rheodyne Instruments). Once the sample is introduced, it is carried by the methanol mobile phase to the column. The Hypercarb column is supplied by Shandon HPLC (100 × 4.6 mm i.d., mean particle diameter 7  $\mu$ m).

At the end of the column, a 100  $\mu$ m i.d. fused-silica capillary (Polymicro Technologies) is attached to serve as a restrictor. The length of the restrictor is reduced as the inlet pressure is decreased in order to maintain a constant pressure drop along the column (3.31× 10<sup>5</sup> Pa (48 psi)/cm). The length of the restrictor and corresponding pressures and flow rate are listed in Table 2.1.

The injector, column, and restrictor are all housed within an oven (Model SM900, Anspec Instruments) that maintains a constant temperature ( $\pm$ 0.1 K) through the use of resistive heating coils. The oven was operated through the temperature range of 296 to 326 K.



Figure 2.3: Schematic diagram for the chromatographic system.

I: injection valve, R: restrictor.

# Table 2.1: Corresponding pressure, flow rate, and length of restrictor in the

Pressure (psi)	Length of restrictor (m)	Flow rate (mL/min) <sup>A</sup>
1000	1.450	0.965
2000	3.777	0.955
3000	5.982	0.956
4000	8.194	0.949
5000	10.345	0.993

chromatographic system.

<sup>A</sup> at room temperature

The spectroscopic technique used for detection is ultraviolet-visible absorbance. As shown in Figure 2.3, a commercially available unit (Model UVIDEC-100-V, JASCO) is directly coupled to the column such that the effluent is directed to a capillary flow cell. The flow cell is a transparent fused-silica capillary with a 180- $\mu$ m i.d., able to hold high pressure in the chromatographic system. The wavelength for detection (210 nm) is chosen based upon the absorption maximum of the solutes. The output from the detector is directed to a data acquisition board (National Instruments) and computer for further data analysis. The data collecting program was written in Labview (National Instruments, v3.1).

# 2.2.3 Data Treatment and Analysis

Since the desired data are zone profiles contained within a multicomponent chromatogram, the first challenge for the data analysis is the reproducible extraction of the individual profiles. The integration limits will affect the accuracy of the analysis results [2]. Once removed, the zone profiles are iteratively fit using a commercially available program (Peakfit v3.18, SYSTAT Software). Since there are many functions available for the analysis of zone profiles, the second obstacle to the analysis is choice of an appropriate function.

The accurate description of asymmetrical peaks usually requires a large number of statistical moments and a large number of data points [3]. In addition, noise can affect the values for the moments [4]. As a result of these limitations, alternative equations such as the exponentially modified Gaussian (EMG) [5], the

nonlinear chromatography (NLC) [6], and the Haarhoff-Van der Linde function [7] have been developed for evaluating non-Gaussian zone profiles. The EMG and NLC models provide variables that can be directly related to experimental parameters. As a result, these two functions were initially chosen to study chromatographic zones. The results of nonlinear regression of a typical experimental zone profile with the Gaussian function and the EMG equation are shown in Figure 2.4. The Gaussian equation (Figure 2.4A) produces nonrandom residuals with a relatively small value for the square of the correlation coefficient ( $R^2 = 0.987$ ). The EMG equation (Figure 2.4B) provides significantly better fit with only small residuals around the maximum of the zone profile ( $R^2 = 0.998$ ). Moreover, the EMG equation yields better statistical results than the NLC and other models mentioned above. On the basis on these results, the EMG model was used throughout the studies in this dissertation. The EMG is a convolution of a Gaussian and an exponential function. The form of the equation is

$$C(t) = \frac{A}{2\tau} \exp\left[\frac{\sigma^2}{2\tau^2} + \frac{t_G - t}{\tau}\right] \left[ erf\left(\frac{t - t_G}{\sqrt{2\sigma}} - \frac{\sigma}{\sqrt{2\tau}}\right) + 1 \right] \quad (2.1)$$

where A is the area,  $t_G$  is the mean of the Gaussian component,  $\sigma$  is the standard deviation of the Gaussian component, and  $\tau$  is the exponential component.

Over the past thirty years, several authors have sought to characterize the use of the EMG function for chromatographic analysis. While Grushka [8,9] and Yau [10] presented some early work, Foley and Dorsey have published two seminal papers reviewing the EMG function in the intervening years [11,12].





**Figure 2.4**: Regression results with the Gaussian equation (A) and the EMG equation (B). Experimental data: (—), regression: ( - - - ).

These reviews have demonstrated the use of the EMG function for a variety of chromatographic applications. More recent studies have compared the EMG to other equations for the analysis of zone profiles [13,14]. The studies have concluded that high-order polynomials that exceed the four parameters used in the EMG function can describe asymmetrical peaks very well. However, the complex nature of such functions makes them impractical for common use. In addition, the parameters for these high-order polynomials may not have any physical significance as do those calculated using the EMG function.

Within this thesis, the EMG is employed predominantly to calculate the thermodynamics and kinetics of retention. The thermodynamic and kinetic parameters can be calculated by substituting the measured values of  $t_G$  and  $\tau$  into Equations 1.3, 1.11, and 1.12 of Chapter 1, where

 $t_r = t_G + \tau$  (2.2)

# 2.4 Results and Discussion

# 2.4.1 Thermodynamic Behavior

#### 2.4.1.1 Retention Factor

The retention factor (k) is the simplest of the measurable parameters that allow for the comparison of the relative strength of interaction. A larger retention factor indicates that the solute has greater affinity for the stationary phase. This comparison is useful to evaluate the effect of different solute structural features.

