Diffusion and Adsorption Coefficients of Aromatic Hydrocarbons in Gas Chromatography Capillary Columns

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A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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DIFFUSION AND ADSORPTION COEFFICIENTS OF AROMATIC HYDROCARBONS IN GAS CHROMATOGRAPHY CAPILLARY COLUMNS

(Thesis format: Monograph)

by

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Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

This study focuses on a mathematical description of aromatic species elution peaks from a gas chromatographic (GC) 30m x 0.25mm x 0.25µm BPX5 capillary column. Using the recorded chromatographic peaks, statistical moments of different order are calculated for toluene, naphthalene, phenol and 2-naphthol. This thesis reports two modelling approaches involving laminar gas flow, distribution coefficients ($K_s$) and diffusion coefficients in the stationary phase ($D_s$).

Firstly, a linear isotherm model with adsorption at equilibrium is considered in order to describe symmetric peaks for toluene and naphthalene. Moreover, a linear isotherm model with non-equilibrium adsorption is also proposed in order to describe asymmetric chromatographic peaks generated by phenol and 2-naphthol. In addition to the $K_s$ and $D_s$ parameters, this model involves adsorption kinetic constants ($k_{ads}$).

Validation of both mathematical models is developed by performing experiments at different carrier gas velocities and GC column temperatures ($T_c$). The model with adsorption at equilibrium, reports that the carrier gas velocity does not affect the first statistical moment ($M_1$) or the second statistical moment ($M_2$). Thus, the equilibrium coefficients, $K_s$, and the diffusion coefficients ($D_s$), solely depend on the solute and stationary phase properties. Furthermore, the model under non-equilibrium adsorption conditions provides $k_{ads}$ parameters for phenol and 2-naphthol. However, and in order for the second moments, $M_2_{model}$ to fit the second moment, $M_2_{exp}$, a revised model for the BPX5 capillary column involving two classes of sites for solute adsorption is considered: one site with adsorption at equilibrium and the other site with adsorption at non-equilibrium.

Thus, this PhD thesis establishes two chromatographic models that provide both adsorption and diffusion parameters for aromatic hydrocarbon species peaks eluted from a BPX5 capillary column. Both mathematical models represent an important contribution to the knowledge of solute interactions in capillary columns for GC. These models may potentially have a significant impact on the future of GC analysis of complex mixtures such as tars from biomass gasification.
Keywords

Gas Chromatography; Capillary Columns; Elution Chromatography; Chromatographic Modelling; Distribution Coefficient; Diffusion Coefficient; Adsorption Coefficient; Finite Volume Method.
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Nomenclature

\( A \)  
Eddy diffusion parameter in \textit{van Deemter} Equation (3.1)

\( a_v \)  
Specific area \((1/r_c)\) (1/cm)

\( a_t \)  
Transfer area; \( a_v=2\pi(r_c+d_f)^2 \)

\( B \)  
Longitudinal molecular diffusion parameter in \textit{van Deemter} Equation (3.1)

\( C \)  
Mass transfer in stationary phase parameter in \textit{van Deemter} Equation (3.1)

\( CDS \)  
Central Differencing Scheme

\( c_m \)  
Mobile phase solute concentration (mg/cm\(^3\) of gas phase)

\( c_{mean} \)  
Mean gas phase solute concentration (mg/cm\(^3\))

\( c_o \)  
Strength of the inlet pulse

\( c_s \)  
Stationary phase solute concentration (mg/cm\(^2\) of polymer)

\( CV \)  
Control Volume

\( D_{12} \)  
Molecular diffusion (cm\(^2\)/s)

\( d_f \)  
Film thickness (cm)

\( D_G \)  
Axial dispersion coefficient (cm\(^2\)/s)

\( D_{Go} \)  
Axial dispersion coefficient (cm\(^2\)/s) at reference temperature of 25ºC and atmospheric pressure

\( D_L \)  
Diffusion coefficient in a liquid phase (cm\(^3\)/s)

\( D_s \)  
Solute diffusion coefficient in the stationary phase (cm\(^2\)/s)

\( D_{so} \)  
Solute diffusion coefficient in the stationary phase (cm\(^2\)/s) at reference temperature

\( E \)  
Dimensionless time \( E = \bar{u}t / L \)

\( f_1 \)  
Dimensionless coefficient: \( f_1 = a_v k_{ad} \Delta t / K_s \)

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Dimensionless coefficient:

- $f_2 = \bar{u}(\Delta t / \Delta z) + D_o(\Delta t / \Delta z^2)$

- $f_3 = 1 + \bar{u}(\Delta t / \Delta z) + 2D_o(\Delta t / \Delta z^2) + a_i k_{ads} \Delta t$

- $f_{s2} = D_s(\Delta t / \Delta r^2)$

- $f_{s3} = 1 + 2D_s(\Delta t / \Delta r^2)$

- $f_4 = D_G(\Delta t / \Delta z^2)$

**GC** Gas Chromatography

**H** Theoretical plate height

**HETP** Height Equivalent to a Theoretical Plate

- $i$ Control node point in time
- $j$ Control node point in axial direction
- $k$ Control node point in radial direction
- $k'$ Capacity factor; $k' = t'_R/t_M$
- $k_{ads}$ Adsorption constant (m/s)
- $K_s$ Distribution constant following IUPAC designation ($K_s = c_s/c_m$)
- $K_{s,exp}$ Distribution coefficient obtained from first statistical moment with Eq 5.13
- $K_{s0,i}$ Equilibrium coefficient at the average temperature $T_o$, obtained with Eq 5.14
- $L$ Column length (cm)
- $l(logL^{16})$ Solvation parameter of solute-stationary phase dispersión interaction as Eq (3.5)
- $M^{*\text{2,exp}}$ Experimental second statistical moment obtained for phenol and 2-naphthol (min$^2$)
- $M^{*\text{2,model}}$ Second statistical moment obtained by linear model isotherm with non-equilibrium adsorption for phenol and 2-naphtol (min$^2$)
\( M_0 \) Zeroth statistical moment 
\( M_1 \) First statistical moment (min) 
\( M_{1,\text{exp}} \) Experimental first statistical moment obtained for phenol and 2-naphthol (min) 
\( m_{1,2} \) Molecular gas components for Eq (3.4) 
\( M_{1,\text{model}} \) First statistical moment obtained by linear model isotherm with non-equilibrium adsorption for phenol and 2-naphthol (min) 
\( M_2 \) Second statistical moment (min\(^2\)) 
\( M^*_2 \) Second central statistical moment or variance of the concentration distribution (min\(^2\)) 
\( M^*_3 \) Third central statistical moment (min\(^3\)) 
\( M^*_{3,\text{exp}} \) Experimental third central statistical moment obtained for phenol and 2-naphthol (min\(^3\)) 
\( M^*_{3,\text{model}} \) Third central statistical moment obtained by linear model isotherm with non-equilibrium adsorption for phenol and 2-naphthol (min\(^3\)) 
\( MS \) Mass Spectrometry 
\( N \) Theoretical plate number; \( N=(t_R/w_h) \) 
\( n_o \) Number density obtained from ideal gas law for Eq (3.4) 
\( nr \) Number of nodes in radial direction 
\( ns \) Number of nodes in axial direction 
\( nt \) Number of nodes in time 
\( p \) Total pressure in the system (kPa) 
\( p_o \) Atmospheric pressure (kPa) 
\( Q \) Flow rate (cm\(^3\)/s) 
\( q \) Dimensionless \( c_s \) in the stationary phase \( q = c_s L / c_o K \bar{u} \) 
\( r \) Radial coordinate 
\( R \) Ideal gas constant (kJ/mol K)
\( r_c \)  
Radius of the column (cm)

\( rR_2 \)  
Solvation parameter of contribution from lone pair \( n \) and \( \pi \) electrons interactions as Eq (3.5)

\( S \)  
Skewness (\( S=M_3/M_2^{3/2} \))

\( SP \)  
Free energy related with solute properties by solvation parameter model as Eq (3.5)

\( t \)  
Time (s)

\( t' R \)  
Adjusted retention time (min); \( t' R = t_R - t_M \)

\( T_b \)  
Boiling temperature (K)

\( T_c \)  
Column temperature (K)

\( T_{co} \)  
Average column temperature (K)

\( t_M \)  
Retention time of an unretained compound or residence time (s); 
\( t_M = L / \bar{u} \)

\( \bar{u} \)  
Average linear velocity (cm/s)

\( u_{max} \)  
Maximum velocity of the carrier gas (cm/s)

\( V \)  
Volume; \( V=2\pi(r_c+d_f)^2 \Delta z \)

\( V_M \)  
Hold up volume (cm\(^3\))

\( V_R \)  
Retention volume (cm\(^3\)); \( V_R = t_R Q \)

\( w_b \)  
Base width of the chromatographic peak; \( 4\sigma \)

\( x \)  
Dimensionless axial length, \( x = z / L \)

\( y \)  
Dimensionless solute concentration in the mobile phase, 
\( y = c_{mean} L / c_o \bar{u} \)

\( z \)  
Axial coordinate
Greek Letters

\( \gamma \)  
Dimensionless axial dispersion parameter, \( \gamma = \frac{D_g}{\bar{u}L} \)

\( \delta(t) \)  
Dirac Delta function

\( \Delta_c \)  
Variation of the local concentration for the mean concentration (mg/cm\(^3\))

\( s\pi_{2}^{H} \)  
Solvation parameter of contribution from dipole-dipole interactions as Eq (3.5)

\( a\sum\alpha_{2}^{H} \)  
Solvation parameter of solute hydrogen bond with the stationary phase as Eq (3.5)

\( b\sum\beta_{2}^{H} \)  
Solvation parameter of contribution from cavity formation as Eq (3.5)

\( \kappa_B \)  
Boltzmann constant

\( \sigma_{12} \)  
Average molecular ratio of each species for Eq (3.4)

\( \Delta H_{ads} \)  
Energy of adsorption of the solute in the stationary phase (kJ/mol)

\( \Delta M_{2,\text{model}}^{*} \)  
Second statistical model by subtracting numerical error in linear isotherm model with non-equilibrium adsorption (Eq. 6.11)

\( \Delta M_{3,\text{model}} \)  
Third statistical model by subtracting numerical error in linear isotherm model with non-equilibrium adsorption (Eq. 6.12)

\( \Delta r \)  
Width of control volume in radial coordinate (cm) \( \Delta r = \frac{d_j}{(nr + 1)} \)

\( \Delta t \)  
Width of control volume in time (s) \( \Delta t = \frac{t_{exp}}{(nt + 1)} \)

\( \Delta z \)  
Width of control volume in radial coordinate (cm) \( \Delta z = \frac{L}{(ns + 1)} \)

\( \Omega_{12} \)  
Lennard-Jones potential potential

\( \kappa \)  
Dimensionless diffusion parameter, \( \kappa^2 = d_j^2 \bar{u} / D_x L \)

\( \sigma \)  
Variance of the chromatographic peak (min\(^2\))

\( \rho \)  
Mobile phase density (g/cm\(^3\))

\( \zeta \)  
Dimensionless film thickness, \( \zeta = \frac{(r - r_c)}{d_f} \)

\( \omega \)  
Dimensionless adsorption coefficient, \( \omega = \frac{r_c}{K_s d_j} \)
Chapter 1

1 Introduction

Gas Chromatography (GC) is one of the most widespread techniques for analyzing chemical species. It consists of a physical separation of chemical species, taking advantage of different species distributions between gas and solid or liquid phases. The mobile gas phase, transports chemical compounds in contact with a stationary phase. As a result, species separation is due to the different degree of interactions between the analyte and the stationary phase (Miller, 2005; Sparkman, et al., 2011). To achieve a physical separation, solutes and chromatographic phases have to interact with each other via intermolecular forces, such as Van der Waal forces. Chemical bonding has to be prevented given that this bonding may allow a solute to modify the stationary phase and as a result the column may no longer be able to be used (Vitha and Carr, 2006).

Chromatography is a complex process that has been described by several authors since 1941, when Martin and Synge presented the plate theory for the elution of a given solute in a packed chromatographic column. This theory, modifies the van Deemter’s equation and assigns mathematical parameters to the adsorption and diffusion phenomena between a solute and stationary phase (Martin and Synge, 1941).

Proposed models in the technical literature are based on the Martin and Synge model, which uses a macroscopic mass balance. Alternatively, these models can be based on the Giddings and Eyring model using a microscopic mass balance or statistical approach (Giddings and Eyring, 1955). One can, in fact, opt for any of these two approaches since they has been proved to be equivalent (Felinger, et al., 2004). Both chromatographic model approaches consider that the interaction of any analyte in the system is affected by a number of factors, such as: a) axial and radial diffusions taking place in the mobile phase, b) axial and radial diffusions in the stationary phase, c) flow in the cross section of the capillary column (laminar or turbulent flow), and d) adsorption-desorption processes of mobile and stationary phases (Chen, 2007). Furthermore, mathematical models may consider not only linear or non-linear isotherms but also the equilibrium between phases.
or non-equilibrium adsorption-desorption processes (Jönsson, 1984; Kong, et al., 2004; Yamaoka, et al., 1974).

As a result, a set of partial differential equations is obtained to describe the elution of a chromatographic peak. Moreover, many authors report statistical moments of different order (first, second and third order) as an alternative way to find the adsorption and kinetic parameters from these equations as follows (Gao, et al., 2010; Grubner, 1971; Grubner, et al., 1967; Grushka, 1972):

a) The first statistical moment ($M_1$) can be related to the adsorption equilibrium parameters, such as the distribution (partition) coefficient ($K_s$) with this parameter only being a function of the analyte and stationary phase properties.

b) The second statistical moment ($M_2$) or the variance (width of the peak) can be related to convection and diffusion parameters such as the diffusion coefficient in both stationary and mobile phases ($D_G$ and $D_S$).

c) The third statistical moment ($M_3$) can be used to represent mass transfer exchange between phases including the adsorption rates and the $k_{ads}$ adsorption rate constants (Gritti and Guiochon, 2012; Miyabe, et al., 2010).

Moreover, the modelling of chromatographic systems has evolved, following the changes in chromatographic column development and applications. The first chromatographic columns were of the packed type and used 0.1-0.2 mm porous sorbent particles (Grob and Barry, 2004). In 1958, Golay suggested the possible use of open columns with a wall coated stationary phase as a way to improve the resolution in chromatograms (Golay, 1958). As a result of this, open columns were introduced in GCs, given that they had a number of advantages over packed columns: a) the two phases rapidly reached adsorption equilibrium; b) they displayed a low pressure drop per unit length allowing the manufacture of longer columns c) they showed a reduction of the gas dispersion into the column; d) they gave more symmetric chromatographic peaks e) they were very stable with only a small amount of polymer coating depleted during extended gas analysis. On this basis, narrow bore capillary columns were designed with average inner diameters of 0.1 mm and lengths of 30-60 m. (Rezaii and Lattanzi, 1994).
Regarding packed columns, a number of models are reported in the technical literature (Grubner and Zikanova, 1967; Kucera, 1965; Vidal-Madjar and Guiochon, 1977). Following Golay's (1958) work with open columns, a number of models were also reported for these columns. These models considered linear or nonlinear isotherms and various others manufacturing considerations such as: a) characteristics of the stationary phase, film thickness and porosity; b) axial dispersion and convection assumptions and c) mass transfer terms (Chen, 2007, 2011; Ching-Chih and Chung-Sung, 1995; Medi and Amanullah, 2011; Pawlisch, et al., 1987).

It is important to notice however, that in spite of these advances, the available information regarding open columns for gas chromatography is still very limited. For instance, there is no available unsteady state model for capillary columns, such as the commercial BPX5 column. The BPX5 capillary column is one of the most used capillary columns to analyse a diversity of samples including hydrocarbon compounds from biomass gasification. It is our view that an unsteady state model for a BPX5 column would provide a valuable basis to improve its performance and potentially influence the design of capillary columns in the future.

To accomplish this, a capillary column model based on a macroscopic balance approach is considered to obtain both equilibrium and kinetic adsorption parameters. To address these issues, this Ph.D dissertation is organized in six more chapters. Chapter 2 contains a relevant literature review including the general information about gas chromatography, capillary columns and available mathematical models. Chapter 3 outlines the main and particular objectives of the research project. Chapter 4 describes the experimental methods and materials used to develop the present study. Chapter 5 reports the validation of an adsorption equilibrium model with the experimental chromatographic analysis of aromatic species. Chapter 6 addresses the validation of an adsorption non-equilibrium model by using the experimental results of oxygenated aromatic species. Finally, Chapter 7 provides the conclusions and recommendations for future work.
Chapter 2
Literature Review

2 Introduction

The present PhD study considers the principles of gas phase chromatography. This is accomplished in the context of both experimental methods and mathematical modeling. A literature review is reported in this section, considering important matters such as a) basic terminology: namely mobile and stationary phases, retention times and hold up times, b) relevant gas chromatography phenomena: equilibrium adsorption and adsorption kinetics and c) available mathematical models and associated parameters for capillary gas chromatography such as convective and film diffusivities. Lastly, this chapter offers a conclusion regarding the present state-of-the-art methods in this area of study.

2.1 General Features of Gas Chromatography

Chromatography from Greek *chroma* “colour” and *graphein* “to write” refers to the early designation offered by Tswett of separation processes of chemical species based on color (Miller, 2005). Nowadays, however, the “chromatography” designation has broadened to refer to the collective methods for the separation of complex mixtures of chemical species, not necessarily by color.

Since Martin and James (1941) proposed the separation of chemical species in chromatographic columns (Martin and Synge 1941), this technique has become one of the most important separation methods used for analytical purposes.

In gas chromatography (GC), the mobile phase is a gas phase while the stationary phase is a solid polymer and/or absorbent material. Regarding gas chromatography in packed columns, one can notice that this method is based on the separation of chemical species taking advantage of their relative distribution between two phases (e.g. gas and solid phases). One of these phases is the gas phase, which is designated as the mobile phase, given that its carries and transports the chemical species. On the other hand, the
stationary phase has the ability to selectively adsorb the evolving analytes. This leads to the selective adsorption of species, providing a progressive and selective separation as described in Figure 1 for species “A” and “B”.

Figure 1 reports a typical analysis in a GC unit of species A and B. This analysis shows the progressive separation of A and B chemical species with the help of a solid phase. One can thus, see that the species “A” will be viewed by a detector placed at the outlet of column well before the species “B”. Thus, the relative amounts of “A” and “B” species as in the original gas mixture can be accurately separated and quantified.

![Diagram of GC analysis](image)

**Figure 1 General Representation of the Gas Chromatographic Analysis. Adapted from Miller (2005).**

Given that chemical species have different chemical structures and molecular weights, they experience different interactions with the stationary phase of the chromatographic column. As a result, the system allows separation and quantification of components in a complex mixture (Miller 2005; Sparkman et al. 2011). Furthermore, the study of single analytes in GC is of significant theoretical value. In this case, the mobile phase transports the analyte in continuous interaction with the stationary phase. This type of GC analysis
is called “elution” chromatography. The characteristic chromatographic curve of solute concentration as a function of time can be visualized as an elution curve (Jönnsson, 1987). One of the values of the “elution” curve or “outlet peak” is to be able to obtain information regarding the interaction of a given solute and a particular stationary phase.

2.1.1 Separation of Chemical Species in Gas Chromatography

Figure 2 describes the typical requirements of a basic GC system. There is an injector device placed at the GC system inlet where quick volatilization of the sample takes place. Following injection and vaporization, the carrier gas of the mobile phase transports the volatized sample to the chromatographic column to be separated. A detector placed at the end of the column, converts changes on pressure of the chemical species of the sample to electrical signals. A GC system can work with one or more different detectors: a) A mass spectrometry detector (MS), b) A flame ionization detector (FID) and c) A thermal conductivity detector (TCD) (Sparkman, et al. 2011). The amplifier transfers magnified electrical signals to the software, where signals are transformed in chromatographic peaks to be identified.

More specifically, when using capillary columns, the carrier gas constituted of helium free of oxygen, is supplied to the column by the flow control system. As a result, both the pressure and flow of the carrier gas are accurately controlled. As stated, at the end of the capillary column, a Mass Spectrometry Detector (MS) can be used. Thus, the GC-MS system provides an excellent laboratory unit for separation, characterization and quantification of chemical species (Grant, 1996; Sparkman, et al. 2011).

Furthermore, the elution of chemical species in chromatography can be reported in a chromatogram. Areas of the peaks contained in the chromatogram are proportional to the flux of the carrier and the solute concentration to be analyzed. Generally, chromatograms are obtained at a constant flow of carrier gas and then, reported as a concentration with respect to time or volume (Jönnsson, 1987; Miller, 2005).
Figure 2 Schematic Diagram of Universal Gas Chromatography. Adapted from Spakman, et al. (2011) and Grant (1996).

Regarding parameters in chromatography, one can analyze a single component and deduce the following from the output peaks: a) the retention time ($t_R$), b) the mobile phase hold up time ($t_M$), c) the retention volume ($V_R$), d) the capacity factor ($k'$), e) the average linear velocity, f) the theoretical plate number ($N$) and g) the theoretical plate height ($H$). All these parameters are specific for a solute eluting in a given chromatographic column.

Regarding these various parameters, one should notice that the time required to reach the maximum peak concentration is designated as the retention time ($t_R$). The corresponding volume of the gas phase is the retention volume ($V_R$) and is expressed as $V_R = t_R Q$; where $Q$ is the constant flow rate. If one injects a pulse of an inert compound, the peak retention time becomes the mobile phase hold up time ($t_M$) and its correspondence volume, $V_M$, is the volume of the mobile phase in the column.

Furthermore, the above described concepts can also provide the time that the solute spends in the stationary phase as $t'R = t_R - t_M$, where $t'R$ is the adjusted retention time. Once $t_R, V_R, V_M$ and $t'R$ are determined, the capacity factor ($k'$) can be calculated as $k' = \ldots$
In other words, the capacity factor is a normalized retention time for a given solute and is also related to the equilibrium constant \( \text{Jönsson, 1987} \).

On the other hand, the efficiency of the chromatographic column can be represented using the ‘number of theoretical plates’ \( N \). The number of theoretical plates concept was introduced as an analogy with distillation columns. This is however an empirical concept given that there are no internal plates in chromatographic columns. Regarding the ‘number of plates’, they can be calculated as \( N=(t_R/w_h) \), where \( w_h \) is the base width of the peak and is equal to 4 times the variance \( (\sigma) \). A single \( N \) value can be calculated for a symmetric chromatographic peak. However, for asymmetric peaks, where a peak does not follow a Gaussian distribution, \( N \) may display more than one possible value \( \text{(Grant, 1996; Jönsson, 1987)} \).

van Deemter et al. (1956), introduced an empirical plate height \( (H) \) such that \( H=L/N \) where \( L \) refers to the total length of the column and \( N \) to the number of theoretical plates. One should notice that the plate height \( (H) \) is inversely proportional to the plate number \( (N) \) and that small values of \( H \) indicate a narrow peak, as is desired in chromatography. Plate height can also be considered to include diffusion and mass transfer parameters in packed gas chromatographic columns. In this respect, the van Deemter’s equation expresses the band broadening in terms of \( H \) as a function of the average linear velocity \( (\bar{u}) \) as:

\[
H = A + \frac{B}{\bar{u}} + C\bar{u}
\]

(3.1)

where A, B and C represent the parameters of eddy diffusion, longitudinal molecular diffusion and mass transfer in the stationary phase, respectively. Once \( \bar{u} \) is determined with \( \bar{u} = L/t_M \), then, A, B and C have to be minimized to find the minimum value of \( H \) for the chromatographic system.

Figure 3 illustrates an example of the van Deemter’s equation. It is concluded that the best efficiency in an open tubular GC column is achieved having helium as a carrier gas \( \text{(Miller, 2005)} \). Hence, other variables of the system, such as stationary film thickness and
temperature can be studied using van Deemter’s equation.

![Graph showing comparisons of different carrier gas efficiencies in open GC columns.](image)

**Figure 3 Comparisons of Different Carrier Gas Efficiencies in Open GC Columns. Adapted from Miller 2005.**

Additionally, an alternative way to calculate the plate number is by statistical moment theory where: a) the zeroth moment \((M_0)\) is the peak area, b) the first statistical moment \((M_1)\) is equivalent to the maximum concentration and \(t_E\) is the average retention time for a symmetric peak, c) the second statistical moment \((M_2)\) is the variance of the peak and d) the third statistical moment \((M_3)\) determines the asymmetry of the band (Miller, 2005). A further discussion of statistical moments is presented in section 2.4.

### 2.1.2 Types of Gas Chromatography Columns

There are two types of chromatographic columns for GC: packed and open columns. A packed column consists of a tube packed with porous solid material. The characteristics of the packing material are important since they strongly influence the separation of the mixture compounds. The packing material can have a regular or irregular particle shape and be porous or non-porous. Better performance is obtained, however, with porous particles of regular shape and size.
In this respect, many packing materials are available for GC analysis. Some of these materials can be found in nature such as diatomaceous earth. Some others are inorganically based, such as sodium silicate as a silica-gel, alumina, magnesium silicate, porous graphitic carbon, hydroxyapatite and zirconia. Finally, there are other organic porous polymers, such as polymethyl methacrylate, divinylbenzene and styrene. One should note, however, that the performance of these packed materials can be influenced by the surface energy, the pH compatibility and the crushing strength of the packing material under pressure (Miller, 2005).

In 1957, Golay suggested the use of coated open columns to improve the gas chromatography analysis (Golay, 1958). Open columns, also called “capillary columns” offer many advantages over packed columns. One of the most relevant gains is an enhanced chromatographic separation, with high reproducibility. Nowadays, the development of open columns has focused on narrow bore capillary columns 60 m long with an inner diameter of 0.25 mm.

Table 1 summarizes the main differences between packed and open chromatographic columns for GC applications. Thus the several advantages of open columns with respect to packed columns can be stated follows:

a) There is a small amount of polymer coating required in the open column. This makes the detailed analysis of many complex mixtures feasible.

b) A small amount of analyte is required for GC analysis. This is critical when limited amounts of samples are available.

c) The pressure drop per unit length is several orders of magnitude lower than in packed columns. Then, long open columns up to 60 m length can be used.

Thus, the superior performance of open capillary columns can be explained, as a result of its special geometry, and given both the flow conditions, as well as the extent of analyte diffusion in the thin film coating of the capillary column (Grant, 1996; Grob and Barry 2004).
<table>
<thead>
<tr>
<th></th>
<th>Packed</th>
<th>Capillary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (m)</td>
<td>1-5</td>
<td>5-60</td>
</tr>
<tr>
<td>Inner diameter (mm)</td>
<td>2-4</td>
<td>0.10-0.53</td>
</tr>
<tr>
<td>Plates per meter</td>
<td>1000</td>
<td>5000</td>
</tr>
<tr>
<td>Total plates</td>
<td>5000</td>
<td>300 000</td>
</tr>
<tr>
<td>Resolution</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Flow Rate (mL/min)</td>
<td>10-60</td>
<td>0.515</td>
</tr>
<tr>
<td>Permeability ($10^7$ cm$^2$)</td>
<td>1-10</td>
<td>10-1000</td>
</tr>
<tr>
<td>Capacity</td>
<td>10 µg/peak</td>
<td>&gt; 100 ng/peak</td>
</tr>
</tbody>
</table>

Nowadays, capillary columns are made from fused silica, instead of glass. Fused silica capillary columns are extruded at a high temperature. Following fused silica glass capillary column manufacturing, a “deactivation” step of the inner fused silica surface is required. This “deactivation” of the inner surface refers to the removal of silanol groups from the silica surface using polymers. A typical example of a polymer than can be used with this objective is Carbowax 20. Deactivation is essential to obtain a uniform thin film along the inner wall of the silica column. Furthermore, once the “deactivation” of the fused silica is completed, the thin film (stationary phase) is added. This thin film is attached by covalent linking to the inner column surface. The most used common stationary phases in capillary columns are non-polar and moderately polar polysiloxanes, such as found in the BPX5 capillary column (Grob and Barry, 2004; Miller, 2005).
2.1.3 Solute Interaction Parameters in Gas Chromatography

The migration of a solute along the capillary column is determined by the equilibrium, the kinetics and the transport properties of the thin film coating of the fused silica capillary column. One should note that, in particular, the equilibrium properties are related to the distribution of a solute between the mobile phase and the stationary phase. To describe these interactions, one can determine the physical properties of the solute, the carrier gas, the polymer coating and the interface. Furthermore, the polymer-solution interactions, such as: a) partition coefficient, b) enthalpy and entropy changes and c) hydrogen bond strength, are important factors affecting the capillary column performance. On the other hand, kinetic and transport properties can cause a solute peak broadening as it moves along the capillary column. These phenomena are significantly influenced by: i) the diffusivity coefficients in gases and polymers, and ii) the adsorption and desorption rate constants (Conder, 2000).

In this respect, one could infer “a priori”, the type of solutes that can be analyzed in capillary chromatographic columns, on the basis of the polymer and carrier gas to be used. In the case of commercial capillary columns, such a BPX5 capillary column, the manufacturer provides this information in broad terms. It is, however, in the hands of the analyst to determine the specific retention times for his/her specific mixture case. There are, furthermore, other key properties that are seldom reported, such as partition coefficient or distribution constant ($K_s$) and enthalpy changes ($\Delta H_{ads}$). These parameters are required to describe the solute interaction with the mobile and stationary phases. It is the goal of this PhD dissertation to provide an in-depth analysis of these key physicochemical properties.

The affinity of a solute to the stationary phase is given by the partition coefficient or the distribution constant ($K_s$). Martin and Synge introduced this concept as the one relating the solute concentration in a stationary phase to the solute concentration in mobile phase (Martin and Synge, 1941). Figure 1, already reported in Section 3.1, illustrates the $K_s$ parameter by showing the solute migration as two peaks, one peak in the mobile phase and the other in the stationary phase. In this Figure, the component “A” moves faster
through the column than the component “B”. This is the result of “A” molecules spending less time in the stationary phase, as pointed out by a smaller peak in this phase. Therefore, the component “A” has a smaller $K_s$ than “B”. If the chemical species are assumed to evolve close to the adsorption equilibrium, $K_s$ is an equilibrium constant (Miller, 2005). Moreover, the partition coefficient or the distribution constant could be related to thermodynamics. In fact, one important parameter involved in the adsorption phenomena is the enthalpy of adsorption ($\Delta H_{ads}$). This parameter provides key information to describe the energy of interaction between the analyte and the stationary phase. If the adsorption phenomenon in gas chromatography is of a physical type, a typical value of $\Delta H_{ads}$ should be in the 62-64 kJ/mol range (Grob and Barry, 2004).

Regarding the enthalpy of adsorption in a chromatographic column, a possible approach, as reported in this PhD study, is the use of the van Hoff’s equation as follows:

$$K_{sd} = K_{so,i} e^{\frac{\Delta H_{ads}}{RT_c} \left( \frac{1}{T_c} - \frac{1}{T_{co}} \right)}$$

(3.2)

where: a) $K_{so,i}$ represents the equilibrium adsorption (interface) coefficient, b) $T_{co}$ stands for the average temperature selected for the chromatographic column operation, c) $\Delta H_{ads}$ denotes the energy of adsorption of the given chemical species on the polymer coating in kJ/mol, d) $R$ is the ideal gas constant in J/mol K, and e) $T_c$ represents the column temperature in degrees Kelvin (Levenspiel, 1999).

However, the performance of the capillary column can also be affected by kinetic parameters, as previously discussed in section 2.1.1. It was in this section, where van Deemter’s equation was introduced. This equation contains diffusion and mass transfer parameters. In this respect, Golay (1958) described the plate height in GC with open columns using an $H$ mass transfer term with the $c_m$ being the analyte concentration in the gas phase and $c_s$ being the concentration of analyte in the solid phase Golay’s equation can be represented as follows:

$$H = \frac{B}{u} + (c_m + c_s)\bar{u}$$

(3.3)
where

\[ B = 2D_G ; \]
\[ c_m = \frac{(1 + 6k' + 11k')2r^2}{96(1 + k'^2)D_G} \quad \text{and} \quad c_s = \frac{4k'2r^2}{3(1 + k')^2 D_s} \]

Regarding these equations, the values of the inner radius, \( r_c \), and the average linear velocity can be established accurately in modern chromatographic columns. However, there is uncertainty in the definitions of \( D_G \) and \( D_s \) diffusivity coefficients.

In this respect, some predictions of \( D_G \) can be made via equations, using the theory of diffusion in gases which includes collision theory. This type of equations can be represented as follows:

\[ D_{12} = 0.00189T^{3/2} \sqrt{\left( \frac{m_1 + m_2}{m_1 m_2} \right) \frac{1}{p \sigma_{12}^2 \Omega_{12}(T)}} \tag{3.4} \]

where \( T \) is the absolute temperature; \( m_1 \) and \( m_2 \) are molecular masses of the chemical species 1 and 2 in g/mol; \( \sigma_{12} \) is the average molecular ratio of each species and is defined as \( \sigma_{12} = 1/(\sigma_1 + \sigma_2) \); \( p \) is the total pressure of the binary mixture in atm; and \( \Omega_{12}(T) \) is the Lennard-Jones potential (Grant, 1996; Bird et al., 2002).

Regarding the reported molecular diffusion coefficients in the open literature, they are in the 0.1 to 0.6 cm\(^2\)/s range, while diffusion coefficients in the stationary phase (\( D_s \)) are in the 10\(^{-7}\) to 10\(^{-10}\) cm\(^2\)/s range (Grant, 1996; Duda, 1985; George and Thomas, 2001).

### 2.2 Solute-Polymer Phase Physical Forces and Interactions

As is described in section 2.1, chromatography is a physical separation in which the components of a mixture are distributed between two phases. This physical separation could involve absorption, adsorption, electromigration or size exclusion processes. In any case, the intermolecular or physical forces rule the separation phenomena. Typical intermolecular forces in chromatography are: a) ion interaction, b) Van der Waal forces and c) hydrogen bonding (Miller, 2005).
Ion interactions need dissociated molecules in ion form. Ions of opposite charge can be attracted as Coulomb’s law described. Ion interactions are one of the strongest interactions between molecules. Ion interactions are important in liquid chromatography where a polar stationary phase can interact with ionic solutes (Vervoort, et al., 2002; Dorsey and Cooper, 1994).

Other possible intermolecular forces are the van der Waals interactions. van de Waals forces can be classified in dipole-dipole, dipole-induced dipole and induced dipole-induced dipole. Polar molecules have permanent dipoles and non-polar molecules produce momentary dipoles (induced dipoles) due to motion of electrons in the chemical structure. This induction of a dipole depends on the polarizability of the non-polar molecule. In GC having a solid stationary phase, the separation of non-polar molecules, such as alkanes, occurs as a result of van der Waals forces. (Miller, 2005; Vitha and Carr, 2006).

In some cases, however, these interactions also involve hydrogen bonding forces (Wu, et al., 1992). Hydrogen bonding involves molecules with hydrogen atoms bonded to oxygen or nitrogen that have a strong electronegativity character. The surfaces of many polymer phases in chromatography contain hydroxyl groups that can form hydrogen bonds. These can provide an undesirable heterogeneity to the surface, causing tailings in the chromatographic peaks. Furthermore, the insertion of other groups to reduce hydroxyl groups can be used to minimize this problem. An example of hydrogen bonding is liquid chromatography, which uses water and organic solvents as a mobile phase (Sander, et al. 2005; Meyer, et al. 2006; Saldoval and Pesek, 1989; Chowdhury, et al., 2000).

Mobile-stationary phase interactions and their physicochemical explanations present indeed, a challenging topic, with this becoming even more complex given that: a) there is a heterogeneity of stationary phases and b) the several possible interactions between solute, mobile and stationary phases. It is important to note, however, that dispersion interactions and intermolecular forces may also affect the molecular selectivity for some columns. These phenomena can be quantified by some parameters, such as the SP
solvation parameter that can be used to calculate retention properties of stationary phases in chromatographic columns as follows:

$$\log SP = c + rR_2 + s\pi_2^H + a \sum \alpha_2^H + b \sum \beta_2^H + l(\log L^{16}) \tag{3.5}$$

where SP is a free energy related solute property equivalent to a partition coefficient.

This SP free energy related solute property is a function of the retention factor, the retention volume and the capacity factor. As shown in Eq (3.5), SP can be expressed as a function of $c$, $r$, $s$, $a$, $b$ and $l$ system constants. The other variables in Eq (3.5) are solute descriptors as follows: a) the contribution from lone pair $n$- and $\pi$-electron interactions is given by $rR_2$; b) the interactions of dipole-dipole are contained in $s\pi_2^H$; c) the solute hydrogen bond with the stationary phase are represented by $a \sum \alpha_2^H$ and $b \sum \beta_2^H$; and d) the contribution from the cavity formation and solute-stationary phase dispersion interactions are given by $l(\log L^{16})$ (Poole, et al., 2000).

Regarding this study, a BPX5 capillary column was employed to model adsorption-desorption processes using both, polar and non-polar aromatic compounds. Figure 4 reports the general chemical structure of BPX5 polymer and also, the analyzed chemical species. The stationary phase in a BPX5 capillary column is manufactured with 5% phenyl-95% polysilphenyesiloxane polymer, making this, a non-polar polymer thin film with 5% of polar sites. Therefore, Van der Waals forces are involved in the solute interactions. One can notice that for similar stationary phases, such as 5% phenyl methylsilicone, a “s” solvation parameter is observed, showing a strong contribution of intermolecular forces (Vitha and Carr, 2006). It is noticed that the aromatic sites in the polymer can also interact with aromatic species in the solute by “$\pi$ staking forces”.
Solute eluted through a BPX5 capillary column

Nonpolar aromatic compounds

\begin{align*}
 & \text{Toluene} & \text{Naphthalene} \\
 & \text{Phenol} & \text{2-Naphthol}
\end{align*}

Polar aromatic compounds

Chemical structure of the BPX5 polymer coating

\begin{align*}
\text{Phenyl-polysilphenyenesiloxane}
\end{align*}

Figure 4 General Chemical Structure of Phenyl-Polysilphenyenesiloxane in BPX5 Capillary Column

Before mentioning specific adsorption-desorption models, a description of the isotherm adsorption in chromatography has to be assessed. This review will be developed in the upcoming literature section.

2.2.1 Adsorption Isotherms in Chromatography

An adsorption isotherm provides a description of the fraction of the adsorbed solute on the solid phase in dynamic equilibrium with the analyte in the solution (gas or liquid mobile phase) at a given temperature. This ratio is called the partition coefficient or distribution constant and is defined as follows:

\[ K_s = \frac{c_s}{c_m} \]  \hspace{1cm} (3.5)

where \(c_s\) is the concentration of an analyte in a stationary phase and \(c_m\) is the
concentration of the analyte in the mobile phase or at the gas phase (mg/m$^3$).