Using Equation 1.3, the retention factor for each solute on PGC was calculated. The results of these calculations are summarized in Tables 2.2 and 2.3. For the homologous series of alkylbenzenes, the retention factor increases

Solute	k <sup>A</sup>	к <sup>в</sup>	∆k/k (%)	kc	k <sup>D</sup>	∆k/k (%)
Benzene	0.16	0.16	-4.9	0.16	0.16	1.90
Toluene	0.36	0.31	-16.2	0.34	0.33	-1.19
Ethylbenzene	0.37	0.30	-17.2	0.34	0.33	-0.89
Propylbenzene	0.53	0.43	-18.4	0.49	0.49	-0.41
Butylbenzene	0.80	0.62	-23.1	0.71	0.71	-0.14
Pentylbenzene	1.43	1.04	-27.8	1.23	1.24	1.30
Hexylbenzene	2.34	1.56	-33.3	1.90	1.93	1.53

 Table 2.2: Retention factors (k) for alkylbenzenes on porous graphitic carbon.

<sup>A</sup> Retention factor calculated at  $3.28 \times 10^7$  Pa (4760 psi) and 298 K <sup>B</sup> Retention factor calculated at  $3.28 \times 10^7$  Pa (4760 psi) and 326 K <sup>C</sup> Retention factor calculated at  $5.24 \times 10^6$  Pa (760 psi) and 309 K <sup>D</sup> Retention factor calculated at  $3.28 \times 10^7$  Pa (4760 psi) and 309 K

Solute	к <sup>A</sup>	К <sup>в</sup>	∆k/k (%)	ۍ ۲	<b>-</b>	∆k/k (%)
Benzene	0.16	0.16	<b>4</b> .9	0.16	0.16	1.90
Toluene	0.36	0.31	-16.2	0.34	0.33	-1.19
o-Xylene	0.99	0.75	-24.5	0.87	0.87	-0.23
<i>m</i> -Xylene	0.82	0.64	-22.0	0.73	0.73	-0.14
p-Xylene	0.96	0.72	-25.5	0.83	0.85	3.39
1,2,3-Trimethylbenzene	2.98	2.03	-32.0	2.48	2.50	0.89
1,2,4-Trimethylbenzene	2.52	1.72	-31.6	2.08	2.14	2.93
1,3,5-Trimethylbenzene	1.80	1.28	-28.9	1.52	1.55	1.84
1,2,3,5-Tetramethylbenzene	7.00	4.36	-37.6	5.53	5.63	1.70
1,2,4,5-Tetramethylbenzene	7.19	4.48	-37.6	5.69	5.88	3.39
Pentamethylbenzene	24.46	15.17	-38.0	20.50	20.87	1.78
Hexamethylbenzene	100.07	50.83	49.2	70.99	74.76	5.31

Table 2.3: Retention factors (k) for methylbenzenes on porous graphitic carbon.

<sup>A</sup> Retention factor calculated at  $3.28 \times 10^7$  Pa (4760 psi) and 298 K <sup>B</sup> Retention factor calculated at  $3.28 \times 10^7$  Pa (4760 psi) and 326 K <sup>C</sup> Retention factor calculated at  $5.24 \times 10^6$  Pa (760 psi) and 309 K <sup>D</sup> Retention factor calculated at  $3.28 \times 10^7$  Pa (4760 psi) and 309 K

with alkyl chain length at all temperatures and pressures. Solutes with longer alkyl chains are more retained due to increased dispersion forces from methylene groups with stationary phase. The only exception is toluene and ethylbenzene, which produce very similar retention factors. This might be due to the greater effect on retention that a methyl group produces, which is discussed below.

The effect of temperature on the retention factor is very pronounced on porous graphitic carbon. For all alkylbenzenes, an increase in temperature results in a decrease in the retention factor. Solutes with longer alkyl chain demonstrate a greater change in retention factor.

In contrast, the effect of pressure is much smaller on PGC. The retention factors for all alkylbenzenes nearly do not change with pressure considering the error in measurement. The reason is that the robust stationary phase does not change with pressure.

For the homologous series of methylbenzenes, the retention factor increases with the number of methyl substituents at all temperatures and pressures. Solutes with more methyl substituents are more retained due to the increased interactions with the stationary phase that result from the increased dispersion forces and the increased electron density of the phenyl ring from electron-donating methyl groups.

The effect of temperature on the retention factor again is very pronounced. For all methylbenzenes, an increase in temperature results in a decrease in the

retention factor. Solutes with more methyl substituents demonstrate a greater change of retention factor.

In contrast, the effect of pressure is again much smaller on PGC. The retention factors for all methylbenzenes change very little with pressure, due to the robust stationary phase.

For the methylbenzenes, each group of positional isomers produces similar retention factors. For example, the *o*-, *m*-, and *p*-xylenes have similar retention factors at the same temperature and pressure. But *m*-xylene is least retained because it has the lowest electron density of the phenyl ring among the isomers. Again, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene have similar retention factors. But 1,3,5-trimethylbenzene is least retained for the same reasons. 1,2,3,5-Tetramethylbenzene and 1,2,4,5-tetramethylbenzene also have similar retention factors.

Comparing the retention factors between the alkylbenzene and methylbenzene series, it can be concluded that the addition of a methyl group produces a greater effect on retention than a methylene group. This is because the methyl group can change the electron density of the phenyl ring to a greater extent than the methylene group.

### **2.4.1.2 Molar Enthalpy**

Using Equation 1.8 and the methods described in Section 1.2.1, the change in molar enthalpy was calculated. A representative graph used in the calculation of the change in molar enthalpy is shown in Figure 2.5. For all solutes at all pressures, the data are linear ( $R^2 = 0.973-0.999$ ) and the slope of the line is



Figure 2.5: Representative graph of the retention factor (k) versus inverse temperature (K<sup>-1</sup>) used to calculate the change in molar enthalpy according to Equation 1.8. Column: porous graphitic carbon. Mobile phase: methanol, 1.21 × 10<sup>7</sup> Pa (1760 psi), 0.955 mL/min. Solutes: toluene (♦), *m*-xylene (■), 1,3,5-trimethylbenzene (▲), pentamethylbenzene (Δ), hexamethylbenzene (

).

positive. A linear graph indicates that the change in molar enthalpy is constant with temperature. A positive slope is demonstrative of a negative change in molar enthalpy, which indicates that the transition from the mobile to stationary phase is an energetically favorable exothermic process. Molar enthalpies for alkylbenzenes and methylbenzenes at different pressures are summarized in Tables 2.4 and 2.5.