The concentration of the analyte on the solid phase, expressed per unit mass of polymer can be plotted with respect to the concentration of the same substance in equilibrium with the mobile phase at the interface. Figure 5 shows three different isotherms; linear, non-linear with a concave shape and non-linear with a convex shape (Grob and Barry, 2004).

In the case of a linear isotherm, the frontal and rear boundaries of the band are symmetric leading to a Gaussian type of peak. In this case the ratio of the concentration $c_s$ per unit mass and the gas phase concentration $c_m$, remain constant as is represented in Figure 5b. Therefore, the distribution constant $K_s$ is not a function of the analyte concentration (Bürgisser, et al., 1993).

On the other hand, in the chromatographic column, non-linear isotherms are caused by a high concentration of the analyte and/or an energetically heterogeneous polymer phase. These energetically heterogeneous stationary phases contain adsorption sites leading to significantly different association/dissociation rates (Poole, 2003). One possible case of a non-linear isotherm with $K_s$, changing with concentration is shown in Figure 5a. This isotherm is convex when $K_s$ increases rapidly with a solute concentration in the gas phase ($d^2c_s/dc_m^2 < 0$). Therefore, when the analyte concentration increases a sharp peak front develops. Furthermore, when the concentration $c_s$ is being depleted, a diffuse front forms in the peak tail. The peak tailing can often be explained by the fact that the retention of the analyte decreases with increasing $c_s$, as all available interaction sites in the stationary phase are occupied by the solute. Furthermore, another type of isotherm is the concave type reported in Figure 5c. In this figure, one can observe a diffuse front peak and a sharp peak rear tail (Bürgisser, et al., 1993; Grob and Barry, 2004).

There are numerous models of adsorption isotherms for pure and mixed compounds, in a chromatographic column. Models such as linear, Langmuir, Bilangmuir, Langmuir-Freundlich and Tóth are commonly found in the open literature to describe chromatographic adsorption/desorption events (Kaczmarski, et al., 2003; Zhang, et al., 2006; Zhang, et al., 2008; Gritti and Guiochon, 2012).
To avoid complex models, one can limit the amount of the analyte. This allows one to convert convex or concave isotherms into linear ones. This approach provides an easier solution to the mathematical models described in section 2.3.3 (Bürgisser, et al., 1993; Grob and Barry, 2004). Then, a linear isotherm equation can be used consistently and expressed as:

\[ c_m = K_s c_s \] (3.2)

Figure 5 Linear and Non-linear Isotherm Chromatography. (a) convex isotherm, (b) linear isotherm and (c) concave isotherm. Adapted from Grob and Barry (2004) and Bürgisser et al., 1993.

2.2.2 Mathematical Chromatographic Models

Studies in the open literature consider two different approaches to describe the chromatographic elution of a solute: a) the macroscopic balance or bulk perspective, and b) the microscopic balance or ensemble perspective. The first approach utilizes
macroscopic species expressed as differential equations in an open or packed chromatography column. On the other hand, the microscopic balance considers statistical based methods to describe the retention processes inside the column (Felinger, et al., 2004). Macroscopic balances are considered to involve less demanding numerical calculations. This PhD dissertation focuses on the use of a macroscopic species balance to describe the elution of aromatic compounds in a GC capillary column.

In this respect, these GC models, based on macroscopic balances, can involve ideal and non-ideal chromatograms with linear and non-linear isotherms. An ideal model defines a thermodynamic reversible mass transfer between both, mobile and stationary phases. This species transfer is very high and therefore other diffusion processes can be neglected while setting the model. On the other hand, non-ideal chromatography does not involve these assumptions. Therefore, there are four types of chromatographic models available; with all of them assessed in the upcoming section of this review. One should note that these macroscopic based equations have been used to describe single or multiple compound elutions in both packed and open chromatographic columns.

2.2.2.1 Linear Chromatography at the Equilibrium

A linear isotherm from the eluted solute, leads to symmetric chromatographic peaks. When several chemical species are carried by the same mobile phase, peak separation is achieved with limited peak broadening. In other words, species mass transport is high enough with species staying at the conditions of adsorption equilibrium (Golay, 1958; Aris, 1959).

In spite of the fact that adsorption equilibrium phenomena neglect mass transfer processes; they have been proven to be good descriptors for some gas chromatography analyses. Additionally, some authors also neglect axial dispersion, calculating adsorption and diffusivity parameters using statistical moments (Yamaoka, 1974; Pawlisch, et al. 1987; Romdhane and Danner, 1993; Ching-Chih and Chung-Sung, 1995).
2.2.2.2  Linear Chromatography at Non-Equilibrium

The linear chromatography at non-equilibrium, leads to band broadening, given diffusion effects or/and non-equilibrium adsorption of the analyte. This broadening mechanism is typically asymmetric (Guiochon and Lin, 2003; Grob and Barry, 2004). Khan (1960) and Kucera (1965) presented the first linear isotherm models, considering the longitudinal diffusion in the mobile phase, the radial diffusion inside of the porous grains of the packing material and the finite mass transfer rate. These publication also provided both adsorption and diffusivity parameters through statistical moment equations (Kucera, 1965; Khan, 1960). Later on, Grubner et al. (1967) and Vidal-Madjar and Guiochon (1977) also considered the Plate Theory, to solve the same model for gas chromatography. Furthermore, Lee et al. (1988) developed an equation that could be expanded to five different kinetic models (Grubner and Zikanova, 1967; Vidal-Madjar and Guiochon, 1977; Lee, et al., 1988).

2.2.2.3  Non-Linear Chromatography at the Equilibrium

This type of modeling approach accounts for both the hydrodynamics and the thermodynamics at equilibrium, using a non-linear isotherm adsorption. This type of model also considers fast interphase mass transport and neglects axial dispersion. Applications for this model are found in liquid-solid chromatography given that in those cases the influence of non-linear isotherms is usually appreciable. The net result of the non-linear isotherm is that peaks develop with sharp fronts and diffuse rear boundaries (Guiochon and Lin, 2003; Grob and Barry, 2004). Jaulmes et al. (1984) reported an application of this model in a capillary column (Jaulmes, et al., 1984). This model can also be used to represent two analytes eluting in the mobile phase. Thus, it leads to two coupled partial differential equations. The equations have an analytical solution if the solute adsorption is represented by Langmuir competitive isotherm model.

The equations for two analytes are reported in Table 2 (Guiochon and Lin, 2003). It is expected, however, that a non-linear isotherm is rarely required in gas chromatography, given the low amounts of analytes involved.
Table 2 Mathematical Model Equations to Describe Elution Chromatography by Adsorption and Diffusion Parameters

<table>
<thead>
<tr>
<th>Type of Chromatography</th>
<th>General Equations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear equilibrium elution in gas chromatography with capillary column</td>
<td>$H = \frac{d u}{d x} = 2 \frac{D_G}{u} + \frac{1 + 6k' + 11k'^2}{24(1 + k')^2} \frac{w_c^2}{D_G}$</td>
<td>(Aris, 1959; Golay, 1958)</td>
</tr>
<tr>
<td>Linear non-equilibrium elution in gas-liquid chromatography</td>
<td>$H = 2\lambda d_p + 2\gamma D_G u + \frac{2}{3} \left( \frac{a_2 k_1}{a_1 k_2} \right)^2 \frac{u}{D_s}$</td>
<td>(Khan, 1960)¹</td>
</tr>
<tr>
<td></td>
<td>$+2 \left( \frac{a_2 k_1}{a_1 k_2} \right)^2 \frac{u}{1 + a_2 k_1 \sigma k_2} \frac{D_s}{D_r}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+2 \frac{a_2 k_1}{a_1 k_2} \frac{D_s}{u}$</td>
<td>(Grubner and Zikanova, 1967)³</td>
</tr>
<tr>
<td>Linear non-equilibrium elution in gas chromatography with packed column</td>
<td>$\frac{\partial c_m}{\partial t} + u \frac{\partial c_m}{\partial z} - D_s \frac{\partial^2 c_m}{\partial z^2} = Q_c$</td>
<td>(Kucera, 1965)²</td>
</tr>
<tr>
<td>Linear non-equilibrium elution in gas chromatography with packed column</td>
<td>$H = \frac{M_2}{M_1} L = 2A + 2\frac{D_G}{u}$</td>
<td>(Grubner and Zikanova, 1967)³</td>
</tr>
<tr>
<td></td>
<td>$+\frac{2}{15} \frac{\phi(1 + K_s)^2}{(1 + \phi K_s)^2} \frac{r_p}{D_r} u$</td>
<td></td>
</tr>
<tr>
<td>Linear equilibrium elution in gas chromatography with packed column</td>
<td>$(1 + k') \frac{\partial c_s}{\partial t} = D_p \frac{\partial^2 c_s}{\partial z^2} - u \frac{\partial c_s}{\partial z}$</td>
<td>(Yamaoka, 1974)</td>
</tr>
<tr>
<td>Type of Chromatography</td>
<td>General Equations</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------------------------------------------</td>
<td>-------------------------------------------------------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Linear non-equilibrium elution in gas chromatography with packed column</td>
<td>[ H = \frac{M_2}{M_1} L = \frac{2D_g}{u} + \frac{2k'}{(1+k')^2} \frac{d_f^2}{3D_s} u ]</td>
<td>(Vidal-Madjar and Guiochon, 1977)</td>
</tr>
<tr>
<td>Non-linear equilibrium elution in gas chromatography with open column</td>
<td>[ \frac{\partial X}{\partial t} (1+k') + \frac{\partial(uX)}{\partial z} = D_g \frac{\partial^2 X}{\partial z^2} ]</td>
<td>(Jaulmes, et al., 1984)</td>
</tr>
<tr>
<td></td>
<td>[ \frac{\partial X}{\partial t} = \frac{\partial [u(1-X)]}{\partial z} - D_g \frac{\partial^2 X}{\partial z^2} ]</td>
<td></td>
</tr>
<tr>
<td>Linear equilibrium elution inverse in gas chromatography with open column</td>
<td>[ \frac{\partial c_{mean}}{\partial t} + u \frac{\partial c_{mean}}{\partial z} = D_g \frac{\partial^2 c_{mean}}{\partial z^2} + \frac{D_s}{r_c} \frac{\partial c(r=r_c)}{\partial r} ]</td>
<td>(Pawlisch, et al., 1987)</td>
</tr>
<tr>
<td></td>
<td>[ \frac{\partial c}{\partial t} = D_s \frac{1}{r} \frac{\partial}{\partial r} \frac{r}{\partial r} c ]</td>
<td></td>
</tr>
<tr>
<td>Linear non-equilibrium elution in gas chromatography with packed column</td>
<td>[ \varepsilon \frac{\partial c_e}{\partial t} = -\frac{Q}{A_c} \frac{\partial c_m}{\partial z} + \varepsilon \frac{D_s}{r_c} \frac{\partial^2 c_m}{\partial z^2} + R ]</td>
<td>(Lee, et al., 1988)</td>
</tr>
<tr>
<td></td>
<td>[ \varepsilon \frac{\partial c_m}{\partial t} = \pm \frac{Q}{2\pi L_z} \frac{\partial c_m}{\partial z} + \varepsilon \frac{\partial}{\partial z} \left( D_c \frac{\partial c_m}{\partial z} \right) + R ]</td>
<td></td>
</tr>
<tr>
<td>Linear equilibrium model inverse in gas-liquid chromatography with packed column</td>
<td>[ \frac{\partial c_s}{\partial t} = D_s \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_s}{\partial r} \right) ]</td>
<td>(Romdhane and Danner, 1993)</td>
</tr>
<tr>
<td></td>
<td>[ \frac{\partial c_m}{\partial t} + \varepsilon \frac{\partial c_m}{\partial t} + u \frac{\partial c_m}{\partial z} - D_s \frac{\partial^2 c_m}{\partial z^2} = 0 ]</td>
<td></td>
</tr>
<tr>
<td>Linear equilibrium model in chromatographic peak broadening technique</td>
<td>[ \frac{\partial c_m}{\partial t} + 2u \left[ 1 - \left( \frac{r}{r_c} \right)^2 \right] \frac{\partial c_m}{\partial z} = D_s \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_m}{\partial r} \right) ]</td>
<td>(Ching-Chih and Chung-Sung, 1995)</td>
</tr>
<tr>
<td>Type of Chromatography</td>
<td>General Equations</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------------------</td>
<td>-----------</td>
</tr>
</tbody>
</table>
| Non-linear isotherm at the equilibrium model for two analytes in liquid chromatography in packed columns | \[
\frac{\partial c_{L1}}{\partial t} + F \frac{\partial q_1}{\partial t} + u \frac{\partial c_{L1}}{\partial z} = 0 \\
\frac{\partial c_{L2}}{\partial t} + F \frac{\partial q_2}{\partial t} + u \frac{\partial c_{L2}}{\partial z} = 0 \\
q_1 = f_1 = (c_{L1}, c_{L2}) \\
q_2 = f_2 = (c_{L1}, c_{L2})
\] | (Guiochon and Lin, 2003)\(^6\) |
| Non-linear isotherm with chemical reaction in liquid chromatography in packed columns | \[
\frac{\partial c_{L1}}{\partial t} + F \frac{\partial q_1}{\partial t} + u \frac{\partial c_{L1}}{\partial z} = 0 \\
\frac{\partial c_{L2}}{\partial t} + F \frac{\partial q_2}{\partial t} + u \frac{\partial c_{L2}}{\partial z} = 0 \\
\frac{\partial q_1}{\partial t} = \frac{\partial f_1(c_{L1}, c_{L2})}{\partial t} + k_f(c_{L1}, c_{L2}) \\
\frac{\partial q_2}{\partial t} = \frac{\partial f_2(c_{L1}, c_{L2})}{\partial t} - k_r(c_{L1}, c_{L2})
\] | (Guiochon and Lin, 2003)\(^6\) |
| Non-linear equilibrium model with two sites of adsorption in liquid chromatography | \[
\frac{\partial c_L}{\partial t} + F \frac{\partial q}{\partial t} - \frac{\partial c_L}{\partial z} = D_L \frac{\partial^2 c_L}{\partial z^2}
\] | (Asnin, et al., 2007)\(^6\) |

\(^1\) \(d_p\) is particle radius, \(d_f\) and \(d_c\) are effective depths of the gas and liquid phases, \(a/\alpha_j\) is the ratio of the area of the cross-section of the liquid to that of gas phase, \(\sigma\) is the surface area per unit length, \(\gamma\) is a van Deemter’s constant and \(\lambda\) is the particle shape.  
\(^2\) \(Q_c\) is the flux of a component \(c\).  
\(^3\) \(A\) refers to the van Deemter’s constant for eddy diffusion phenomena, \(\phi\) (or \(F\)) is porosity of the stationary phase, and \(r_p\) is the particle radius.  
\(^4\) \(X\) is the fraction of the eluted component.  
\(^5\) \(\varepsilon\) is the void fraction of the stationary phase polymer.  
\(^6\) \(c_L\), \(c_{L1}\), and \(c_{L2}\) are the solute concentrations in the liquid phase, \(q\), \(q_1\) and \(q_2\) are the sites of adsorption in the stationary phase, \(k_f\) is the solute reaction constant and \(F\) is the phase ratio defined by \((1-\varepsilon)/\varepsilon\).
2.2.2.4 Non-Linear Chromatography at Non-Equilibrium

Non-equilibrium adsorption-desorption processes displaying a non-linear isotherm at non-equilibrium can show both diffuse peak fronts and peaks tails. These models, are more realistic and also very complex mathematically. They can be solved, however, if the proper assumptions are considered (Guiochon and Lin, 2003; Grob and Barry, 2004). In this respect, Asnin et al. (2007) presented a mathematical solution including a Langmuir isotherm for two adsorption sites in a liquid chromatographic system. It is anticipated however, that a non-equilibrium model requiring a non-linear isotherm should not be needed in gas chromatography given the low amounts of analytes involved.

2.2.2.5 Non-Linear Reaction Chromatography

Chemical reaction in a chromatographic column is a phenomenon of infrequent occurrence. It may happen, when a binary mixture reacts during its elution in a chromatographic column. Therefore, a reaction term is needed in the chemical species balance equations.

2.2.2.6 General Strategy for GC Capillary Column Studies

A number of studies reported that competitive isotherms could be derived from the single-component isotherms of a mixture of compounds (Guichon, et al. 1984; Gritti, et al. 2003; Gritti and Guiochon, 2012). Following this, one can take the information generated from single chromatography peaks and predict the physicochemical parameters of the same analytes in a mixture.

Moreover, it has also been described in these chromatographic models that an asymmetrical peak means a stronger non-linear behavior and, also a lower resolution of this peak with respect to its neighbours (Gritti and Guiochon, 2003). However, this possibility is considered of less importance in gas phase chromatography given the small amounts of analyte injected.

Therefore, in this study, a linear adsorption isotherm is considered consistently for both symmetric and asymmetric peaks. Peak asymmetry is thus, explained, considering the
state of non-equilibrium species mobile and static phases.

2.3 Statistical Moments of Different Order: $M_1$, $M_2$ and $M_3$

Since early 1960’s, many authors have used central statistical to extract information from chromatographic peaks (Kucera, 1965; Yamaoka, 1974; Grubner, 1971; Gao, et al., 2010; Lan and Jorgenson, 2000).

Basically, statistical moments are the simplest mathematical description, allowing one to quantify chromatographic peak deviations from Gaussian distributions. Table 3 reports the equations for the statistical moments from order zero to order three: from $M_0$ to $M_3$. One should note that the moments of different order allow one to establish the properties of the peak distribution data in a chromatographic plot (Chen, 2011). Furthermore, the moment theory, has the distinct advantage of being able to provide a mathematical solution for the output concentration in Laplace transform domain (Carbonell and McCoy 1975).

Regarding the moments of different order, one should notice that if a mass of solute pulse is fed to the GC column, the zeroth moment ($M_0$) represents the area under the effluent curve. This means that the total area calculated, in terms of dimensionless concentration and dimensionless time, is always equal one (Grubner, 1971). One significant property of $M_0$ is that, it is independent of the system size and column used (Carbonell and McCoy, 1975). In fact, having a dimensionless $M_0$, close to 1, provides a good indicator of the quality of the gas chromatographic data collected.

Concerning the first peak statistical moment ($M_1$), one should mention that it provides the location of the centroid of the area under the curve. For a highly symmetrical chromatographic peak, $M_1$ is equal to the average retention time ($t_R$). However, for asymmetrical peaks, one should consider that $M_1$ is affected by parameters such as the equilibrium constant ($K_s$). On the other hand, it can be predicted, that the kinetic adsorption constants ($k_{ads}$) or the kinetic desorption constants ($k_{des}$) do not influence $M_1$ (Grubner, 1971; Yau, 1977; Moscariello, et al., 2005).
Table 3 Statistical Moments to Describe Chromatography Peaks

<table>
<thead>
<tr>
<th>Statistical moment</th>
<th>Meaning</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeroth moment</td>
<td>Area under the curve</td>
<td>$M_0 = \frac{\int_0^\infty c(t)dt}{\int_0^\infty c(t)dt}$</td>
</tr>
<tr>
<td>First moment</td>
<td>Centroid of the peak</td>
<td>$M_1 = \frac{\int_0^\infty tc(t)dt}{\int_0^\infty c(t)dt}$</td>
</tr>
<tr>
<td>Second central moment</td>
<td>Peak variance</td>
<td>$M_2^* = \frac{\int_0^\infty (t-M_1)^2 c(t)dt}{\int_0^\infty c(t)dt}$</td>
</tr>
<tr>
<td>Third central moment</td>
<td>Peak Skew</td>
<td>$M_3^* = \frac{\int_0^\infty (t-M_1)^3 c(t)dt}{\int_0^\infty c(t)dt}$</td>
</tr>
</tbody>
</table>


Furthermore, regarding the second peak statistical moment ($M_2$), one can note that it represents the variance of the probability density distribution curve. A second central statistical moment ($M_2^*$) stands for a second statistical moment with respect to the centroid of the peak or $M_1$. This moment also describes the peak width and is affected by the diffusion in the mobile and stationary phases (Grubner, 1971; Grubner and Zikanova, 1967; Yau, 1977; Moscariello, et al., 2005). As is mentioned in section 2.1.1, the column HETP or height plate ($H$) can be related to $M_1$ and $M_2$ as follows (Guiochon, et al., 1994):

$$H = L \left( M_2 / M_1^2 \right)$$

Finally, the third central statistical moment ($M_3^*$) provides a quantification of the peak asymmetry. A positive value of $M_3^*$ indicates a tailing of the peak, while a negative value represents a leading diffuse peak front. Furthermore, the $M_3 / M_2^{3/2}$ ratio of the second and
third statistical moments gives the peak skewness (S). One should mention that the skewness value, being influenced by both $M^*_2$ and $M^*_3$ (Grubner, 1971; Guiochon and Lin, 2003), becomes a function of the diffusion in the mobile and stationary phases as well as the adsorption kinetics parameters.

Regarding the first, the second and third statistical moments, one should note that they do not depend on the amount of the analyte. These three moments are, in fact, normalized to the peak area as shown in Table 3. One should also note that while the peak traverses the column, its variance increases due to axial diffusion and other transport processes in the stationary phase. The observed peak variance is, in fact, an additive quantity. That means that the total peak variance results as the sum of the individual variances coming from various phenomena contributing to peak dispersion (Moscariello, et al. 2005).

Apart from statistical moments, several models have been considered to describe characteristic asymmetric peaks, such as: a) Exponentially Modified Gaussian functions (EMG), b) Polynomially Modified Gaussian function, c) Edgeworth-Cramer series function, d) Chesler-Cram function, e) bi-Gaussian function, and, f) Exponential-Gaussian Hybrid function. The EMG model is the most popular of these models because it provides a very good fit for a broad range of chromatographic peaks. However, model parameters are not easy to obtain from graphical measurements. Furthermore, calculations involving peaks with low asymmetries may lead to unstable EMG calculations (Lan and Jorgenson, 2000; Howerton, et al., 2003).

2.3.1 Calculation of Statistical Moments of Different Order

The statistical moments of chromatographic peaks are relatively simple to calculate. They require both the accurate measurements of outlet peaks as well as the implementation of numerical integration of the resulting functions. Furthermore, the first and second moments are frequently considered, given that they are relatively easy to calculate accurately. However, as is well established, the first and second moments are not enough to fully characterize the sorption process affecting a chromatographic peak. This is particularly true if the peak shape deviates considerably from the Gaussian shape. Hence, in principle, the higher moments such as the third order moment, are needed to describe
quantitatively the asymmetry of a chromatographic peak.

A significant number of researchers have used statistical moments of orders higher than two to obtain adsorption and diffusion parameters from chromatographic peaks. Vidal-Madjar and Guiochon (1977) pointed out the significant measurement errors that could potentially affect the moments of order higher than two. Thus, special efforts have been made to improve both peak measurements and calculation accuracy.

In spite of the technical challenges, the application of statistical moments higher than two is still an attractive approach in modern gas chromatography. This is the case, given that, as stated, these statistical moments can be related to the physicochemical adsorption processes taking place in capillary columns. Regarding these matters, Gao, et al. (2010) showed that if one wants to improve the experimental conditions for the measurement of the third central moment, the following considerations are important: a) the S/N ratio of the eluted peak profile needs to be high and the slowly descending tails should be avoided, b) the determination of both the starting and ending points of a peak is especially important for the calculations of moments of higher order (Gao, et al., 2010).

Furthermore, it is significant to emphasize that equations for statistical moments are usually estimated by discrete summation. The accurate description of asymmetric peaks usually requires a large number of data points. Thus, statistical moments can be affected by noise. Therefore, it should be considered, that, when a numerical integration is applied, the tails of the curves, especially for the second moment, and more notably for the third moment could contain errors. In this respect, either the square of the time variable or the cube of the time variable can magnify small errors in the peak tails. As a result, extrapolations to large times are preferably made via curve fitting, assuming a peak exponential decay with respect to the time variable (Carbonell and McCoy, 1975). As a result, and in spite of application challenges, many authors have chosen to use the statistical moment analysis, given that it requires fewer model assumptions and does not require the numerical solution of the chemical species differential equations (Grubner and Zikanova, 1967; Carbonell and McCoy, 1975; Lan and Jorgenson, 2000; Gao, et al., 2010; Pawlisch, et al., 1987).
2.4 Conclusions and Goals for the Present Ph.D Study

This chapter describes the general concepts and issues in gas chromatography. In particular, the value of the macroscopic balance approach in narrow bore capillary columns is stressed. To accomplish this, various chemical species differential equations and possible model assumptions influencing adsorption equilibrium and kinetics are discussed in detail.

As described in this review chapter, in spite of the significance, there is not adequate information to address the modelling and parameter estimation of elution peaks in 30m-60m capillary columns. This is particularly relevant if one considers that a GC capillary column is one of the most important modern analytic techniques (a work horse of analytical methods). Therefore, more phenomenologically based models describing interactions of the analyte with the mobile and stationary phases are required. Findings in this area, together with the establishment of adsorption-desorption parameters could lead to the development of new analytical techniques and the manufacture of capillary columns with enhanced performance.
Chapter 3

3 Scope of the Research

The main objective of this PhD research is to establish a mathematical model allowing the description of the elution of oxygenated and non-oxygenated aromatic compounds in a 30m x 0.25 mm x 0.25 µm BPX5 narrow bore capillary column. More specifically, the purpose of this PhD study is to gain understanding on the interacting processes between selected chemical analytes (mobile phase) and thin film capillary column (stationary phase). The ultimate aim is to contribute to the understanding of the physicochemical processes involved in thin-coated capillary columns when analyzing complex tar samples from biomass gasification. It is anticipated that to accomplish this, it is required to calculate both adsorption and diffusivity parameters, linking them with chemical structure.

Therefore, the specific proposed objectives for this study are the following:

a) The experimental determination of the elution of toluene and naphthalene (aromatics) and phenol and 2- naphthol (oxygenates) at isothermal conditions. The planned experiments aim to validate the proposed mathematical models; therefore, the eluted chromatograms were carried out under several temperatures and carrier gas flows.

b) The calculation of statistical moments of different order ($M_1$, $M_2^*$ and $M_3^*$) from the experimental chromatographic peaks for toluene, phenol, naphthalene and 2-naphthol.

c) The validation of a linear at equilibrium model for aromatic chemical species displaying symmetric elution chromatographic peaks. This model involves an analytical solution and the calculation of statistical moments of different order using Laplace transform.

d) The validation of a linear non-equilibrium model to describe the elution of oxygenated compounds displaying asymmetric chromatographic peaks. This
model requires a numerical solution and the concurrent calculation of the statistical moment of different order.

e) The evaluation of the adsorption and diffusivity parameters under both equilibrium and non-equilibrium adsorption conditions, using model and experimentally calculated statistical moments.
Chapter 4
Experimental Methods

4 Introduction

The experimental methods of this PhD dissertation were established with the specific goal of providing adequate validation to the proposed model for gas chromatography in capillary columns. In this respect, one has to have the confidence that the various assumptions considered in the modeling analysis of the present study apply to the experiments developed. This is especially relevant in the following areas: a) analyte injections should be close to a concentration impulse and b) the adsorbed and gas phase analyte concentrations should be linearly related at equilibrium. In addition, it is required for the experimental set-up used to provide an ample range of temperatures and of linear gas velocities for adequate model validation.

4.1 Model Compound Solution Preparation and Elution in a BPX5 Capillary Column

Experiments were carried out with $5 \times 10^{-2}$ mg/cm$^3$ solutions of each chemical compound in high purity acetone (>99%, Caledon Laboratory). All chemical reactants were >99% pure and obtained from Sigma-Aldrich Co., except toluene which was obtained from Fisher Scientific Co. The selected concentration of analytes was established by conducting an analysis of toluene at different concentrations, from $0.75 \times 10^{-2}$ to $5 \times 10^{-2}$ mg/cm$^3$. The parameters of adsorption and diffusivity ($K$ and $D_s$) for all tested concentrations are detailed in Appendix A. This range of concentration is in the linear range of the isotherm. Therefore, concentrations of $5 \times 10^{-2}$ mg/cm$^3$ were accurate to perform further experiments.

Four model compounds were chosen to perform the experiments for the validation of the mathematical models. Toluene and naphthalene were selected for the linear isotherm model at equilibrium as they present symmetric chromatographic peaks. Phenol and 2-naphthol experiments were performed to validate the linear isotherm model at non-
equilibrium due to these compounds having asymmetric chromatographic peak. The chemical structures of these compounds are shown in Figure 4.

4.2 Experimental Set-Up

The chromatographic elution peaks of the analytes were obtained in a Shimadzu GC-MS QP2010S unit equipped with a BPX5 capillary column of 30 m, 0.25mm i.d., and 0.25μm film thickness (Mandel Scientific, Australia). The general experimental conditions of the Gas Chromatography system and Mass Detector are reported in Table 4.

Table 4 Gas Chromatograph and Mass Detector Parameters

<table>
<thead>
<tr>
<th>Parameter in GC-MS</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>BPX5 capillary column. 30 m length, 0.25mm inner diameter, 0.25 μm film thickness. Polymer coating made of 5% Phenyl-95% polysilphenyenesiloxane.</td>
</tr>
<tr>
<td>Injection oven temperature (K)</td>
<td>573</td>
</tr>
<tr>
<td>Injection volume (μL)</td>
<td>1</td>
</tr>
<tr>
<td>Injection mode</td>
<td>Split 1:25</td>
</tr>
<tr>
<td>Flow control mode</td>
<td>Lineal velocity</td>
</tr>
<tr>
<td>Purge flow (mL/min)</td>
<td>1</td>
</tr>
<tr>
<td>High pressure injector</td>
<td>OFF</td>
</tr>
<tr>
<td>Carrier gas saver</td>
<td>ON</td>
</tr>
<tr>
<td>Splitter hold</td>
<td>OFF</td>
</tr>
<tr>
<td>ACQ Mode</td>
<td>Scan</td>
</tr>
<tr>
<td>Event time (s)</td>
<td>0.18</td>
</tr>
<tr>
<td>Scan speed</td>
<td>2000</td>
</tr>
<tr>
<td>Ion source temperature (K)</td>
<td>493</td>
</tr>
<tr>
<td>Interface temperature (K)</td>
<td>493</td>
</tr>
<tr>
<td>Detector gain mode</td>
<td>Relative</td>
</tr>
<tr>
<td>Detector Gain Mode [kV]</td>
<td>-0.2</td>
</tr>
</tbody>
</table>
One should notice that there are important parameters in the GC-MS analysis as follows:

a) *Injection oven temperature.* This was set to $T=573$ K, being always higher than the boiling temperature ($T_b$) of all chemical species analysed (Toluene, $T_b=384$ K; Phenol, $T_b=455$ K; Naphthalene, $T_b=491$ K; 2-Naphthol; $T_b=553$ K).

b) *Sample Injection.* A 1$\mu$L of solution of each sample was manually and consistently injected using a 5$\mu$L syringe. The selected injection mode was the split mode with a 1:25 split ratio. As a result, one part of the sample solution was mixed with 25 parts of the carrier gas before entering into the capillary column. This allowed a homogeneous sample to be fed into the column.

c) *Flow Control.* The selected carrier gas linear velocities are reported in Table 5. These gas linear velocities are set in the gas chromatographic system taking advantage of compensations accounting for variation of carrier gas viscosity during the analysis (if temperature changes). This is accomplished by increasing the head pressure in order to maintain constant linear velocity of the carrier gas in the capillary column.

d) *Mass Spectrometric Detector.* The parameters set in the Mass Spectrometry Detector (MS) unit were such that they allowed accurate detection of the chemical species eluted in the GC unit. For instance, it was shown that the ion source temperature at 493 K was adequate to fragment aromatic molecules into ions. Furthermore, event time was set to 0.18s and scan speed was set to 2000 (units). These values allowed for the chromatographic peak definition with 30 data points or more. As a result, having elution peaks with a high number of data points was critical for adsorption-desorption model validation.

e) *Column Temperature and Carrier Flow:* Table 5 reports the column temperatures ($T_c$) used to validate the mathematical models utilizing toluene, phenol, naphthalene and 2-naphthol. At each isothermal condition, three carrier flows were employed: 1, 2 and 3.5 mL/min.

f) *Capillary Chromatographic Column.* The selected capillary column was a BPX5. As it was previously discussed in Chapter 2, the BPX5 column is a narrow bore capillary
column with a polymer coating manufactured with 5% phenyl polysilphenylenesiloxane. The coating allows the separation of a wide variety of different chemical species, such as, aromatics and polyaromatics (Grob and Barry, 2004; Miller, 2005). Previous studies in the CREC Laboratory used a BPX5 capillary column to separate tar-derived species from biomass gasification tar products, such as phenol, toluene, naphthalene and 2-naphthol (Salaices, 2010). This work was developed for the Mandel and Shimadzu companies. Therefore, it was judged valuable to develop the present experimental elution runs using the same aromatic species and BPX5 capillary column as in previous research.

Table 5 Isotherm Conditions for Aromatic Species Tested

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (K)</th>
<th>Compound</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>313</td>
<td>Phenol</td>
<td>323</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>343</td>
</tr>
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<td>343</td>
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<td>353</td>
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<td>353</td>
<td></td>
<td>373</td>
</tr>
<tr>
<td></td>
<td>363</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>363</td>
<td>2-Naphthol</td>
<td>393</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td></td>
<td>413</td>
</tr>
<tr>
<td></td>
<td>393</td>
<td></td>
<td>433</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td></td>
<td>453</td>
</tr>
<tr>
<td></td>
<td>433</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a All temperatures were performed under three carrier gas flows: 1, 2 and 3.5 mL/min.*
4.3 SEM Images of a Radial Cut of the Narrow Bore BPX5 Capillary Column

Mandel Co. reports that the polymer phase film thickness ($d_f$) of the BPX5 capillary column is 0.25 µm. As is observed in Eqs 5.11 and 5.12, the $d_f$ is a factor to the power of three. Therefore a change in the film thickness value can drastically affect the results of the model. Therefore, SEM images of a radial cut of the BPX5 capillary column were obtained in order to confirm the $d_f$ value. The microscopic analysis was done in a Hitachi S-4500 field emission SEM with a Quartz XOne EDX system in the Surface Science Laboratory at The University of Western Ontario.

4.4 Conclusions

This chapter describes the experimental set-up and the experimental methods developed in the GC-MS unit with the BPX5 capillary column capabilities of the present research. The studies developed using toluene, naphthalene, phenol and 2-naphthol as analytes were adequate to validate a linear adsorption isotherm at equilibrium. In this respect, experimental data as well as model results are discussed in Chapters 5 and 6.
Chapter 5
Mathematical Model with Equilibrium Adsorption in a BPX5 Capillary Column

5 Introduction

There are several models, reported in the technical literature, for describing elution peaks of a given analyte in a GC capillary column. The general characteristics of these models are described in Chapter 2. To the knowledge of this author, there is no report, in the open literature, regarding the experimental validation of mathematical models in commercial capillary columns such as the BPX5.

Therefore, to adequately simulate experimental chromatograms, the present PhD dissertation started from a simple model and to move progressively towards a more complex model, as required using the experimental data obtained.

Regarding the first model studies of this PhD dissertation, an isothermal adsorption process at adsorption equilibrium is considered. The model is established for aromatic hydrocarbons, such as toluene and naphthalene. This chapter provides the required unsteady species equations, and their validation, for the case of adsorption of an analyte at equilibrium, using statistical moments of different order. The model developed is applied to both toluene and naphthalene eluted peaks from a BPX5 capillary column.

5.1 Adsorption at Equilibrium Model in Capillary Column

This PhD dissertation considers the elution of both toluene and naphthalene in a narrow bore BPX5 capillary column. The capillary column is modeled as a straight cylindrical tube with a polymer coating stationary phase. The following applicable equations and assumptions as proposed by Pawlisch et al. (1987) are considered.

a) The polymer coating with thickness \(d_p\) is selected to be completely inert to the various chemical species analysed. Thus, there is no chemical reaction between the solute and the stationary phase. This is required to preserve both, the column
performance during numerous analyses as well as to secure adequate analyte quantification.

b) The polymer stationary phase is manufactured to be both homogeneous and to have a constant film thickness \( (d_f) \). This is typically achieved in the GC commercial capillary columns such as the BPX5, which, according to Mandel Co., is manufactured with an inner diameter of \( 0.25 \pm 5 \times 10^{-4} \text{ mm} \). Figure 6 shows the SEM image of a radial cut of the BPX5 capillary column. This image confirms the inner diameter and film thickness value of the chromatographic column. This is an important measurement for the calculations, as it will be shown later.

![Figure 6 SEM image (x200) of a Radial Cross-Section of a BPX5 Capillary Column.](image)

The small window in the upper right hand provides an expanded view of the thin inner polymer film.

a) The capillary column-gas interaction takes place via solute transfer at the
polymer-gas interface with solute adsorption on the polymer coating.

b) Distribution constant \( (K_s) \) and diffusion coefficients in the stationary phase \( (D_s) \) are assumed to be concentration independent, with their axial diffusion being negligible. This is consistent given the respectively low analyte concentrations used and the very high length/polymer thickness ratio of capillary columns. In the Appendix A, a comparison of \( K_s \) and \( D_s \) at different solute concentration is provided to verify this assumption.

c) The carrier gas (Helium) complies with the ideal gas law. This is reasonable considering the near atmospheric pressure conditions employed and, as a result, the expected compressibility factors close to one.

d) The carrier gas flow in the capillary column occurs at nearly constant pressure and as a result near constant average cross-section flow velocity, as shown in the Appendix A of the present Ph.D study.

e) The analyte samples are injected manually into the carrier flow entering the capillary column as a concentration pulse. This concentration change can be approximated using the Impulse Delta Dirac (\( \delta \)).

f) The various capillary column analyses are developed at a constant temperature. This is adequate, as a result of the negligible influence of the heats of adsorption/desorption of the chemical species, given the small analyte amounts involved in each one of the capillary column experiments.