For the alkylbenzenes (Table 2.4), the change in molar enthalpy with pressure is very small. At constant pressure, the homologous series illustrates a trend of decreasing molar enthalpy, where retention becomes more exothermic as the number of methylene groups increases. The differential change in molar enthalpy ( $\Delta\Delta H_{sm}$ ) versus carbon number for alkylbenzenes is shown in Figure 2.6. From benzene to toluene,  $\Delta H_{sm}$  changes about –3 kJ/mol. But from toluene to propylbenzene, the change in  $\Delta H_{sm}$  is very small (–0.5 kJ/mol). This small change indicates the addition of one methylene group at this stage does not significantly affect the retention. Thereafter, the change in  $\Delta H_{sm}$  becomes relatively constant at approximately –2 kJ/mol.

The methylbenzenes (Table 2.5) also illustrate decreasing molar enthalpy as the number of methyl groups increases. Solutes with the same number of methyl substituents have similar molar enthalpies. For example, o-, m-, and pxylenes have comparable molar enthalpies of –8 kJ/mol. The same is true for 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene with molar enthalpies of –11 kJ/mol. The differential change in molar enthalpy versus carbon number for methylbenzenes, shown in Figure 2.7, is relatively constant at

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	ΔH <sub>sm</sub>				
Solute	(kJ/mol) <sup>A</sup>	(kJ/mol) <sup>B</sup>	(kJ/mol) <sup>C</sup>	(kJ/mol) <sup>D</sup>	(kJ/mol) <sup>E</sup>
Benzene	-2.28 ± 0.84	-2.00 ± 0.97	-2.01 ± 0.54	-2.03 ± 0.88	-1.63 ± 0.21
Toluene	-5.11 ± 0.48	-5.08 ± 0.21	-4.96 ± 0.14	-4.97 ± 0.87	-4.96 ± 0.29
Ethylbenzene	-5.55 ± 0.52	-5.47 ± 0.54	-5.40 ± 0.45	-5.40 ± 0.76	-5.41 ± 0.35
Propylbenzene	-5.83 ± 0.29	-6.04 ± 0.53	-6.00 ± 0.20	-5.64 ± 0.43	-5.70 ± 0.42
Butylbenzene	-7.62 ± 0.44	-7.71 ± 0.41	-7.35 ± 0.39	-7.51 ± 0.65	-7.30 ± 0.29
Pentylbenzene	-9.37 ± 0.31	-9.69 ± 0.77	-8.97 ± 0.09	-9.08 ± 0.31	-9.13 ± 0.30
Hexylbenzene	-11.66 ± 0.35	-11.66 ± 0.39	-10.90 ± 0.41	-11.42 ± 0.80	-11.23 ± 0.42

<sup>A</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 5.24 × 10<sup>6</sup> Pa (760 psi) and T = 295 to 327 K <sup>B</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 1.21 × 10<sup>7</sup> Pa (1760 psi) and T = 296 to 327 K <sup>C</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 1.90 × 10<sup>7</sup> Pa (2760 psi) and T = 295 to 328 K <sup>D</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 2.59 × 10<sup>7</sup> Pa (3760 psi) and T = 296 to 327 K <sup>D</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 2.58 × 10<sup>7</sup> Pa (4760 psi) and T = 296 to 327 K <sup>D</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 2.58 × 10<sup>7</sup> Pa (4760 psi) and T = 297 to 326 K

	∆Hsm	∆H <sub>sm</sub>	∆H <sub>sm</sub>	∆Hsm	∆Hsm
Solute	(kJ/mol) <sup>A</sup>	(kJ/mol) <sup>B</sup>	(kJ/mol) <sup>c</sup>	(kJ/mol) <sup>D</sup>	(kJ/mol) <sup>E</sup>
Benzene	<b>-</b> 2.28 ± 0.84	-2.00 ± 0.97	-2.01 ± 0.54	-2.03 ± 0.88	<b>-1.63 ± 0.21</b>
Toluene	-5.11 ± 0.48	<b>-5.08 ± 0.21</b>	<b>-4.96 ± 0.14</b>	<b>-4.97 ± 0.87</b>	<b>-4.96 ± 0.29</b>
o-Xylene	<b>-8.21 ± 0.16</b>	-8.10 ± 0.45	-7.67 ± 0.18	-7.92 ± 0.49	-7.93 ± 0.30
<i>m</i> -Xylene	-7.71 ± 0.52	-7.60 ± 0.20	-7.49 ± 0.17	-7.06 ± 0.35	-7.13 ± 0.38
<i>p</i> -Xylene	<b>-8.30 ± 0.32</b>	-8.50 ± 0.24	<b>-8.68 ± 0.12</b>	-8.56 ± 0.16	<b>-8.55 ± 0.34</b>
rimethylbenzene	-11.10 ± 0.13	-11.71 ± 0.30	-11.44 ± 0.09	-11.04 ± 0.40	-10.88 ± 0.22
rimethylbenzene	-11.11 ± 0.21	-11.08 ± 0.16	-11.16 ± 0.14	-11.35 ± 0.04	-10.82 ± 0.16
rimethylbenzene	-10.10 ± 0.13	-9.40 ± 0.20	-9.70 ± 0.13	-9.67 ± 0.26	-9.61 ± 0.21
etramethylbenzene	<b>-13.65 ± 0.10</b>	<b>-13.38 ± 0.22</b>	-13.69 ± 0.03	-13.46 ± 0.35	-13.26 ± 0.34
etramethylbenzene	-13.88 ± 0.21	-13.94 ± 0.08	<b>-13.65 ± 0.11</b>	-13.98 ± 0.04	-13.39 ± 0.14
methylbenzene	-16.48 ± 0.28	-16.00± 0.09	-15.38 ± 0.10	-16.05 ± 0.25	-15.61 ± 0.12
nethylbenzene	-20.08 ± 0.43	-20.24 ± 0.31	-19.54 ± 0.14	-19.28 ± 0.27	-19.56 ± 0.36

Table 2.5: Molar enthalpy for methylbenzenes on porous graphitic carbon.