The coordinates in the straight capillary tube are as the Figure 7 shows. Thus, these conditions and approximations lead to the chemical species conservation equations of this mathematical model:

a) \textit{Gas Phase (Mobile Phase) Chemical Species Balance}. The first term on the left side of Eq (5.1) describes the solute accumulation. The second term relates the concentration in a \( \Delta z \) of the column length, \( L \). Terms in the right side of Eq (5.1) are axial dispersion in the mobile phase and diffusivity in the stationary phase, respectively.
\[
\frac{\partial c_{\text{mean}}}{\partial t} + u \left( \frac{\partial c_{\text{mean}}}{\partial z} \right) = D_g \frac{\partial^2 c_{\text{mean}}}{\partial z^2} + \frac{2D_s}{r_c} \frac{\partial c_s (r = r_c)}{\partial r}
\] (5.1)

Figure 7 Capillary Column Coordinates and the BPX5 Column. The BPX5 column is considered as a straight cylindrical tube with a \(d_f\) film thickness. The injected sample is modeled as a Delta Dirac Impulse (\(\delta\)) with a \(c_o\) initial concentration (mg/cm\(^3\)) and is average linear velocity (cm/s). Solute migrates through all column length, \(L\).

b) **Solid Phase (Stationary Phase) Chemical Species Balance.** In Eq (5.2) the term on the left side defines the concentration in the stationary phase at time \(t\), and the left side term relates the stationary phase diffusion of the solute in the radial direction.

\[
\frac{\partial c_s}{\partial t} = D_s \frac{1}{r} + \frac{\partial}{\partial r} \frac{\partial c_s}{\partial r}
\] (5.2)

Eqs (5.1) and (5.2) can be solved using a set of physical initial and boundary conditions:

i. At the beginning of the GC analysis, the capillary column is eluted of any analyte remaining from a previous experiment. Thus, initial concentrations of the solute in the mobile and stationary phases are zero in the capillary column:

\[
c_m(r,z,t) = c_s(r,z,t) = 0 \quad \text{at } t=0 \quad \text{and } z > 0
\]
ii. The volume of solute injected into the system is constant and introduced quickly at the entrance of the unit. Hence, the initial mass of the analyte in the capillary column is constant and can be approximated as a Impulse Delta Dirac Function:

\[ c_m(r,z,t) = d(t) \ c_o \quad \text{at } z > 0 \]

iii. At the interphase between the gas and polymer phases \((r=r_c)\), the analyte concentrations in both phases, are related via a distribution constant \((K_s)\) as follows:

\[ c_m(r,z,t) = c_s(r,z,t)/K_s \quad \text{at } r=r_c \]

iv. The diffusivity of the solute in both mobile and stationary phases is the same at the interphase \((r=r_c)\):

\[ D_G \left( \frac{\partial c_m}{\partial r} \right) = D_s \left( \frac{\partial c_s}{\partial r} \right) \quad \text{at } r=r_c \]

v. The analyte concentration does not change at the center of the capillary column \((r=0)\):

\[ \frac{\partial c_m}{\partial r} \quad \text{at } r=0 \]

vi. Any solute injected in the GC system is recovered at the exit. Therefore, the analyte is not chemically linked to the polymer coating or does not migrate to the polymer-column interphase:

\[ \frac{\partial c_s}{\partial r} = 0 \quad \text{at } r = r_c + d_f \]

One can simplify the solution for both, Eqs (5.1) and (5.2) by using the following dimensionless concentrations, space and time variables:

\[ y = (c_{\text{mean}} L / c_o \bar{u}) \quad \text{(5.3.1)} \]

\[ q = c_s L / c_o K_s \bar{u} \quad \text{(5.3.2)} \]

\[ x = z / L \quad \text{(5.3.3)} \]
\[ \varsigma = \frac{(r - r_c)}{d_f} \]  \hspace{1cm} (5.3.4)

\[ E = \frac{\tilde{u}}{L} \]  \hspace{1cm} (5.3.5)

where, \( y \) and \( q \) define the dimensionless solute concentration in the mobile and stationary phases, respectively; \( x \) corresponds to the dimensionless axial coordinate; \( \varsigma \) is the dimensionless film thickness of the polymer phase and \( E \) represents the dimensionless time variable.

Then, the substitution of these dimensionless variables from Eqs (5.3.1) to (5.3.5) in Eqs (5.1) and (5.2) leads to Eqs (5.4) and (5.5)

\[ \frac{\partial y}{\partial E} + \frac{\partial y}{\partial x} = \gamma \frac{\partial^2 y}{\partial x^2} + \frac{2}{\omega \kappa^2} \frac{\partial q(0)}{\partial \varsigma} \]  \hspace{1cm} (5.4)

\[ \frac{\partial q}{\partial E} = \frac{1}{\kappa^2} \frac{\partial^2 q}{\partial \varsigma^2} \]  \hspace{1cm} \text{if} \ d_f << r_c \hspace{1cm} (5.5)

where \( \omega \) is the dimensionless equilibrium adsorption constant defined by \( \omega = r_c / K_d \); \( \gamma \) is the dimensionless axial dispersion parameter given by \( \gamma = D_G / \tilde{u}L \) and \( \kappa \) defines the dimensionless diffusion parameter in the stationary phase as \( \kappa^2 = d_f^2 \tilde{u} / D_s L \).

It is important to notice that the second term in the right hand of Eq (5.4) includes a \( 2/\omega \kappa^2 \) coefficient. This coefficient is needed for mathematical consistency and represents a change with respect to a similar equation published for GC open columns (Pawlisch, et al., 1987).

Furthermore, the dimensionless initial and boundary conditions for Eqs (5.4) and (5.5) are as follows:

\[ y = q = 0 \] \hspace{1cm} \text{at} \ \ \theta = 0
\[ y = \delta(\theta) \] \hspace{1cm} \text{at} \ \ \ x = 0
\[ y = q \] \hspace{1cm} \text{at} \ \ \varsigma = 0
\[ \frac{\partial q}{\partial \varsigma} = 0 \] \hspace{1cm} \text{at} \ \ \varsigma = 1
Appendix B contents a detailed description of these mathematical model equations. This description is important for showing the differences between this model and a similar model published for open columns with lengths of 10 meters (Pawlisch et al. 1987). One of the differences is that the second term in the right hand of Eq (5.4) includes a \( \frac{2}{\omega k^2} \) coefficient. This coefficient is needed for mathematical consistency.

Moreover, the coupled Eqs (5.4) and (5.5) can be solved using Laplace Transforms yielding Eq (5.6). This transformation is also included in Appendix B.

\[
\bar{Y}(s,x) = e^{(1/2)\gamma x} e^{-1/2\gamma(4\Psi(s))^{1/2} x}
\]  

(5.6)

Where:
\[
\Psi(s) = s + (2s^{1/2}/\alpha \beta) \tanh(\beta s^{1/2})
\]

Thus, a solution at \( x=1 \), which represents the transfer function at the exit column, is provided by Eq (5.7).

\[
Y(s,1) = e^{1/2\gamma} e^{-1/2\gamma(1+4\Psi(s))^{1/2}}
\]  

(5.7)

5.2 Statistical Moment Descriptors for an Adsorption at Equilibrium Model in GC Capillary Column

As it is mentioned in Chapter 2, statistical moments of different order can be related with adsorption and diffusivity parameters in equations modeling the chromatographic elution of a given analyte. In this case, Eq (5.8) shows that the statistical moments \( M_i \) can be obtained from the derivatives of Laplace Transforms given by the Eq (5.6)

\[
M_i = (-1)^i (L/ u_a)^i \lim_{s \to 0} \frac{d^i Y(s)}{ds^i}
\]  

(5.8)

\[
M_i = \frac{\int_0^\infty t^i c_{\text{mean}}(t) dt}{\int_0^\infty c_{\text{mean}}(t) dt}
\]  

(5.9)

where:

The chromatographic peaks can also be characterized using central statistical moments
(\(M_i^*\)) as reported in Equation (5.10):

\[
M_i^* = \frac{\int_0^\infty (t - M_1) \hat{Y}(t) dt}{\int_0^\infty \hat{C}_{\text{mean}}(t) dt}
\]

(5.10)

Furthermore, if Eqs (5.8), (5.9) and (5.10) are applied to the specific cases of the first and second statistical moments \((M_1\) and \(M_2\)), the following equations hold true:

\[
M_1 = \left(1 + \frac{2d f K_s}{r_c}\right)t_M
\]

(5.11)

\[
M_2^* = \left[\frac{d^3 f K_s}{t_M D_{r_c}} + \frac{2D_{c f r_c}}{L^2} \left(1 + \frac{2d f K_s}{r_c}\right)^2\right]t_M^2
\]

(5.12)

Thus, Eqs (5.11) and (5.12) provide a link between the \(M_1\) and \(M_2^*\) and adsorption and transport parameters, such as adsorption distribution constant, establishing the interaction between the solute and the stationary phase in a capillary column.

Therefore, one can calculate the experimental statistical moments \(M_1\) and \(M_2^*\) of the analyzed chemical species and then, relate those values to the mathematical model. To validate the results a non-linear regression of the data can be applied as it is described in the following sections.

### 5.3 General Description of Elution of Aromatic Species in BPX5 capillary Column

Chromatographic data of toluene and naphthalene were obtained as described in Chapter 4. In this respect, one should mention that accurate and reproducible GC capillary column moments require carefully acquired experimental data. For instance, some temperature ranges lead to GC chromatographic peaks with less noise or baseline drift. The reported chromatograms in this study are those with the best reproducibility (\(\pm 5\%\)). The recorded chromatographic peaks were processed with Peak Fit Software to reduce noise that could affect the statistical moment calculations. Once the “smoothed” peaks were obtained, \(M_i\)
and $M_2$ moments were calculated with Eqs (5.9) and (5.10).

Figures 8a and 8b show example of two characteristic chromatograms for both toluene and naphthalene. One can notice the quasi-symmetry of these peaks, which is characteristic for both toluene and naphthalene in a BPX5 capillary column elution. As it was previously discussed in Chapter 3, the asymmetry of a peak can be measured by the skewness ($M_3/M_2^{3/2}$). For symmetric bands, $(S=M_3/M_2^{3/2})$ is lower than 1 (Doane & Seward 2011). It is interesting to note that skewness of both toluene and naphthalene peaks remained in the 0.3 to 0.9 ranges, in all cases (see Appendix A). Moreover, if adsorption at the equilibrium model generates symmetric peaks, therefore, toluene and naphthalene elution in a BPX5 capillary column can be used to validate this mathematical model.

![Figure 8 Characteristic Chromatograms Obtained in a GM-MS Shimadzu Mandel QP2010S unit and 30m x 25mm BPX5 capillary column. (a) Toluene: $T_e=353$K and $=37$ cm/s and (b) Naphthalene: $T_e=433$ K and $=37$ cm/s. Note: Symbols in this figure refer to data points for individual runs, while the solid line represents the calculated average values obtained with data from individual injections (triplicates). Individual runs were performed at the same conditions of flow and temperature.](image-url)
5.4 Validation of an Adsorption at Equilibrium Model for a BPX5 Capillary Column

The adsorption at equilibrium model was the first approach made to describe the elution of aromatic chemical species in a commercial BPX5 capillary column. Thus, the evaluation of the adsorption and diffusion parameters for toluene and naphthalene are presented in the following sections.

5.4.1 Evaluation of the Adsorption Parameters in BPX5 Capillary Column Using First Order Statistical Moment \((M_1)\)

As it is mentioned in Chapter 2, first statistical moment \((M_1)\) defines the centroid of the chromatographic peak. In a Gaussian chromatographic peak, \(M_1\) is equal to the retention time \((t_R)\) of the corresponding analyte (Carbonell and McCoy, 1975). Moreover, \(t_R\) is unique for any analyte in a given chromatographic column and is defined by distribution constant, \(K_s\). As the value of \(K_s\) increases, the retention time and the affinity with the stationary phase increase as well (Armstrong and Nome, 1981).

One can obtain the experimental distribution constant values \((K_{s,exp})\) of the analyzed compounds by using Eq. (5.11). This equation shows that distribution constant determination could be affected by the carrier gas flow. Then, \(M_1/t_M\) ratios versus hold up time \((t_M=L/\bar{u})\) are presented in Figures 9a and 9b. These plots demonstrate that the observed \(M_1/t_M\) ratios for toluene and naphthalene, respectively, differ by less than ±1% at set temperatures and different gas carrier flow. Therefore, the experimental distribution constants \((K_{s,exp})\) obtained using Eq (5.11), are only function of the properties of the BPX5 polymer coating and its interactions with toluene and naphthalene.

As a result, the following equation was considered for further analysis of the \(K_{s,exp}\) using the first statistical moment:

\[
\frac{M_1}{t_w} = 1 + \frac{2d_fK_s}{r_c} \quad K_{s,exp} = \left( \frac{M_1}{t_M} - 1 \right) \frac{r_c}{2d_f} \quad \text{Or} \quad \left( 5.13 \right)
\]

Furthermore, the distribution constant for the “i” species \((K_{s,i})\) can be also related to the
operating temperature as follows.

\[
K_{s,i} = K_{so,i} e^{\frac{\Delta H_{ads}}{R} \left( \frac{1}{T_c} - \frac{1}{T_{co}} \right)}
\]  

(5.14)

**Figure 9 Influence of the Average Linear Velocity on the \( M_1/t_M \) Ratios for Toluene (a) and Naphthalene (b), at Various Column Temperatures \( (T_c) \).**

where: a) \( K_{so,i} \) represents the distribution constant (interface), b) \( T_{co} \) stands for the average temperature selected for the chromatographic column, c) \( \Delta H_{ads} \) denotes the energy of adsorption of the given chemical species on the polymer coating in kJ/mol, d) \( R \) is the ideal gas constant in kJ/mol K, and e) \( T_c \) represents the column temperature in Kelvin degrees. The \( T_{co} \) variable is considered to minimize cross-correlation between adsorption parameters (Moreira, et al., 2012).

The \( K_{s,exp} \) distribution constant can be determined from the first order moments as described in Eq (5.13). Following this, the \( K_{so,i} \) and \( \Delta H_{ads} \) parameters for both toluene and naphthalene can be numerically regressed with minimization of the \( \Sigma (K_{s,exp} - K_{s,i})^2 \).

Then, Figures 10a and 10b report the reconciliation plots for the experimentally determined distribution constant \( (K_{s,exp}) \) and the model calculated constant \( (K_{s,i}) \). It can be observed that the non-linear parameter regression provides good fitting of the chromatographic data. Thus, Table 6 reports the determined \( K_{so,i} \) and \( \Delta H_{ads} \) parameters.
These parameters are reported with limited spans for the 95% confidence intervals and low cross-correlation. This is encouraging given that both show the adequacy of the model as well as the significant phenomenological value of the determined parameters.

According to this analysis, $-34.5 \pm 2.43\% \Delta H_{ads}$ is obtained for toluene while $-46.1 \pm 3.28\%$ is acquired for naphthalene. This increase in the heat of adsorption can be justified given that the larger molecular weight of naphthalene molecules requires bigger energies for molecules to be adsorbed on the polymer phase.

Figure 10 Comparison of $K_{s,exp}$ and $K_{s,i}$ for (a) Toluene and (b) Naphthalene. Carrier gas flow: 0.6-3.5 mL/min. Temperature for toluene: 313, 323, 343, 353 and 363 K. Temperatures for naphthalene: 373, 393, 413, 433 and 453K. Note: The reported points represent at least 9 to 10 experiments performed at various gas carrier flows.

Furthermore, considering the results obtained, one can notice that the adsorption energy for toluene has the same magnitude as the $\Delta H_{ads} = -29.3$ kJ/mol reported in a previous study using a DB-5 commercial capillary column coated with (5%-Phenyl)-methylpolysiloxane. In addition, it is interesting to mention that this is an expected result, given that the (5%-Phenyl)-methylpolysiloxane is a similar polymer, with respect to the one used in the manufacturing of the BPX5 capillary column (Li, 1994).
Table 6 Adsorption Parameters Obtained from the Model as per Eq (5.13) for Both Toluene and Naphthalene in a BPX5 Capillary Column*

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>$\log K_{so,i} \pm SD$</th>
<th>$\Delta H_{ads} (kJ/mol) \pm SD$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.07 ± 0.05</td>
<td>-34.5 ± 0.84</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2.55 ± 0.07</td>
<td>-46.1 ± 1.51</td>
</tr>
</tbody>
</table>

aDegree of freedom was 34. Reference temperature ($T_{co}$) for toluene: 353 K and for naphthalene 413 K

In summary, regarding the proposed model and the moments of first order ($M_i$) for toluene and naphthalene, this is a valuable approach for adsorption parameter determination under the dynamic conditions of the narrow bore BPX5 capillary column study. Thus, on this basis, Eq (5.14) provides an adequate and phenomenologically based relation for the $K_s$ distribution constant and its changes with temperature.

5.4.2 Evaluation of the Axial Mixing and Diffusivity in a Capillary Column Using Second Order Statistical Moment ($M_2$)

As the first statistical moment ($M_i$) is linked to the adsorption parameters, the second central statistical moment ($M_2$) is related with the dispersion parameters, such as axial dispersion and diffusivity in the gas and polymer phase. This statistical moment descriptor provides the variance of the concentration in the chromatographic peak. In other words, $M_2$ is the width of the peak (Carbonell and McCoy, 1975).

Regarding the axial mixing ($D_G$), one can consider that this parameter may be affected by the superficial fluid velocity or the equivalent hold up time ($t_M$), with this being a function of the Bodenstein dimensionless number (Levenspiel, 1999).

$$D_G = D_{Go} \frac{P_o}{P} \left( \frac{\bar{u}}{u_o} \right)^n = D_{Go} \frac{P_o}{P} \left( \frac{t_{Mo}}{t_M} \right)^n \quad n=0 \text{ or } n=2 \quad (5.15)$$

where $D_G$ is the diffusivity parameter (cm$^2$/s), $D_{Go}$ is the diffusivity parameter defined at
1 atmosphere and \( n \) is the power in Eq (5.15) affecting \( t_M/t_M^0 \). The power for \( t_M/t_M^0 \) may be either “0” for the diffusionally controlled regime and “2” for the convective controlled regime.

Under these conditions, the \( (M^*/t_M)_{\text{model}} \) group as in Eq (5.12) becomes:

\[
\frac{M^*_t}{t_M} = a + b t_{M}^{(-n+2)}
\]  

(5.16)

where the values of the constants “\( a \)” and “\( b \)” are given by the following expressions:

\[
a = \frac{d^3 K_{s}}{r_c} \cdot \frac{1}{D_s} \quad b = \frac{2 D_G p_o}{L^2 p_M} t_{M}^{n} \left( 1 + \frac{2 d f K_{s} p}{r_c} \right)^2
\]  

(5.17)

Evaluation of the coefficient \( M^*/t_M \) in Eq (5.16) is presented in Figure 11 where the \( (M^*_2/t_M)/(M^*_2/t_M)_{\text{av}} \) group is plotted as a function of \( t_M \), at various temperatures, for both toluene and naphthalene. It can be noted that the \( (M^*_2/t_M)/(M^*_2/t_M)_{\text{av}} \) group remained essentially unchanged. Typical standard deviations are ±20%. This behaviour can be justified for a "\( n=2 \)” or "\( -n+2=0 \)” exponents in Eq (5.16).

Figure 11 Influence of the Average Linear Velocity on the \( (M^*/t_M)/(M^*_2/t_M)_{\text{av}} \) Ratios for Toluene (a) and Naphthalene (b), at Various Column Temperatures \( (T_c) \). Note: Each of the reported symbols is an average value of 3 experimental points. Standard deviations for repeats are ±7%.
This value for "n" is consistent with the expected dimensionless Bodenstein numbers, which are in the 4.5-10 for toluene and 4-12 for naphthalene as is shown in Appendix A. It has been suggested that under these conditions, the flow regime in tubes with $L >> r_c$ remains in the convective or near convective flow regime (Levenspiel, 1999).

Furthermore, differences between $M^*/t_M$ and "b" constant for $n=2$ are reported in Table 7. One can notice that $M^*/t_M$ is always larger than "b". Therefore, one can conclude that the "b" parameter which is related with axial dispersion in the narrow bore capillary column has, for all practical purposes, a negligible influence on the $M^*/t_M$ group and can thus, be neglected. It is however, for the case of $t_M = 104$ s (the lowest flow studied) where $M^*/t_M$ group at the n=0 condition can affect $M^*/t_M$. It was as a result of this finding, that this condition of low flow was discarded for further analysis.