<sup>A</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 5.24 × 10<sup>6</sup> Pa (760 psi) and T = 295 to 327 K <sup>B</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 1.21 × 10<sup>7</sup> Pa (1760 psi) and T = 296 to 327 K <sup>C</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 1.90 × 10<sup>7</sup> Pa (2760 psi) and T = 295 to 328 K <sup>D</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 2.59 × 10<sup>7</sup> Pa (3760 psi) and T = 296 to 327 K <sup>D</sup> Molar enthalpy ( $\Delta H_{sm}$ ) calculated at P = 2.58 × 10<sup>7</sup> Pa (4760 psi) and T = 297 to 326 K



Figure 2.6







around –2.5 kJ/mol. This value is slightly larger than that for the alkylbenzenes when the carbon number is greater than three. The constant change suggests that the addition of each methyl group produces a similar effect on retention. The methylbenzenes also demonstrate very small differences in molar enthalpies at different pressures.

For the high-density octadecylsilica stationary phase, the change in molar enthalpy ( $\Delta H_{sm}$ ) ranges from -44 kJ/mol to -128 kJ/mol for fatty acids ranging from C<sub>10</sub> to C<sub>22</sub>, respectively, at 303 K and 1.01 × 10<sup>7</sup> Pa (1470 psi) [15]. The differential change in molar enthalpy per ethylene group remains constant for solutes C<sub>10</sub> to C<sub>18</sub> with an average value of -15 kJ/mol [15]. Thus, when PGC is compared with octadecylsilica, the addition of each methylene group has less effect on retention.

# 2.4.1.3 Molar Volume

Similar to the molar enthalpy, the molar volume also provides insight into the effects that arise from structure. Using Equation 1.10 and the methods described in Section 1.2.1, the change in molar volume was calculated. A representative graph used in the calculation of the change in molar volume is depicted in Figure 2.8. For all solutes at all temperatures, the data are relatively linear. However, because of the small change in retention factor with pressure, the square of the correlation coefficient is small ( $R^2 = 0.549-0.889$ ). A linear graph indicates that the molar volume is constant with pressure. The slope of the line is slightly positive or negative. A negative slope results in a positive change in molar volume, which indicates that the molecule occupies more space in the





Figure 2.8

stationary phase than in the mobile phase. Conversely, a positive slope indicates that the transition from the mobile to stationary phase results in a smaller volume. Representative data are contained in Tables 2.6 and 2.7

Overall, the change in molar volume is very small on PGC, compared with that of polycyclic aromatic hydrocarbons (PAHs) on octadecylsilica, which is around  $-2 \text{ cm}^3/\text{mol}$  [16]. The change in molar volume for methylene homologues on high-density octadecylsilica ranges from -40 to  $-110 \text{ cm}^3/\text{mol}$  [15], which is much greater than that on PGC. Considering the uncertainty in measurement, the change in molar volume on PGC is very close to zero. This is consistent with the retention mechanism on PGC, which is based on adsorption and desorption of the solute molecules from the solid surface, rather than partition of the solute molecules into the stationary phase as on octadecylsilica..

	$\Delta V_{sm}$	$\Delta V_{sm}$
Solute	(cm <sup>3</sup> /mol) <sup>A</sup>	(cm <sup>3</sup> /mol) <sup>B</sup>
Benzene	-0.24 ± 0.22	0.23 ± 0.20
Toluene	0.25 ± 0.19	0.16 ± 0.09
Ethylbenzene	0.18 ± 0.17	-0.25 ± 0.21
Propylbenzene	$-0.35 \pm 0.21$	0.25 ± 0.19
Butylbenzene	0.23 ± 0.20	0.29 ± 0.15
Pentylbenzene	-0.29 ± 0.15	0.36 ± 0.26
Hexylbenzene	0.33 ± 0.26	-0.24 ± 0.20

 Table 2.6: Molar volume for alkylbenzenes on porous graphitic carbon.

- <sup>A</sup> Molar volume ( $\Delta V_{sm}$ ) calculated at T = 296 K and P = 5.24 × 10<sup>6</sup> Pa (760 psi) to 3.28 × 10<sup>7</sup> Pa (4760 psi) <sup>B</sup> Molar volume ( $\Delta V_{sm}$ ) calculated at T = 327 K and P = 5.24 × 10<sup>6</sup> Pa (760 psi) to 3.28 × 10<sup>7</sup> Pa (4760 psi)

	$\Delta V_{sm}$	$\Delta V_{sm}$
Solute	(cm <sup>3</sup> /mol) <sup>A</sup>	(cm <sup>3</sup> /mol) <sup>B</sup>
Benzene	$-0.24 \pm 0.22$	0.23 ± 0.20
Toluene	0.25 ± 0.19	0.16 ± 0.09
o-Xylene	0.28 ± 0.19	-0.22 ± 0.21
<i>m</i> -Xylene	-0.35 ± 0.21	0.23 ± 0.19
<i>p</i> -Xylene	0.24 ± 0.20	0.21 ± 0.15
1,2,3-Trimethylbenzene	0.29 ± 0.15	-0.36 ± 0.26
1,2,4-Trimethylbenzene	0.33 ± 0.26	0.24 ± 0.20
1,3,5-Trimethylbenzene	$-0.34 \pm 0.23$	0.29 ± 0.20
1,2,3,5-Tetramethylbenzene	0.36 ± 0.26	$-0.46 \pm 0.39$
1,2,4,5-Tetramethylbenzene	0.34 ± 0.17	0.37 ± 0.21
Pentamethylbenzene	-0.55 ± 0.21	0.61 ± 0.36
Hexamethylbenzene	$0.63 \pm 0.28$	0.69 ± 0.34

- <sup>A</sup> Molar volume (ΔV<sub>sm</sub>) calculated at T = 296 K and P =  $5.24 \times 10^{6}$  Pa (760 psi) to  $3.28 \times 10^{7}$  Pa (4760 psi) <sup>B</sup> Molar volume (ΔV<sub>sm</sub>) calculated at T = 327 K and P =  $5.24 \times 10^{6}$  Pa (760 psi) to  $3.28 \times 10^{7}$  Pa (4760 psi)

# 2.4.2 Kinetic Behavior

# 2.4.2.1 Rate Constants

Although the thermodynamic data demonstrate the steady-state aspects, they do not fully explain the mechanism of retention. Using Equations 1.11, 1.12, 1.14, and 1.16 and the method described in Section 1.2.2, the pseudo-first-order rate constants, activation enthalpies, and activation volumes were calculated. These values help to quantify the kinetic aspects of solute transfer between the mobile and stationary phases.

Representative values of the rate constants are summarized in Tables 2.8 and 2.9. For the alkylbenzenes (Table 2.8), the structures with longer alkyl chains result in larger rate constants for the mobile to stationary phase ( $k_{sm}$ ), and stationary to mobile phase ( $k_{ms}$ ) transitions. From benzene to butylbenzene, the rate-limiting step is the transfer from mobile to stationary phase (i.e.,  $k_{ms} > k_{sm}$ ) because the retention factor, which is the ratio of  $k_{sm}$  and  $k_{ms}$ , is less than 1.

Solute	k <sub>ms</sub> (s⁻¹) <sup>A</sup>	k <sub>sm</sub> (s⁻¹) <sup>B</sup>
Benzene	5.9	1.0
Toluene	13.1	4.9
Ethylbenzene	11.8	4.5
Propylbenzene	15.0	8.4
Butylbenzene	16.7	14.0
Pentylbenzene	16.3	24.5
Hexylbenzene	15.4	37.4

Table 2.8: Kinetic rate constants for alkylbenzenes on porous graphitic carbon.

- <sup>A</sup> Rate constants for the stationary to mobile phase transition at  $5.24 \times 10^{6}$  Pa (760 psi) and 295 K. <sup>B</sup> Rate constants for the mobile to stationary phase transition at  $5.24 \times 10^6$  Pa
- (760 psi) and 295 K.

Table 2.9: Kinetic rate constants for methylbenzenes on porous graphitic carbon.

Solute	k <sub>ms</sub> (s⁻¹) <sup>A</sup>	k <sub>sm</sub> (s <sup>-1</sup> ) <sup>B</sup>
Benzene	5.9	1.0
Toluene	13.1	4.9
o-Xylene	13.9	14.2
<i>m</i> -Xylene	16.3	14.0
<i>p</i> -Xylene	15.0	14.9
1,2,3-Trimethylbenzene	14.5	44.9
1,2,4-Trimethylbenzene	14.5	38.1
1,3,5-Trimethylbenzene	20.4	38.4
1,2,3,5-Tetramethylbenzene	3.5	25.5
1,2,4,5-Tetramethylbenzene	16.0	120.6
Pentamethylbenzene	3.5	99.0
Hexamethylbenzene	2.6	292.0

<sup>A</sup> Rate constants for the stationary to mobile phase transition at  $5.24 \times 10^{6}$  Pa (760 psi) and 295 K  $^{\rm B}$  Rate constants for the mobile to stationary phase transition at 5.24  $\times$  10<sup>6</sup> Pa

(760 psi) and 295 K

However, for pentylbenzene and hexylbenzene, the rate-limiting step is the transfer from stationary to mobile phase (i.e.,  $k_{ms} < k_{sm}$ ) because the retention factor is greater than 1.

For the methylbenzenes (Table 2.9), generally the molecules with more methyl substituents produce larger rate constants for the mobile to stationary phase ( $k_{sm}$ ), and stationary to mobile phase ( $k_{ms}$ ) transitions. For benzene, toluene, and the xylenes, the rate-limiting step is the transfer from mobile to stationary phase (i.e.,  $k_{ms} > k_{sm}$ ) because the retention factor is less than 1. But for the trimethylbenzenes, tetramethylbenzenes, pentamethylbenzene, and hexamethylbenzene, the rate-limiting step is the transfer from stationary to mobile phase (i.e.,  $k_{ms} < k_{sm}$ ) because the retention factor is greater than 1.

In addition, an increase in temperature yields an increase in the rate constants for all molecules. For example, the rate constant ( $k_{ms}$ ) for hexylbenzene ranges from 15.4 to 32.8 s<sup>-1</sup> for temperatures from 295 to 327 K, respectively, at 5.24 × 10<sup>6</sup> Pa (760 psi). In contrast, an increase in pressure yields only slight changes. The rate constant ( $k_{ms}$ ) for hexylbenzene ranges from 23.6 to 20.4 s<sup>-1</sup> for pressures from 5.24 × 10<sup>6</sup> to 3.28 × 10<sup>7</sup> Pa (760 to 4760 psi), respectively, at 309 K.

Overall, the data indicate that the rate constants ( $k_{ms}$  and  $k_{sm}$ ) increase as the retention factor increases, which is the reverse order of the rate constants on octadecylsilica for PAHs [16].

# 2.4.2.2 Activation Enthalpy

Using Equation 1.14 and 1.15 and the methods described in Section 1.2.2, the activation enthalpies were calculated. Figure 2.9 illustrates a typical graph of the natural logarithm of the rate constant versus inverse temperature used in the calculation of the activation enthalpy. For all solutes at all pressures, the data are linear ( $R^2 = 0.443$ -0.869) and the slope of the line is negative. A linear graph indicates that the change in activation enthalpy is constant with temperature. A negative slope is demonstrative of a positive change in activation enthalpy, which is the energy barrier for the transfer from mobile or stationary phase to the transition state. Tables 2.10 and 2.11 contain the activation enthalpies for alkylbenzenes and methylbenzenes.