Table 7 Values of Constants "a" and "b" in Eq (5.16) when $n=2$ and n=0 for Toluene and Naphthalene*

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$M^*/t_M \times 10^2$</th>
<th>$n=2$, for all $t_M$</th>
<th>$n=0$, for $t_M=104$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$b \times 10^4$ (s)</td>
<td>$b \times 10^4$ (s)</td>
<td>$b t_M^2 \times 10^3$ (s)</td>
</tr>
<tr>
<td><strong>Toluene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>1.47</td>
<td>1.82</td>
<td>1.51</td>
</tr>
<tr>
<td>323</td>
<td>0.66</td>
<td>1.77</td>
<td>1.07</td>
</tr>
<tr>
<td>343</td>
<td>0.31</td>
<td>0.81</td>
<td>0.67</td>
</tr>
<tr>
<td>353</td>
<td>0.77</td>
<td>0.68</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Naphthalene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>4.81</td>
<td>6.07</td>
<td>5.03</td>
</tr>
<tr>
<td>373</td>
<td>1.42</td>
<td>2.68</td>
<td>2.23</td>
</tr>
<tr>
<td>393</td>
<td>1.10</td>
<td>1.40</td>
<td>1.15</td>
</tr>
<tr>
<td>433</td>
<td>1.11</td>
<td>0.65</td>
<td>0.50</td>
</tr>
</tbody>
</table>

$t_M = 52$ s, $D_{go} = 0.20$ cm$^2$/s for toluene and 0.17 cm$^2$/s for naphthalene at 25°C and 1atm. $D_{go}$ was approximated with the molecular diffusivity.
Finally, the polymer diffusion coefficient ($D_s$) values for both toluene and naphthalene were obtained from the constant “$a$” using Eq (5.16). Figure 12 shows values of $D_s$ as function of absolute temperature for toluene and naphthalene. One can notice in this plot that for both chemical species, $D_s$ values slightly increase with temperature. This mild increment in the $D_s$ diffusivity with the thermal level is in agreement with the polysiloxane polymer behaviour in capillary columns. Furthermore, $D_s$ values of $4.45-5.83 \times 10^{-8}$ cm$^2$/s for toluene and $4.47-5.91 \times 10^{-8}$ cm$^2$/s for naphthalene seem to be consistent with molecular weight. It is important to notice that despite the range of temperature for both analytes is different, a temperature point at 353 K makes clear that $D_s$ value for toluene ($5.83 \times 10^{-8}$ cm$^2$/s) is higher that $D_s$ value for naphthalene ($4.47 \times 10^{-8}$ cm$^2$/s). This reduction of $D_s$ for naphthalene while compared with the ones for toluene is in line with the expected increased difficulty of larger molecules to elute in the polymer phase of the BPX5 column. Values of $D_s$ for both toluene and naphthalene are in agreement with the open literature, where one can find that aromatic species diffusivities in polymers are in the range of $10^{-7}$ and $10^{-10}$ (Duda, 1985; George and Thomas, 2001).

![Figure 12 Diffusion of Toluene and Naphthalene in the Polymer Coating of BPX5 Capillary Column. Temperature range used in this Study was 313–433 K. Note: Each of the reported symbols is an average of 3 experimental points](image-url)
Moreover, a reconciliation plot was built once the values of $D_s$ are calculated from $(M^*_2/tM)_{model}$. This plot is presented in Figure 13, where $(M^*_2/tM)_{model}$ values are those obtained from Eq (5.16) and $(M^*_2/tM)_{exp}$ values with $M^*_2$ obtained from Eq (5.10). This comparison shows $R^2$ regression coefficients of 0.86 and 0.89 for toluene and naphthalene, respectively.

![Figure 13](image)

**Figure 13** Comparison Plot for $(M^*_2/tM)_{model}$ as per Eq (5.16) and the $(M^*_2/tM)_{exp}$ for Naphthalene and Toluene. Temperature range used in this study was 313-433 K. $R^2$ is 0.86 and 0.89 for toluene and naphthalene, respectively.

### 5.5 Conclusions

This chapter reports the validation of an adsorption equilibrium model for aromatic species such as, toluene and naphthalene, in a BPX5 thin coated capillary column. It is proven, that the proposed phenomenologically based model allows the calculation of the adsorption parameters in BPX5 capillary columns using the first and second central statistical moments of the eluted peaks ($M_1$ and $M_2^*$). Thus, this chapter provides an in depth analysis of adsorption processes in a BPX5 column. The knowledge gained may lead to their improved design as well as to the modelling for other families of chemical species in capillary columns, as is shown in Chapter 6.
Chapter 6
Mathematical Model with Adsorption at Non-Equilibrium in a BPX5 Capillary Column

6 Introduction

A mathematical model for a GC capillary column was reported in Chapter 5. This model was based on adsorption and adsorption-desorption processes at equilibrium. This model was applied extensively for both toluene and naphthalene.

It was found, however, that this model is unable to describe asymmetric peaks such as the ones observed when using oxygenate chemical species such as phenol and 2-naphthol. Figure 14 reports characteristic phenol and 2-naphthol chromatograms. It can be observed that there is a significant deviation of the observed peaks with respect to the close to Gaussian peaks recorded for toluene and naphthalene (refer to Figure 8 in section 5.3). Additionally, it was also noticed that the skewness values \( S=M_3/M_2^{3/2} \) quantifying the asymmetries of peaks were 1.5-10 times higher for phenol and 2-naphthol than for toluene and naphthalene (refer Appendix A).

Therefore, a mathematical modified model is needed to adequately describe the phenol and 2-naphthol peak asymmetry. As is described in Chapter 2, the peak tailings in chromatograms can be explained by a number of possible considerations: a) non-linear adsorption, b) non-equilibrium adsorption/desorption, c) heterogeneous stationary phase or d) two sites of adsorption on the polymer coating (Kucera, 1965; Lee, et al., 1988; Guiochon and Lin, 2003; Asnin, et al., 2007). Given the low solute concentrations selected for this PhD study, a linear isotherm can always be adopted as explained in Appendix A. Therefore and considering the likely homogeneous polymer film thickness coating \( (d_f) \), a phenomenological model can be adopted to explain phenol and 2-naphthol peaks under adsorption at non-equilibrium conditions.

Given that the proposed model requires the numerical solution of the resulting equations, a major aspect on this analysis is its validation and numerical error analysis. Once these
issues are clarified, calculations of adsorption and diffusion parameters in the column are reported.

![Figure 14 Characteristic Chromatograms Obtained in a GM-MS Shimadzu Mandel QP2010S Unit and a 30m x 25mm BPX5 Capillary Column. (a) Phenol: \( T_c = 353 \text{K} \) and \( \bar{u} = 69 \text{ cm/s} \) and (b) Naphthalene: \( T_c = 433 \text{ K} \) and \( \bar{u} = 69 \text{ cm/s} \). Note: symbols in this figure refer to data points for individual runs, while solid lines represents the calculated average chromatograms obtained with data from individual injections (triplicates).](image)

6.1 Mathematical Model Equations for a Non-Equilibrium Adsorption Model

This proposed non-equilibrium adsorption model adopts similar conditions and approximations as for the equilibrium adsorption model. The assumptions are listed below, and are also detailed in Chapter 5.

- The polymer coating of the stationary phase is inert to the analyte.
- The polymer film thickness, \( d_f \), is \( 0.25 \pm 5 \times 10^{-4} \text{ mm} \) and constant within the BPX5 capillary column.
- The capillary column-gas interaction takes place via solute transfer at the
polymer-gas interface with the solute being absorbed into the polymer coating.

- Diffusion coefficients in the stationary phase are assumed to be concentration independent, with their axial diffusion being negligible. This is shown in Appendix A for an equilibrium adsorption model. This chapter will also report the $D_s$ and $D_G$ effects on the linear adsorption model with non-equilibrium adsorption.

- The carrier gas complies with the ideal gas law.

- The carrier gas flow in the capillary column occurs at nearly constant pressure and, as a result, near constant average cross-section flow velocity, as shown in the Appendix A of the present PhD study.

- The carrier gas displays a parabolic velocity profile in the capillary column.

- The solute initial concentration ($c_0$) can be modeled as an Impulse Delta Dirac ($\delta$).

The various capillary column analyses are developed at a constant temperature.

Thus, under these isothermal conditions and accounting for various approximations, Eqs (6.1) and (6.2) describe the chemical species conservation considering adsorption at non-equilibrium:

\[
\frac{\partial c_m}{\partial t} = -u \frac{\partial c_m}{\partial z} + D_G \frac{\partial^2 c_m}{\partial z^2} + \frac{2D_s}{r_c} \frac{\partial c_s(r = r_c)}{\partial r} \tag{6.1}
\]

\[
\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial r^2} \tag{6.2}
\]

To solve Eqs (6.1) and (6.2), it is required to establish both initial and boundary conditions as follows:

- At the beginning of the GC analysis, the BPX5 capillary column is eluted of any analyte remaining from a previous experiment. Then, the initial concentrations $c_m$ and $c_s$ inside the column are equal to zero:
\[ c_m(t,z,r) = c_s(t,z,r) = 0 \quad \text{at } t = 0 \text{ and } z > 0 \quad (6.3) \]

- The volume of solute injected into the system is constant and introduced rapidly at the inlet port. This assures a constant initial mass of solute that can be approximated as the Impulse Delta Dirac Function (\( \delta \)):

\[ c_m(t,z,r) = d(t) c_o \quad \text{at } z > 0 \quad (6.4) \]

- At the interphase between the mobile and stationary phases, the analyte concentrations in both phases, are related via a non-equilibrium adsorption equation which involves a distribution coefficient (\( K_s \)) as follows:

\[ \frac{2D_s}{r_c} \frac{\partial c_s(r = r_c)}{\partial r} = -a_k k_{ads} \left[ c_m - c_s \left( \frac{r = r_c}{K_s} \right) \right] \quad \text{at } r = r_c \quad (6.5) \]

- The diffusivity flux of the solute in both mobile and polymer phases is the same at the interphase:

\[ D_G \left( \frac{\partial c_m}{\partial r} \right) = D_s \left( \frac{\partial c_s}{\partial r} \right) \quad \text{at } r = r_c \quad (6.6) \]

- The solute concentration does not change radially at the center of the capillary column. Thus at \( r = 0 \), then

\[ \frac{\partial c_m}{\partial r} = 0 \quad r = 0 \quad (6.7) \]

- Any solute injected in the GC unit is recovered at the column exit. This means that there is no BPX5 chemical reaction between the analyte and the polymer coating or no analyte migrate far away from the polymer-glass capillary column interphase

\[ \frac{\partial c_s}{\partial r} = 0 \quad r = r_c + df \quad (6.8) \]

- The axial dispersion term, \( D_G \left( \frac{\partial^2 c_m}{\partial z^2} \right) \) is negligible from Eq (6.1), since it has been proven that it has no influence in a similar model in Chapter 5. Additionally, section 6.2.1 shows that the \( D_G \) term, in a model, at adsorption, at non-equilibrium, and displaying a linear adsorption isotherm, has no effect on the dispersion of the chromatographic peak.
Furthermore, in order to proceed with a numerical solution, eqs (6.1) and (6.2) have to be discretized using a finite element method, as described in Appendix C, with the solute concentration in the mobile phase \(c_m\) and stationary phase \(c_s\) being reported as follows:

\[
c_m(i-1,j) = -f_1(c_s(i,j,1)) - f_2(c_m(i,j-1)) + f_3(c_m(i,j)) - f_4(c_m(i,j+1)) \tag{6.9}
\]

\[
c_s(i-1,j,k) = -f_{s2}(c_s(i,j,k-1)) + f_{s3}(c_s(i,j,k)) - f_{s4}(c_s(i,j,k+1)) \tag{6.10}
\]

where the nodes at various times, axial coordinates and radial coordinates are represented using \(i, j\) and \(k\) subscripts, respectively. As a result, at the gas-polymer interface one can consider \(k=1\).

Furthermore, there are a number of dimensionless coefficients, which result from this discretization analysis as follows:

\[
f_1 = \frac{a_v k_{ads} \Delta t}{K_s} ; \quad f_2 = -\frac{u}{\Delta \zeta} \Delta t + D_s \frac{\Delta \zeta}{\Delta \zeta^2} ; \quad f_3 = 1 + \frac{u}{\Delta \zeta} \Delta t + 2 D_s \frac{\Delta \zeta}{\Delta \zeta^2} + a_v k_{ads} \Delta t ;
\]

\[
f_4 = D_G \frac{\Delta t}{\Delta \zeta^2} ; \quad f_{s2} = D_s \frac{\Delta t}{\Delta \zeta^2} ; \quad f_{s3} = 1 + 2 D_s \frac{\Delta t}{\Delta \zeta^2}.
\]

In the upcoming sections, the validation of the non-equilibrium adsorption model is considered. This includes the evaluation of possible numerical errors, the stability of the obtained parameters \((K_s, D_s \text{ and } D_G)\) and the fitting of the experimental statistical moments \((M_{1,\text{exp}}, M_{2,\text{exp}}^* \text{ and } M_{3,\text{exp}}^*)\) to the statistical moments of the model \((M_{1,\text{model}}, M_{2,\text{model}}^* \text{ and } M_{3,\text{model}}^*)\).

### 6.2 Evaluation of the Numerical Solution

The proposed non-equilibrium adsorption model solution includes three parameters as follows: i) the distribution coefficient \((K_s)\), ii) the diffusion coefficient in stationary phase \((D_s)\) and iii) the adsorption constant \((k_{ads})\). As discussed earlier in Chapter 2, parameters can be related with the statistical moments of a given chromatographic peak. For
instance, $K_s$ determines $M_1$, $D_s$ is related to $M_2^*$ and $k_{ads}$ is associated with $M_3$. Therefore, the values $K_s$, $D_s$ and $k_{ads}$ can be validated by adjusting the statistical moments of the model: $M_{1,model}$, $M_{2,model}^*$ and $M_{3,model}^*$, to the experimental values of the same statistical moments: $M_{1,exp}$, $M_{2,exp}^*$ and $M_{3,exp}^*$. Figure 15 reports a general diagram to determine the values $K_s$, $D_s$ and $k_{ads}$ for various experimental elution chromatograms of phenol and 2-naphthol in a BPX5 capillary column.

Figure 15 Diagram of the Implemented Numerical Method to Determine $K_s$, $D_s$ and $k_{ads}$ with a Non-Equilibrium Adsorption Model in a BPX5 Capillary Column.
Moreover, prior to determining the $K_s$, $D_s$ and $k_{ads}$ parameters, one is advised to check that the mathematical model provides a sound description for the following cases: a) the response of the model to an inert tracer, b) the response of the model to the expected $D_G$ values as in the adsorption in the equilibrium model considered in Chapter 5, c) the response of the model to $D_s$ values obtained, with the equilibrium adsorption model and, d) stable values of the calculated statistical moments ($M_{1,model}$, $M^*_{2,model}$ and $M^*_{3,model}$) at various numbers of nodes in the time scale ($nt$), in the axial coordinate ($ns$) and in the radial coordinate ($nr$).

### 6.2.1 Response to a Tracer Impulse Using the Non-Equilibrium Adsorption Model

The response of the proposed non-equilibrium model was first evaluated by simulating that there were no solute-polymer phase interactions. In other words, adsorption/desorption phenomena and dispersion in the stationary phase were turned “off” in the model, setting both at $D_s=0$ and $k_{ads}=0$. As a result, the mathematical model peaks display chromatograms with $M_{1,model}$ values equivalent to the theoretical expected hold up time ($t_M=L/\bar{u}$) and the experimental $t_{M,exp}$, when air was injected in the GC capillary column at the same linear velocity as is shown in Table 8. Details of the experiments with air as a tracer are described in Appendix A.

**Table 8 Evaluation of a Tracer in the non-equilibrium Adsorption Model**

<table>
<thead>
<tr>
<th>Average linear velocity; ($\bar{u}$) cm/s</th>
<th>Hold up time; $t_M=L/\bar{u}$ (min)</th>
<th>$M_{1,model}$ (min)</th>
<th>$M^*_{2,model}$ x10$^5$ (min)$^2$</th>
<th>$M^*_{3,model}$ x10$^8$ (min)$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.0</td>
<td>0.72</td>
<td>0.72</td>
<td>4.39</td>
<td>0.49</td>
</tr>
<tr>
<td>52.4</td>
<td>0.95</td>
<td>0.95</td>
<td>7.33</td>
<td>1.06</td>
</tr>
<tr>
<td>37.1</td>
<td>1.35</td>
<td>1.34</td>
<td>14.1</td>
<td>2.83</td>
</tr>
</tbody>
</table>

*Average linear velocity ($\bar{u}$) and hold up time ($t_M$) were confirmed by injecting air as an inert compound into the BPX5 capillary column (see details in Appendix A). Parameters in the model were: $D_g=0$, $D_s=0$, $k_{ads}=0$, $nt=3\times10^5$, $ns=1.5\times10^4$ and $nr=5$. 
Furthermore, the statistical moments $M_{2,\text{model}}^\ast$ and $M_{3,\text{model}}^\ast$ were, in this case, $10^1$ and $10^2$ times smaller that the obtained values when $D_s$ and $k_{ads} > 0$ using the mathematical model. Therefore, it was shown that the non-equilibrium model provides outlet peaks for the $D_s=0$ and $k_{ads}=0$ cases that are very close to a Delta Dirac Impulse Function. More information regarding the simulation of like-Delta Dirac Impulse peaks is presented in section 6.2.

6.2.2 Influence of the Diffusion Coefficient in the Mobile Phase ($D_G$) in a Non-Equilibrium Adsorption Model

As described in Chapter 5, the axial dispersion for toluene and naphthalene can be neglected, in a chromatographic model, at the equilibrium applicable to a BPX5 capillary column. Thus, a negligible axial dispersion term $D_G (\partial^2 c_m / \partial z^2)$ can also be an accurate approximation, in the case of the non-equilibrium adsorption model, using the same BPX5 capillary column. However, to secure the adequacy of neglecting $D_G$ a wide range of $D_G$ values were used. In this respect, Table 9 reports the calculated statistical moments of the model, $M_{1,\text{model}}$, $M_{2,\text{model}}^\ast$ and $M_{3,\text{model}}^\ast$ for phenol and 2-naphthol with $D_G$ values changing from $1 \times 10^{-1}$ to $1 \times 10^2 \text{ cm}^2/\text{s}$. It can be observed from this table, that the mathematical model yields statistical moments similar to those obtained when $D_G = 0$ with deviations being limited to 5-10% for $D_G$ values in the $1 \times 10^{-1}$ to $1 \times 10^1 \text{ cm}^2/\text{s}$.

Therefore, if $D_G$ is approximated by the molecular diffusion coefficient, $D_{12}$ ($1.7 \times 10^{-1}$ and $2.0 \times 10^{-1} \text{ cm}^2/\text{s}$) at the expected Reynolds numbers of 0.1-0.7 (as explained in Chapter 5); then, the axial dispersion parameter can be neglected. As a result axial dispersion can be as non-relevant in the mathematical modeling of adsorption at non-equilibrium
Table 9 Influence of Axial Dispersion Coefficient ($D_G$) in the Non-equilibrium Adsorption Model*

<table>
<thead>
<tr>
<th>$D_G$ (cm$^2$/s)</th>
<th>Phenol</th>
<th></th>
<th></th>
<th>2-Naphthol</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_1$ (min)</td>
<td>$M^*_2$ (min$^2$)</td>
<td>$M_3$ (min$^3$)</td>
<td>$M_1$ (min)</td>
<td>$M^*_2$ (min$^2$)</td>
<td>$M_3$ (min$^3$)</td>
</tr>
<tr>
<td>0</td>
<td>1.83</td>
<td>0.96</td>
<td>0.10</td>
<td>2.09</td>
<td>1.32</td>
<td>0.16</td>
</tr>
<tr>
<td>1x10$^{-1}$</td>
<td>1.83</td>
<td>0.97</td>
<td>0.10</td>
<td>2.09</td>
<td>1.33</td>
<td>0.17</td>
</tr>
<tr>
<td>5x10$^{-1}$</td>
<td>1.83</td>
<td>0.98</td>
<td>0.11</td>
<td>2.09</td>
<td>1.35</td>
<td>0.17</td>
</tr>
<tr>
<td>1</td>
<td>1.83</td>
<td>1.00</td>
<td>0.11</td>
<td>2.09</td>
<td>1.37</td>
<td>0.18</td>
</tr>
<tr>
<td>1x10$^{1}$</td>
<td>1.83</td>
<td>1.30</td>
<td>0.19</td>
<td>2.09</td>
<td>1.76</td>
<td>0.32</td>
</tr>
<tr>
<td>1x10$^{2}$</td>
<td>1.91</td>
<td>5.07</td>
<td>5.23</td>
<td>2.18</td>
<td>6.85</td>
<td>8.66</td>
</tr>
</tbody>
</table>

Parameters: $D_f=0$, $u=69$ cm/s, $n_t=3 \times 10^5$, $n_s=1 \times 10^3$, $n_r=1$. For phenol: $K_s=309$ at $T_c=373$K. Experimental statistical moments of phenol: $M_1_{exp}=1.83$ min; $M^*_2_{exp}=0.12 \times 10^{-3}$ min$^2$; $M^*_3_{exp}=0.20 \times 10^{-3}$ min$^3$. For 2-naphthol: $K_s=385$ at $T_c=453$K. Experimental statistical moments of 2-naphthol: $M_1_{exp}=2.1$ min; $M^*_2_{exp}=0.19 \times 10^{-3}$ min$^2$; $M^*_3_{exp}=0.32 \times 10^{-5}$ min$^3$.

6.2.3 Influence of Diffusion Coefficient in the Stationary Phase ($D_s$) in the Non-equilibrium Adsorption Model

As Figure 15 illustrates, diffusion coefficients in the stationary phase $D_s$ for phenol and 2-naphthol, were obtained using the adsorption at the equilibrium model. These values were, in turn, used in the non-equilibrium adsorption model to determine $K_s$ and $k_{ads}$. Furthermore, different values of $D_s$ were considered to analyze the response of the mathematical model to both, phenol and 2-naphthol analytes. For instance, Table 10 reports two cases of statistical moments obtained in the $1 \times 10^8$ to $20 \times 10^8$ cm$^2$/s $D_s$ range. It can be observed that for $1 \times 10^8$ to $10 \times 10^8$ cm$^2$/s at constant $K_s$ and $k_{ads}$, the variation of $M_{1, model}$ was less than 1%, the deviation of $M^*_{2, model}$ was in the 3-10% and the variation of $M^*_{3, model}$ was restricted to 3-15%.

Additionally, the effect of $D_s$ can be analyzed in Figure 16. This Figure shows phenol concentrations $c_s$ and $c_m$ within the capillary column with non-equilibrium adsorption. In Figures 17a, 17b and 17c, one can observe that changes of concentration ($c_s/K_s$) in the
polymer phase are small when an eluted chromatograph is evaluated in the mathematical model (Figure 17a, \( c_v/K_s=0.97 \times 10^{-3} \) g/solute/m\(^2\) polymer phase; Figure 17b, \( c_v/K_s=0.55 \) g/solute/m\(^2\) polymer phase and Figure 17c \( c_v/K_s=0.48 \) g/solute/m\(^2\) polymer phase). Figures representing \( c_v \) in a BPX5 capillary column illustrate that a solute does not diffuse quickly in the polymer phase. Therefore, \( D_s \) provides a small contribution on peak dispersion, and \( M^*_2 \) is not straightforwardly determined by \( D_s \) with non-equilibrium adsorption. Thus, sections 6.5 and 6.6, in this Chapter, explain the selection of \( D_s \) for the experimental chromatographic data of phenol and 2-naphthol.

**Table 10 Influence of Diffusion Coefficient in the Stationary Phase \( (D_s) \) Using the Non-equilibrium Adsorption Model\(^1\).**

<table>
<thead>
<tr>
<th>Phenol</th>
<th>( M_{1,model} ) (min)</th>
<th>( M^*_{2,model} \times 10^3 ) (min(^2))</th>
<th>( M^*_{3,model} \times 10^5 ) (min(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_s ) (cm(^2)/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1x10(^{-8})</td>
<td>1.83</td>
<td>1.53</td>
<td>2.75</td>
</tr>
<tr>
<td>2.5x10(^{-8})</td>
<td>1.83</td>
<td>1.56</td>
<td>2.78</td>
</tr>
<tr>
<td>5x10(^{-8})</td>
<td>1.83</td>
<td>1.39</td>
<td>2.15</td>
</tr>
<tr>
<td>10x10(^{-8})</td>
<td>1.83</td>
<td>1.32</td>
<td>1.90</td>
</tr>
<tr>
<td>20x10(^{-8})</td>
<td>1.83</td>
<td>1.27</td>
<td>1.86</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2-Naphthol</th>
<th>( M_{1,model} ) (min)</th>
<th>( M^*_{2,model} \times 10^3 ) (min(^2))</th>
<th>( M^*_{3,model} \times 10^5 ) (min(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_s ) (cm(^2)/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1x10(^{-8})</td>
<td>3.46</td>
<td>8.52</td>
<td>3.89</td>
</tr>
<tr>
<td>2.5x10(^{-8})</td>
<td>3.46</td>
<td>7.48</td>
<td>2.96</td>
</tr>
<tr>
<td>5x10(^{-8})</td>
<td>3.46</td>
<td>6.83</td>
<td>2.50</td>
</tr>
<tr>
<td>10x10(^{-8})</td>
<td>3.47</td>
<td>6.75</td>
<td>2.58</td>
</tr>
<tr>
<td>20x10(^{-8})</td>
<td>3.48</td>
<td>6.69</td>
<td>2.46</td>
</tr>
</tbody>
</table>

\(^1\) Parameters: \( \bar{u}=69 \) cm/s, \( m=5 \) and \( n_s=1.5 \times 10^4 \). Parameters of phenol at \( T_c=373K \): \( K_s=309 \) and \( k_{ads}=4.80 \times 10^{-3} \) m/s. Experimental statistical moments of phenol: \( M_{1,exp}=1.83 \) min; \( M^*_{2,exp}=0.12 \times 10^{-3} \) min\(^2\); \( M^*_{3,exp}=0.20 \times 10^{-5} \) min\(^3\). Parameters of 2-naphthol at \( 433K \): \( K_s=762 \) and \( k_{ads}=4.6 \times 10^{-3} \) m/s. Experimental statistical moments of 2-naphthol: \( M_{1,exp}=3.46 \) min; \( M^*_{2,exp}=0.71 \times 10^{-3} \) min\(^3\); \( M^*_{3,exp}=2.48 \times 10^{-5} \) min\(^3\).
Figure 16 Phenol Concentrations in the Mobile Phase ($c_m$) and Stationary Phase ($c_s$) using a Non-equilibrium Adsorption Model. Parameters: $\bar{u} = 69$ cm/s, $nr=5$, $nt=3\times10^5$ and $ns=1\times10^3$. At $T_c = 373K$: $K_s=309$, $k_{ads}=5\times10^{-3}$ m/s and $D_s=5\times10^8$ cm$^2$/s. Figures were obtained from the model at different times of analysis ($t_{exp}$). Figure (a): $t_{exp}=26s$ and $L=17.5m$; Figure (b): $t_{exp}=40s$ and $L=12.5m$ and Figure (c): $t_{exp}=95$ and $L=24m$. 
6.2.4 Mesh Independency Test Using the Non-Equilibrium Adsorption Model

Earlier in this Chapter, Eqs (6.9) and (6.10) were reported as the ones providing the numerical solution of the proposed non-equilibrium adsorption model. The discretization of both equations was developed using the Finite Volume Method as detailed in Appendix C. Using this method, the spatial domain is divided into a discrete number of volume elements and the equations (6.1) and (6.2) are integrated over the volume element \(i,j,k\) (refer to Figure C.1 of the Appendix sections).

Thus, the discretization of equations yields a mesh of nodes in the time \((nt)\), axial \((ns)\) and radial \((nr)\) coordinates. In each element of the created mesh, physical parameters such as temperature, average linear velocity and pressure are considered fixed at set values (Cruz, et al., 2005; Webley & He, 2000). Thus, the resulting system of linear equations is solved by obtaining the concentrations \(c_m\) and \(c_s\) in \(i,j,k\) node in time \(i\) \((i>0)\).

One can notice that when using this numerical method, the size of the mesh grid is crucial to find an accurate numerical solution for the model equations. However, increasing the number of nodes of the mesh involves, at some point, an excessive computational time. Thus, one has to compromise the evaluation of the stability of the \(M_{1,model}\), \(M^{*}_{2,model}\) and \(M^{*}_{3,model}\) statistical moments, regarding \(nt\), \(ns\) and \(nr\). This step is critical in order to obtain reliable values for the adsorption and diffusion parameters.

It is important to mention, in this respect, that the gradient of concentration in the stationary phase \((c_s)\) requires an adequate number of radial nodes \((nr)\). Figure 17 reports the values of \(M_{1,model}\), \(M^{*}_{2,model}\) and \(M^{*}_{3,model}\) with respect to the number of radial nodes \((nr)\) for both phenol and 2-naphtol. One can notice that statistical moment values decrease as the \(nr\) number increases. However, statistical moment values did not change when \(nr\) is 5 and 6. For these cases, the variation of \(M_{1,model}\), \(M^{*}_{2,model}\) and \(M^{*}_{3,model}\) remain in the 2%-6% range. Thus, increasing the number of radial nodes \((nr)\) demands more and unjustified extra computational time. As a result \(nr=5\) was selected for further calculations.
Figure 17 Influence of the Number of Radial Nodes (nr) in the Statistical Moments $M_{1,\text{model}}$, $M'_{2,\text{model}}$ and $M'_{3,\text{model}}$ Obtained with the Non-equilibrium Adsorption Model. Parameters: $\bar{u}=69$ cm/s, $ns=1x10^3$ and $nt=3x10^5$. Adsorption and Diffusion Parameters for phenol at 373K: $K_s=309$, $k_{\text{ads}}=5x10^{-3}$ m/s and $D_s=5x10^8$ cm$^2$/s. Adsorption and diffusion parameters for 2-naphthol at $T_c=453$K: $K_s=385$, $k_{\text{ads}}=5.5x10^{-3}$ m/s and $D_s=2x10^8$ cm$^2$/s. Note: nr value was selected once $M'_{3,\text{model}}$ values deviated by less than 5%.

On the other hand, Figure 18 illustrates the influence of the number of time nodes (nt) in $M_{1,\text{model}}$, $M'_{2,\text{model}}$ and $M'_{3,\text{model}}$ statistical moment values for phenol and 2-naphthol. One can observe that the values of $M_{1,\text{model}}$ and $M'_{2,\text{model}}$ for both chemical species do not significantly change in the $3x10^5$ to $10x10^5$ nt range. Statistical moments of third order, $M'_{3,\text{model}}$, are, however, slightly affected by the change of time nodes with 5% variations. Therefore, it can be concluded that nt does not affect the adsorption and diffusion parameter calculation, significantly, in the range considered when using the non-equilibrium adsorption model.

Furthermore, Figure 19 reports the influence of axial number of nodes (ns) on the statistical moment calculations. One can observe that $M_{1,\text{model}}$ values are not influenced by the number of axial nodes. However, $M'_{2,\text{model}}$ and $M'_{3,\text{model}}$ values decrease as ns increases. One can observe less than 5% of variation in the second and third statistical moments when ns is between 15 and $20x10^3$. One can also notice that the increase of ns also leads to extra computational time. Therefore, to reduce the computational time involved in parameter calculations, the following strategy was adopted: a) $K_s$ was adjusted at low values of ns (e.g. $ns=1x10^3$), b) $k_{\text{ads}}$ was determined with an extra number
of axial nodes until the third statistical moment, $M_{3,\text{model}}^*$ had a variation of <5% (e.g. $15 \times 10^3$-$20 \times 10^3$).

Figure 18 Influence of the Number of Time Nodes ($nt$) on the Statistical Moments $M_{1,\text{model}}, M_{2,\text{model}}^*$ and $M_{3,\text{model}}^*$ Calculation Obtained from the Non-equilibrium Adsorption Model. Parameters: $\bar{u} = 69$ cm/s, $nr=5$ and $ns=1 \times 10^3$. Adsorption and diffusion parameters for phenol: $K_c=309$, $k_{\text{adv}}=5 \times 10^{-3}$ m/s and $D_s=5 \times 10^8$ cm$^2$/s. Adsorption and diffusion parameters for 2-naphthol: $K_c=385$ and $k_{\text{adv}}=5.5 \times 10^{-3}$ m/s and $D_s=2 \times 10^8$ cm$^2$/s. Note: $nt$ value was selected once $M_{3,\text{model}}^*$ values deviated by less than 5%.

Figure 19 Influence of the Number of Axial Nodes ($ns$) on the Statistical Moments $M_{1,\text{model}}, M_{2,\text{model}}^*$ and $M_{3,\text{model}}^*$ Obtained for the Non-equilibrium Adsorption Model. Parameters: $\bar{u} = 69$ cm/s, $nr=5$ and $nt=3 \times 10^6$. Adsorption and diffusion parameters for phenol: $K_c=309$, $k_{\text{adv}}=5 \times 10^{-3}$ m/s and $D_s=5 \times 10^8$ cm$^2$/s. Adsorption and diffusion parameters for 2-naphthol: $K_c=385$, $k_{\text{adv}}=5.5 \times 10^{-3}$ m/s and $D_s=2 \times 10^8$ cm$^2$/s. Note: $ns$ value was selected once $M_{3,\text{model}}^*$ values deviated by less than 5%.
6.2.5 Evaluation of the Implemented Numerical Method for Non-Equilibrium Adsorption Model

It was noticed that $M_{2,\text{model}}^*$ calculated was higher than the $M_{2,\text{exp}}^*$ calculated with the experimental peak data. It was hypothesized that this finding could be related to ‘false diffusion’ The designated ‘false diffusion’ is the peak dispersion captured by the model, as a result of numerical errors while of solving fluid convection problems using first order upwind methods (Xu, et al., 2007). Appendix C contains additional details about its application to the numerical solution of the adsorption non-equilibrium model.

In order to evaluate this, numerical simulations were developed for the two following cases:

a) Calculating the chromatographic elution peak with $M_{1,\text{model}}^* = M_{1,\text{exp}}^*$ and no interaction with the stationary phase. To accomplish these parameters $D_s$ and $k_{\text{ads}}$ were both set at zero.

b) Calculating the chromatographic elution peak with $M_{1,\text{model}}^* = M_{1,\text{exp}}^*$ and having the analyte interacting with the polymer phase. In this case, both $D_s$ and $k_{\text{ads}}$ were larger than zero.

Furthermore, the numerical calculations considered were developed using different $n_s$ values for both, phenol and 2-naphthol. Figure 20 reports the results of these simulations. One can observe that the $M_{2,\text{model}}^*$ and $M_{3,\text{model}}^*$ statistical moments from cases a) and b), converge when $n_s$ is 15-20x10$^3$. One should notice that values obtained when $D_s=0$ and $k_{\text{ads}}=0$ at $n_s$ of 15-20x10$^3$, were 5 to 10% different than the ones calculated with $D_s>0$ and $k_{\text{ads}}>0$.

In addition and to cancel the potential effect of ‘false diffusion’, the following correction was applied to the calculated statistical moment data: $\Delta M_{2,\text{model}}^*$

\[
\Delta M_{2,\text{model}}^* = (M_{2,\text{model}}^*)_{D_s>0, k_{\text{ads}}>0} - (M_{2,\text{model}}^*)_{D_s=0, k_{\text{ads}}=0}
\] (6.11)

\[
\Delta M_{3,\text{model}}^* = (M_{3,\text{model}}^*)_{D_s>0, k_{\text{ads}}>0} - (M_{3,\text{model}}^*)_{D_s=0, k_{\text{ads}}=0}
\] (6.12)

Once the $\Delta M_{2,\text{model}}^*$ and $\Delta M_{3,\text{model}}^*$ were established, they were compared with the
experimental statistical moments. Figure 20 reports this information with a comparison of $\Delta M^*_{2,\text{model}}$ and $\Delta M^*_{3,\text{model}}$ with $M^*_{2,\text{exp}}$ and $M^*_{3,\text{model}}$ for phenol. Similar results were also obtained for 2-naphthol.

An important observation from this analysis is that the correction of the moment of second order using the $\Delta M^*_{2,\text{model}}$ for phenol and 2-naphthol is not enough to explain the discrepancy between the second order moments, as predicted by the model and as observed by the experiments. In fact, the $\Delta M^*_{2,\text{model}}$ still remains 10 times higher than the $M^*_{2,\text{exp}}$.

Thus, it can be concluded that the "false diffusion" is inadequate to explain the discrepancy between the predicted and experimentally observed second order moments.

### 6.3 Determination of the Distribution Coefficient ($K_s$) with Non-Equilibrium Adsorption Model

Thus, once these issues were clarified, the various model parameters were evaluated. First, it was attempted to calculate the $K_s$ distribution coefficient. In order to accomplish this, a first guess of $K_s$ was considered using Eq (5.13) from Chapter 5 (equilibrium...
adsorption model). Following this, the $K_s$ values were corrected until the first statistical moment, $M_{1,model}$ was adjusted to the experimental statistical moment $M_{1,exp}$) This was done using four different temperatures. Typical corrections of the initial $K_s$ values and the final converged $K_s$ were 35% different.

Figure 21 reports the reconciliation plot for both of phenol and 2-naphthol. It can be noticed that the correlation between the $M_{1,exp}$ and the $M_{1,model}$ obtained with the $K_s$ converged, was established with regression coefficients $R^2 = 0.99$.

![Figure 21 Comparison of $M_{1,exp}$ and $M_{1,model}$ Using Phenol and 2-Naphthol Analytes.](image)

Experimental parameters for phenol and 2-naphthol: $\bar{u} = 69$ cm/s. Temperature for phenol: 323, 343, 353 and 373 K. Temperature for 2-naphthol: 393, 413, 433, 453 K. Parameters of the model: $\bar{u} = 69$ cm/s, $nr=5$, $nt=3\times10^5$ and $ns=1.5\times10^4$. Note: reported data represent average values for 3 repeats. Standard deviations were +/-1%

Furthermore, Figure 22 reports the converged $K_s$ distribution constant for phenol and 2-naphthol as a function of absolute temperature ($T_c$). It is observed that $K_s$ decreases as temperature increases. Moreover, values of $K_s$ for 2-naphthol were higher than $K_s$ values for phenol. This influence of the molecular weight on $K_s$ is similar to the one reported for
toluene and naphthalene in Chapter 5. It was, in fact, shown in that chapter that the
distribution coefficient ($K_s$) decreased with temperature and augmented with molecular
weight.