As demonstrated for the alkylbenzenes (Table 2.10), an increase in the number of methylene groups results in an increase in the activation enthalpy. The data indicate that the energy barrier from the stationary phase to the transition state  $\Delta H_{\ddagger3}$  increases with the addition of every methylene group. The differential change in  $\Delta H_{\ddagger3}$  versus carbon number for the alkylbenzenes is shown in Figure 2.10. From benzene to toluene,  $\Delta \Delta H_{\ddagger3}$  is about 3 kJ/mol. But from toluene to propylbenzene,  $\Delta \Delta H_{\ddagger3}$  increases only slightly at 0.5 kJ/mol. When the carbon number is greater than three,  $\Delta \Delta H_{\ddagger3}$  is relatively constant at around 2 kJ /mol, indicating that the effect of each methylene group on activation enthalpy is relatively constant.



Figure 2.9



Figure 2.9: Representative graph of the rate constant (ksm) versus inverse temperature (K<sup>-1</sup>) used to calculate the change in activation enthalpy according to Equation 1.14. Column: porous graphitic carbon. Mobile phase: methanol, 1.90×10<sup>7</sup> Pa (2760 psi), 0.956 mL/min. Solutes: toluene (♦), *m*-xylene (■), 1,3,5-trimethylbenzene (▲), pentamethylbenzene (Δ), hexamethylbenzene (
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	(lom)	± 0.66	± 0.57	± 0.26	± 0.94	± 0.54	± 0.69	± 0.65
3	(kJ	1.56	0.74	1.05	1.91	3.93	3.60	3.29
\$4.17	(kJ/mol) <sup>B</sup>	<b>3.94 ± 0.75</b>	5.59 ± 1.03	6.76 ± 0.30	8.25±0.36	11.33± 0.76	12.71± 0.49	14.59 ± 0.44
ΔΠ‡m	(kJ/mol)	1.40 ± 0.94	<b>1.73 ± 0.43</b>	0.77 ± 1.35	<b>2.93 ± 1.14</b>	<b>3.10 ± 0.52</b>	1.87 ± 1.18	2.18 ± 0.67
2H‡s	(kJ/mol) <sup>A</sup>	<b>3.70 ± 1.22</b>	<b>6.86 ± 0.51</b>	6.56 ± 1.21	8.35 ± 1.27	<b>10.76 ± 0.13</b>	<b>11.40 ± 0.72</b>	<b>13.81 ± 0.69</b>
	Solute	Benzene	Toluene	Ethylbenzene	Propylbenzene	Butylbenzene	Pentylbenzene	Hexylbenzene

<sup>A</sup> Activation enthalpies from the stationary phase to transition state ( $\Delta H_{ta}$ ), and from the mobile phase to transition state ( $\Delta H_{tm}$ ) were calculated at 5.24 × 10<sup>6</sup> Pa (760 psi). <sup>B</sup> Activation enthalpies from the stationary phase to transition state ( $\Delta H_{ta}$ ), and from the mobile phase to transition state ( $\Delta H_{tm}$ ) were calculated at 3.28 × 10<sup>7</sup> Pa (4760 psi).

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∆H‡m	(kJ/mol)	1.56 ± 0.66	0.74 ± 0.57	2.87 ± 0.49	4.86 ± 0.64	0.98 ± 1.09	3.90 ± 1.26	5.13±1.73	2.53 ± 1.46	2.48 ± 0.64	5.80 ± 1.96	9.63 ± 1.19	<b>34.00 ± 6.03</b>
∆H≄s	(kJ/mol) <sup>B</sup>	<b>3.94 ± 0.75</b>	5.59 ± 1.03	10.89 ± 0.43	11.99 ± 1.02	<b>9.51 ± 1.27</b>	12.61 ± 0.93	15.31 ± 1.91	<b>13.17 ± 1.54</b>	<b>16.50 ± 0.58</b>	19.67 ± 1.87	25.23 ± 1.21	55.08 ± 5.65
ΔH‡m	(kJ/mol)	1.40 ± 0.94	1.73 ± 0.43	4.23 ± 0.89	2.08 ± 1.39	3.82 ± 1.66	2.04 ± 0.91	3.94 ± 1.45	4.50 ± 1.11	3.86 ± 0.61	2.21 ± 1.05	8.51 ± 1.43	26.14 ± 8.61
∆H≄s	(kJ/mol) <sup>A</sup>	3.70 ± 1.22	<b>6.86 ± 0.51</b>	12.43 ± 0.97	10.78 ± 2.24	12.17 ± 1.75	13.84 ± 1.00	15.04 ± 1.63	14.89 ± 1.19	17.50 ± 0.65	16.09 ± 1.10	25.36±1.52	46.38 ± 8.87
	Solute	Benzene	Toluene	o-Xylene	m-Xylene	p-Xylene	1,2,3-Trimethylbenzene	1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene	1,2,3,5-Tetramethylbenzene	1,2,4,5-Tetramethylbenzene	Pentamethylbenzene	Hexamethylbenzene

<sup>A</sup> Activation enthalpies from the stationary phase to transition state ( $\Delta H_{ts}$ ), and from the mobile phase to transition state ( $\Delta H_{tm}$ ) were calculated at 5.24 × 10<sup>6</sup> Pa (760 psi). <sup>B</sup> Activation enthalpies from the stationary phase to transition state ( $\Delta H_{ts}$ ), and from the mobile phase to transition state ( $\Delta H_{tm}$ ) were calculated at 3.28 × 10<sup>7</sup> Pa (4760 psi)



Figure 2.10



carbon number for alkylbenzene at  $5.24 \times 10^{6}$  Pa (760 psi)

For the methylbenzenes (Table 2.11), the activation enthalpy from the stationary phase to the transition state  $\Delta H_{ps}$  increases with increasing number of methyl substituents. This result suggests that with the addition of each methyl group, the energy barrier from the stationary phase to the transition state increases. Figure 2.11 shows the differential change in  $\Delta H_{ps}$  versus carbon number for the methylbenzenes. From benzene to tetramethylbenzenes, the differential change in activation enthalpy  $\Delta \Delta H_{ps}$  is relatively constant at around 3 kJ /mol. But for pentamethylbenzene and hexamethylbenzene,  $\Delta \Delta H_{ps}$  is much greater.

For both alkylbenzenes and methylbenzenes, the change in activation enthalpy from the mobile phase to transition state  $\Delta H_{\pm m}$  is nearly constant, considering the uncertainty in the kinetic data. But  $\Delta H_{\pm m}$  for pentamethylbenzene and hexamethylbenzene is greater than that of other solutes in the same homologous series. Comparison between  $\Delta H_{\pm s}$  and  $\Delta H_{\pm m}$  indicates that the retention on PGC is controlled by desorption, which is decided by the molecular structures of the solutes. Thus, the structure of the molecules affects the energy needed to transfer between mobile and stationary phases. Comparing the activation enthalpy with the absolute value of molar enthalpy, the trend is  $\Delta H_{\pm s} >$  $\Delta H_{\pm m} > \Delta H_{\pm m}$ . As expected,  $\Delta H_{\pm m}$  is nearly equal to the difference between  $\Delta H_{\pm s}$ and  $\Delta H_{\pm m}$ .

Comparing with the activation enthalpy for PAHs on octadecylsilica [16], the activation enthalpy for PGC is much smaller. This indicates that the energy barrier for retention on PGC is much smaller than that on octadecylsilica.





Figure 2.11

## 2.4.2.3 Activation Volume

Using Equation 1.16 and the methods described in Section 1.2.2, the activation volumes were calculated. A representative graph of the natural logarithm of the rate constant versus pressure is depicted in Figure 2.12 and resulting values for the activation volume are presented in Tables 2.12 and 2.13. The slope of the line is either slightly positive or slightly negative. The activation volumes for the stationary phase to transition state ( $\Delta V_{\pm n}$ ) and the mobile phase to transition state ( $\Delta V_{\pm n}$ ) appear to be larger than the change in molar volume ( $\Delta V_{\pm m}$ ) because of greater uncertainty of the kinetic data. However, these values are also nearly zero. They are much smaller than the activation volumes reported for methylene and benzene homologues on octadecylsilica [15]. This suggests that the volume barrier on PGC is much smaller than that on octadecylsilica stationary phase.




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Figure 2.12

	∆V <b>‡s</b>	ΔV‡m	∆V <b>‡s</b>	ΔV‡m
Solute	(cm <sup>3</sup> /mol) <sup>A</sup>	(cm <sup>3</sup> /mol)	(cm <sup>3</sup> /mol) <sup>B</sup>	(cm <sup>3</sup> /mol)
Benzene	-0.94 ± 0.92	0.93 ± 0.70	-1.24 ± 0.92	1.23 ± 1.20
Toluene	1.15 ± 0.69	0.76 ± 0.89	1.25 ± 1.19	-1.16 ± 0.99
Ethylbenzene	1.18 ± 0.97	$-1.05 \pm 0.91$	-0.98 ± 0.87	-0.95 ± 0.91
Propylbenzene	1.35 ± 1.21	0.95 ± 0.69	-1.15 ± 1.21	1.25 ± 0.89
Butylbenzene	1.33 ± 0.90	$-1.29 \pm 0.85$	0.99 ± 0.80	0.73 ± 1.15
Pentylbenzene	-1.29 ± 0.85	0.96 ± 0.76	-1.36 ± 1.25	0.99 ± 0.76
Hexylbenzene	1.33 ± 0.76	-0.84 ± 0.70	1.33 ± 0.96	-1.24 ± 0.90

 Table 2.12: Activation volume for alkylbenzenes on porous graphitic carbon.

<sup>A</sup> Activation volumes for the stationary phase to transition state ( $\Delta V_{\ddaggers}$ ), and mobile phase to transition state ( $\Delta V_{\ddaggerm}$ ) were calculated at T = 296 K and P = 5.24 × 10<sup>6</sup> Pa (760 psi) to 3.28 × 10<sup>7</sup> Pa (4760 psi) <sup>B</sup> Activation volumes for the stationary phase to transition state ( $\Delta V_{\ddaggers}$ ), and mobile phase to transition state ( $\Delta V_{\ddaggerm}$ ) were calculated at T = 327 K and P = 5.24 × 10<sup>6</sup> Pa (760 psi) to 3.28 × 10<sup>7</sup> Pa (4760 psi)

ΔV <sub>‡m</sub> (cm <sup>3</sup> /mol)	1.23 ± 1.20	-1.16 ± 0.99	-0.98 ± 0.89	- 1.35 ± 1.41	1.94 ± 1.90	1.96 ± 1.26	1.44 ± 1.30	1.29 ± 1.30	2.04 ± 2.26	1.97 ± 2.21	-2.41 ± 2.36	-1.83 ± 1.28
∆V <sub>‡s</sub> (cm³/mol) <sup>B</sup>	-1.24 ± 0.92	1.25 ± 1.19	1.52 ± 0.81	1.73 ± 1.49	2.21 ± 2.15	-2.29 ± 2.15	-2.33 ± 2.25	-2.18 ± 1.78	-2.46 ± 2.39	2.54 ± 2.17	2.55 ± 1.91	2.69 ± 2.44
∆V <sub>‡m</sub> (cm³/mol)	0.93 ± 0.70	0.76 ± 0.89	-1.22 ± 1.21	1.23 ± 1.19	-1.71 ± 1.15	1.29 ± 1.15	-1.83 ± 1.46	1.34 ± 1.23	-1.96 ± 1.69	1.94 ± 1.87	1.61 ± 1.46	2.33 ± 2.28
∆V <sub>‡s</sub> (cm <sup>3</sup> /mol) <sup>A</sup>	-0.94 ± 0.92	1.15 ± 0.69	1.28 ± 0.99	-1.35 ± 1.21	1.24 ± 1.20	-2.36 ± 1.76	2.24 ± 2.20	2.29 ± 1.90	2.36 ± 2.26	-2.07 ± 2.21	- 2.55 ± 2.21	-2.49 ± 1.34
Solute	Benzene	Toluene	o-Xylene	m-Xylene	p-Xylene	1,2,3-Trimethylbenzene	1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene	1,2,3,5-Tetramethylbenzene	1,2,4,5-Tetramethylbenzene	Pentamethylbenzene	Hexamethylbenzene

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<sup>A</sup> Defined in Table 2.12 A. <sup>B</sup> Defined in Table 2.12 B.

### **2.5 Conclusions**

To illustrate the full implications of the data presented above, it is helpful to describe the entire retention event for a single solute. For example, as hexylbenzene transfers from the mobile to stationary phase, it passes through a high-energy transition state. The creation of this transition state requires an enthalpy change of 2 kJ/mol and a volume change of -0.84 cm<sup>3</sup>/mol. This transfer occurs with a rate constant of 37 s<sup>-1</sup>. As hexylbenzene transfers from the stationary to mobile phase, it passes through another high-energy transition state. This transition state requires an enthalpy change of 1.33 cm<sup>3</sup>/mol. This transfer occurs with a rate constant for mobile change of 14 kJ/mol and a volume change of 1.33 cm<sup>3</sup>/mol. This transfer occurs with a rate constant of 15 s<sup>-1</sup>, which is only half of the rate constant for mobile to stationary phase transfer. Hence, the rate-limiting step is the transfer from stationary to mobile phase.

This description illustrates that both the thermodynamics and kinetics are necessary to fully describe the retention event. By using the necessary theoretical foundation and instrumentation, this dissertation demonstrates a comprehensive study of retention for two series of known pollutants on porous graphitic carbon.

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# **Chapter 3: Conclusions and Future Directions**

Porous graphitic carbon (PGC) is a nonpolar reversed-phase adsorbent. With aqueous or aqueous-organic mobile phases, porous graphitic carbon has stronger retention for the same solutes than the alkyl-bonded silica gels. Increasing the hydrophobicity of a solute by the addition of a methylene group or other nonpolar groups increases retention. In addition, by virtue of its great adsorptive strength, PGC can be used with nonpolar mobile phases for the retention of polar analytes.

Porous graphitic carbon has proven to have a number of unsuspected properties, which have substantially enlarged its area of applications and opened up entirely new possibilities. However, the investigations of molecular contributions to retention on PGC have been limited primarily to selectivity factor [1,2]. Virtually no experimentation has sought to characterize the change in molar enthalpy and molar volume, which provide insight into how molecules interact with the stationary phase. In addition to thermodynamic information, the kinetics of retention have also been largely overlooked. The kinetics of retention are important because they provide insight into the rate at which transitions occur, as well as the energy barriers that exist for a molecule to move from one phase to another.

#### 3.1 Results

In the research presented in this dissertation, solute transfer of two series of aromatic hydrocarbons (alkylbenzenes and methylbenzenes) has been studied as a function of molecular structure. By quantitating the thermodynamics and

kinetics together, a better description of retention on PGC is made, providing a more accurate comparison of different solutes and stationary phases.

In the thermodynamic studies, the retention factor of alkylbenzenes increases with increasing number of methylene groups, and the retention factor of methylbenzenes increases with increasing number of methyl substituents. For the same solute, the retention factor (k) decreases with an increase in temperature, but does not change significantly with pressure. The data from this study indicate that increases in the number of methylene and methyl groups result in more negative changes in molar enthalpy ( $\Delta H_{sm}$ ). The more negative change in  $\Delta H_{sm}$  suggests that the transition from the mobile to stationary phase is a more energetically favorable exothermic process with a methylene or methyl group added. The data also show that the change in molar volume ( $\Delta V_{sm}$ ) is close to zero on PGC, which indicates that during the retention, the solute molecules adsorb on the surface of PGC instead of penetrating further into the stationary phase, as in octadecylsilica.

In the kinetic studies, the rate constants of alkylbenzenes and methylbenzenes increase with increasing number of methylene and methyl groups. The enthalpic barriers between the stationary phase and transition state  $(\Delta H_{\pm s})$  were found to increase with increasing number of methylene and methyl groups as well. But the enthalpic barriers between the mobile phase and transition state  $(\Delta H_{\pm m})$  were much smaller than  $\Delta H_{\pm s}$  and, at the same time, very similar for all the solutes. The values of enthalpic barriers suggest that the retention on PGC is controlled by the adsorption and desorption of the solutes on

the stationary phase. The volume barriers  $\Delta V_{\ddagger s}$  and  $\Delta V_{\ddagger m}$  again are very close to zero due to the adsorption mechanism on porous graphitic carbon.

#### **3.2 Future Directions**

In order for a complete and quantitative description of retention to be presented, a series of experiments beyond those presented herein can be done. The first series of experiments that could lead to a more comprehensive explanation of retention would be a systematic study of the effect of mobile phase composition, such as methanol/water or acetonitrile/water, on the derived values.

Similar to varying the mobile phase, a series of stationary phases, such as phenylsilica, octadecylsilica, and polystyrene divinylbenzene, could be used to compare the effect of solute structure on retention.

Porous graphitic carbon exhibits unexpected and largely unexplained retentive properties for molecules containing polar groups. This property makes PGC particularly useful for the separation of highly polar compounds that would be difficult to retain on octadecylsilica phases. To help understand the retention of polar solutes on PGC better, a number of environmentally important polar solutes, such as atrazine and its polar metabolites can be used [3].

Porous graphitic carbon also shows unusual discrimination of closely related stereoisomers [4]. Chiral separations can be achieved when the molecule is very flexible and can adapt to the flat surface of PGC. The study of the retention of some stereoisomers on PGC can help to better understand the



retention mechanism. These position isomers can be the *o*-, *m*-, *p*- substituted benzene derivatives.

In conclusion, the adsorption retention mechanism on PGC is totally different from that of octadecylsilica, the most widely used stationary phase in liquid chromatography. A better understanding of the retention mechanism on PGC will advance its applications in separation.

## **3.3 References**

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