![Figure 22 Influence of Column Temperature ($T_c$) on the Distribution Coefficient ($K_s$)
of Phenol and 2-Naphthol Analytes using Non-equilibrium Adsorption Model. $K_s$
values were obtained with $nr=5$, $nt=3-8x10^5$ and $ns=1.5x10^4$

One can calculate the energy of adsorption ($\Delta H_{ads}$) as previously
described by Eq (5.14). Table 11 reports the $K_{sa}$ and $\Delta H_{ads}$ determined parameters. According to these results, the
$\Delta H_{ads}$ of phenol is -47.8 +/- 4.37% while $\Delta H_{ads}$ of 2-naphthol is -59.2 +/- 5.85%. As
already mentioned, for toluene and naphthalene, this increase in the heat of adsorption
can be justified given that molecules with larger molecular size require bigger energies to
be adsorbed on the stationary phase.
Table 11 Adsorption Parameters Obtained from the Model as per Eq (5.13) for both Toluene and Naphthalene in a BPX5 Capillary Column*

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>log $K_{so}$ ± SD</th>
<th>$\Delta H_{ads}$ (kJ/mol) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>2.84 ± 0.17</td>
<td>-47.8 ± 2.09</td>
</tr>
<tr>
<td>2-Naphthol</td>
<td>3.22 ± 0.29</td>
<td>-59.2 ± 3.46</td>
</tr>
</tbody>
</table>

*Reference temperatures $T_{co}$ for toluene, 353 K and for naphthalene 413 K

6.4 Determination of the Adsorption Constant ($k_{ads}$) with a Non-Equilibrium Adsorption Model

The adsorption constant, $k_{ads}$ (m/s) determined with non-equilibrium adsorption refers to the adsorption/desorption kinetic parameter involved once the gas phase analyte interacts with the stationary phase. In other words, $k_{ads}$ represents the rate at which the solute molecules are transferred into and out of the polymer phase surface.

As a result of non-equilibrium adsorption, analyte molecules may spend different times on the polymer coating of the capillary column. Then, molecules spending extended periods in the stationary phase, delay their return to the gas mobile phase, resulting in band broadening and tailing (Muzenda, 2012).

As a result and to calculate $k_{ads}$, the following methodological steps were considered as follows: a) The calculation of the $K_s$ distribution coefficients for phenol and 2-naphthol with $D_s$ values were set as explained in section 6.2.3, b) The calculation of $k_{ads}$ values numerically regressing this parameter until the $M^*_{3, model}$ to the $M^*_{3, exp}$ were adjusted as described in Figure 15. Then, Figure 23 reports the obtained reconciliation plot for $M^*_{3, model}$ and $M^*_{3, exp}$. $R^2$ regression coefficients were consistently 0.99 for phenol and 2-naphthol.

Furthermore, the temperature effect on the adsorption constant, $k_{ads}$, for phenol and 2-naphthol, is reported in Figure 24. It is interesting to notice two consistent trends in this Figure:
a) when the column temperature ($T_c$) was 353 and 373 K for phenol and 433 and 453 K for 2-naphthol; the determined adsorption constants ($k_{ads}$) augmented with temperature,

b) when the column temperature ($T_c$) was 343 and 323 K for phenol and 413 and 393 K for 2-naphthol, the determined $k_{ads}$ decreases when temperature increased.

These observed trends for $k_{ads}$, regarding temperature, were assigned to the chemical structure of the stationary phase: 5% Phenyl Polysilphenylene-Siloxane. As can be observed in Figure 4, Chapter 2, the BPX5 polymer consists of a 95wt% non-polar chain and 5wt% of phenyl of polar sites. Temperature ($T_c$) can affect the position of the polar phenyl radicals in the polymer chain. Position of polar radicals in the polymer can determine the type of interaction with the eluted analyte in the capillary column.

Figure 23 Comparison of $\Delta M_{3,exp}^*$ and $M_{3,model}^*$ for Phenol and 2-naphthol Analytes. Experimental parameters for phenol and 2-naphthol: Average linear velocity of 69 cm/s. Absolute temperatures for phenol: 323, 343, 353 and 373. Temperatures for 2-naphthol: 393, 413, 433, 453. $M_{3,model}^*$ values were obtained with $nr=5$, $nt=3.8x10^5$ and $ns=1.5x10^4$. Note: reported data represent average $M_{3,exp}^*$ values for 3 repeats. Standard deviations were +/-1%.
Regarding the selected chemical species, phenol and 2-naphthol, studied in a BPX5 capillary column, one can argue that “π stacking forces” occur between the analytes and the polymer phase. These types of intermolecular interactions are similar to London forces and are highly dependent on the aromatic ring geometry (Morph and Pommerening, 1985; Paton, et al., 2009; Martinez and Iverson, 2012). Thus, experimental results may indicate that there are two geometries of phenyl radical groups in the stationary phase; with their abundance being a function of the column temperature ($T_c$).

Therefore, the determined $k_{ads}$ for phenol at 353-373 K and for 2-naphthol at 433-453 K suggests a solute adsorption accessibility in the polymer phase following an Arrhenius energy activated process. On the other hand, in the 323-343 K range for phenol, and in the 393-413 K range for 2-naphthol, it appears that the geometry of phenyl radicals, in the stationary phase, favors an increased accessibility of sites at lower temperatures. Regarding 2-naphthol, the same trend as the one observed for phenol is observed at lower temperatures. However, this effect is noticed, now, at a higher thermal range, with this being assigned to the larger 2-phenol molecular size versus the smaller molecular seize for phenol.

![Figure 24 Influence of the Column Temperature ($T_c$) on the Adsorption Constants ($k_{ads}$) for Phenol and 2-naphthol Analytes. $k_{ads}$ values were obtained with $nr$=5, $nt$=3-8$x10^5$ and $ns$=1.5$x10^4$.](image-url)
6.5 Determination of the Diffusion Coefficient in the Stationary Phase \((D_s)\) Using an Adsorption Non-Equilibrium Model

The effect of the diffusion coefficient on the stationary phase \((D_s)\), for the non-equilibrium adsorption model, was determined by using Eq (5.16) already described in Chapter 5 for adsorption at equilibrium.

Figure 25 reports these diffusion coefficient values. One can also notice that Figure 16 shows small solute concentration \((c_s)\) changes in the polymer phase. Hence, this establishes the low \(D_s\) influence in peak broadening. Thus, the determined \(D_s\) values were considered a good approximation.

Figure 26 reports a reconciliation plot of second statistical moments. This plot shows that the \(M^*_{2,\text{model}}\) does not fit the experimental \(M^*_{2,\text{exp}}\) values yielding \(M^*_{2,\text{model}}\) 10 times larger than \(M^*_{2,\text{exp}}\). Therefore, while the proposed non-equilibrium adsorption model is able to predict the peak asymmetry, fails to represent undoubtedly the variance of the chromatographic peaks.

![Figure 25 Influence of Temperature Using on the Approximate Diffusion Coefficients \((D_s)\) for Phenol and 2-naphthol Analytes. Note: Model considered is the one of adsorption-desorption at equilibrium adsorption (Eq 5.16).](image)
Figure 26 Comparison of $M_{2,exp}$ and $M_{2,model}$ of Phenol and 2-naphthol. Experimental parameters for phenol and 2-naphthol: Average linear velocity of 69 cm/s. Absolute temperature for phenol: 323, 343, 353 and 373. Absolute temperature for 2-naphthol: 393, 413, 433, 453. $M_{2,model}^*$ values were obtained with $nr=5$, $nt=3-8 \times 10^5$ and $ns=1.5 \times 10^4$.

6.6 A Revised Model with Allowance for Equilibrium and Non-equilibrium Adsorption Sites

Regarding the development of an adsorption model applicable for GC capillary columns. One can notice that the proposed model of section 6.1 provides good prediction of both distribution coefficients ($K_s$) and adsorption coefficients ($k_{ads}$) for phenol and 2-naphthol. This can be accomplished by adjusting $M_{1,model}$ and $M_{3,model}$ to $M_{1,exp}$ and $M_{3,exp}$, respectively.

Furthermore, concerning the diffusion coefficient ($D_s$), it was also observed while using the adsorption equilibrium model (refer to Chapter 5), that this parameter strongly influences the width of the chromatographic peak (e.g. variance or second statistical moment, $M_2^*$). In the case, the adsorption at non-equilibrium model; however, this influence was noticed, as discussed in section 6.2.3. The $M_2^*$ statistical moments for phenol and 2-naphthol display a small influence of $D_s$. As well and in all the cases
reported in this Chapter, the $M_{*2,\text{model}}$ was 10 times higher than $M_{*2,\text{exp}}$.

The state of analyte transport under adsorption at non-equilibrium is schematically represented in Figure 27a with a molecule of solute moving throughout the capillary column (from 0 to $L$), interacting with ‘y’ sites only. As stated, this type of analyte transport allows the description of both $M_{1,\text{model}}$ and $M_{*3,\text{model}}$, including the peak tailing. The adsorption at non-equilibrium model is however, inadequate for $M_{*2}$ prediction and one has to envision that there are other site of interactions.

On the other hand, one can consider, as in Figure 27b, an adsorption-desorption with all surface molecule interactions taking place at equilibrium or the equivalent having very large local $k_{\text{ads}}$ values. This type of ‘x’ sites leads to symmetric chromatographic peaks, more in line with the $10^{-4}$ magnitude of $M_{*2,\text{exp}}$ calculated for experimental eluted species (phenol and 2-naphthol). The $M_{*3,\text{model}}$ values; however, are in this case considerably smaller than the ones observed for $M_{*3,\text{exp}}$.

Given these issues, a revised adsorption model is proposed in this PhD dissertation picturing adsorption phenomenon in capillary columns as a process where there are two stationary phase coexisting sites: a) sites with adsorption at equilibrium, and b) sites with adsorption at non-equilibrium.

One can notice that the revised model is able to provide both good second and third order statistical moments ($M_{*2,\text{model}}$ and $M_{*3,\text{model}}$) simultaneously, with this being in line with the experimental values. It is, in this respect, suggested, that molecules of the analyte are transported throughout the capillary column by gas convection. At some point, however, molecules interact with the stationary phase being either via adsorption at equilibrium with non-polar sites of polysilphenylene-siloxane main chain or alternatively via adsorption at non-equilibrium with polar phenyl sites of the stationary phase. The process repeats itself many times, with molecules evolving sequentially in the gas phase, interacting later and at some point, with either polar or non-polar phenyl sites. As a result, the transit of a molecule, throughout the capillary column, is a summation of equilibrium and non-equilibrium adsorption-desorption steps, as shown in Figures 27c and 27d. Furthermore, summation of many individual molecules paths as in Figures 27c and 27d.
yields the observed elution peak at the end of the capillary column.

Since the capillary column used in this study has 95% of non-polar polymer sites and 5% of polar sites, the probability of having an influence of equilibrium adsorption sites (‘x’ sites) is higher than being affected by non-equilibrium adsorption (‘y’ sites). In spite of this, and in order to be able to calculate $M_{2,\text{exp}}^*$ and $M_{3,\text{exp}}^*$ adequately, both type of interactions with polar and non-polar phenyl sites have to be included in an adsorption model.

Therefore, it is found in this PhD dissertation, that in order to be able to adequately calculate $K_s$, $D_s$ and $k_{ads}$ parameters for oxygenated chemical species, such as phenol and 2-naphthol in a BPX5 GC capillary column, one is required to proceed as follows: a) To establish the evolution of chemical species in the capillary column as a sequence of equilibrium and non-equilibrium adsorption events in the two different sites, b) To revise the models accounting for these sequential equilibrium and non-equilibrium adsorption events.
Figure 27 Schematic Representation of a Model with Equilibrium Adsorption sites ‘x’ and Non-equilibrium Adsorption sites ‘y’ in a BPX5 capillary column.
6.7 Conclusions

1) A non-equilibrium adsorption model was established and solved numerically for eluted solutes in BPX5 capillary columns. To accomplish this a numerical methodology was successfully established.

2) The numerical solution of the adsorption non-equilibrium model was carefully validated making sure that the $M_{1,\text{model}}$, $M_{2,\text{model}}^*$, and $M_{3,\text{model}}^*$ were independent of the number of time mesh nodes ($nt$).

3) The $M_{1,\text{model}}$, and $M_{3,\text{model}}^*$ statistical moments of the adsorption at non-equilibrium model matched closely the experimentally derived $M_{1,\text{exp}}$ and $M_{3,\text{exp}}^*$ values for both phenol and 2-naphtol analytes.

4) The resulting $k_{ads}$ kinetic adsorption constants, increased with temperature in the 353-373K range for phenol and 433-453K range for 2-naphthol. On the other hand, in the 323-343K range for phenol and 393-413K for 2-naphthol, $k_{ads}$ decreased with temperatures. It is suggested, that at lower temperatures, there are more favorable “π staking forces” affecting the BPX5 polymer stationary phase and oxygenate molecule interactions.

5) The joint determination of $K_s$, $D_s$ and $k_{ads}$ parameters for the oxygenated chemical species, such as phenol and 2-naphthol, requires to revise the adsorption models including two types of sites. These two types of sites are required for accounting for the sequential equilibrium and non-equilibrium adsorption experienced by analyte molecules evolving in the BPX5 GC capillary column.
Chapter 7

7 Conclusions and Recommendations

This chapter reports the main conclusions and contributions of this PhD dissertation. Recommendations and future work are also provided.

7.1 Conclusions

a) It is proven that eluting peaks can be determined for toluene, naphthalene, phenol and 2-naphthol at various temperatures and different carrier gas flows in a 30m x 0.25 mm x 0.25 µm BPX5 capillary column. These eluting peaks at the exit of the BPX5 capillary column allowed the validation of the proposed mathematical adsorption-desorption models.

b) It is shown that the statistical moments of different order \((M_1, M'_2\) and \(M'_3)\) can be calculated for toluene, phenol, naphthalene and 2-naphthol chromatographic peaks. Skewness values \((S)\) were also assessed using the \(M_3/M_2^{3/2}\) group. Phenol and 2-naphthol showed \(S\) values from 1.5 to 10 times larger than \(S\) values for toluene and naphthalene. This suggests that oxygenated aromatic species generated asymmetric peaks when eluted in a BXP5 capillary column at isothermal conditions.

c) It is demonstrated that a linear equilibrium isotherm was adequate to describe the adsorption of aromatic chemical species, displaying symmetric chromatographic peaks. It was noticed that in these cases, distribution constants \((\log K_s)\) varied from 2.08 to 2.86 for toluene and 2.06 to 2.35 for naphthalene. In addition, it was observed that the diffusion coefficient \((D_s)\) changed in the \(4.45-5.83 \times 10^{-8}\) cm²/s range for toluene and in the \(4.47-5.91 \times 10^{-8}\) cm²/s for naphthalene ranges. In this respect, it was observed that both parameters were functions of the type of solute used and the stationary phase properties employed.

d) It was established that a linear non-equilibrium adsorption model could be considered adequate to describe asymmetric chromatographic elution peaks for
both phenol and 2-naphthol. The numerical solution of this model was developed using a finite volume method considering similar assumptions as the ones for the equilibrium adsorption model. The numerical solution of the model was tested using air pulses, and $D_G$ axial dispersions from $1 \times 10^{-1}$ to $1 \times 10^1 \text{ cm}^2/\text{s}$. In addition, the numerical model was useful to establish the influence of $D_s$ diffusivity in the polymer phase. This allowed us to show that this parameter has a small influence on the peak shapes with values in the $2.5 \times 10^{-8}$ to $10 \times 10^{-8} \text{ cm}^2/\text{s}$ range.

e) It was observed that the log $K_s$ changed in the 2.49-3.50 range for phenol and in the 2.58-3.60 range for 2-naphthol. It was also noticed that adsorption constant, $k_{ads}$, increased with temperature in the 353-373K range for phenol and 433-453K range for 2-naphthol. Furthermore, in the 323-343K range for phenol and 393-413K for 2-naphthol, $k_{ads}$ displayed an unexpected behaviour: it increased at lower temperatures instead of decreasing. It is, in this respect, suggested, that lower temperatures could favor strong “π stacking forces” between stationary phase and aromatic solutes.

f) It was proven that joint determination of $K_s$, $D_s$ and $k_{ads}$ parameters for oxygenated chemical species, such as phenol and 2-naphthol, requires a revision of the adsorption non-equilibrium models including two types of sites. These two types of sites are required for accounting for the sequential equilibrium and non-equilibrium adsorption experienced by analyte molecules evolving in the BPX5 GC capillary column.

7.2 Recommendations for Future Work

The following recommendations can be proposed by taking into account the results and conclusions of this thesis:

a) The mathematical models proposed in this PhD dissertation are aimed at providing information concerning the solute interaction in a commercial capillary column such as a BPX5. Therefore, it is recommended to extend elution
chromatography experiments to other aromatic chemical species to compare results with those presented in this work.

b) The mathematical model of the present study accounts for a linear isotherm model with non-equilibrium adsorption. This appears to be quite adequate to describe the elution of phenol and 2-naphthol in a BPX5 capillary column. It is, however recommended, to incorporate two different sites of adsorption into the model: one experiencing non-equilibrium adsorption and the other displaying adsorption at equilibrium.

c) The experimentally obtained analyte elution peaks of this PhD thesis show that phenyl groups in the polymer phase of the BPX5 capillary column are affected by temperature. This favors adsorption phenomena of chemical species, with likely “π staking forces”, affecting analyte polymer phase interactions. Molecular modeling of a polymer with phenyl groups interacting with aromatic solute species at various temperatures is recommended to clarify these issues.
References


Appendices

Appendix A: Modeling the Elution of Toluene, Naphthalene, Phenol and 2-Naphthol in a BPX5 GC capillary column

This appendix contains a description of four important considerations regarding the mathematical models presented in this Ph.D study:

A. Solute concentration \( (c_o) \) eluted in the tested BPX5 capillary column is in a linear isotherm curve.
B. Hold up retention times \( (t_M) \) indicates that changes of total pressure in the capillary column can be neglected.
C. Predicted Bodenstein numbers in the capillary column are consistent with flow regime in the convective or near to convective flow regime.
D. Oxygenated aromatic species such as phenol and 2-naphthol, have higher values of skewness \( (S=M_3/M_2^{3/2}) \) than non-oxygenated aromatic compounds as toluene and naphthalene.

As it has been described in this Ph.D thesis, mathematical models with linear isotherm adsorption require both, constant temperature \( (T_c) \) within the chromatographic column and low concentrations of analyte \( (c_o) \); where the ratio of solute concentration in the mobile phase, \( c_m \), and solute concentration in the stationary phase, \( c_s \), remain constant in the equation: \( c_m = K_s c_s \). Therefore, the concentration of the eluted analyte does not modify the distribution constant \( (K_s) \). This is illustrated in Figure 5b. Furthermore, one of the considerations described in Chapter 5 is that distribution constant \( (K_s) \) and diffusion coefficient in the stationary phase \( (D_s) \) are independent of the solute concentration when toluene and naphthalene are eluted in a BPX5 capillary column.

Subsequently, various initial solute concentration \( (c_o) \) where injected in the GC-MS unit with a BPX5 capillary column. General conditions for the equipment are described in Chapter 4. Tested solute concentration of toluene and 2-naphthol were from \( 0.75 \times 10^{-2} \) to \( 5 \times 10^{-2} \) mg/cm\(^3\). Thus, Table A.1 reports the average distribution constant \( (K_s) \) and average diffusion coefficient \( D_s \) of toluene and naphthalene at column temperature.
$T_c=343$K and 393 K, respectively. These values were obtained with Eqs (5.11) and (5.12). One can observe that standard deviation of the average $K_s$ at different concentrations was 1-2%. In the same way, standard deviation for the average $D_s$ was 6-7%. Therefore, the subsequent experiments for the validation of a linear isotherm mathematical model with adsorption at the equilibrium were performed with $5\times10^{-2}$ mg/cm$^3$ of solute concentration. An equal consideration was applied in Chapter 6 for a linear isotherm model with non-equilibrium adsorption when phenol and 2-naphthalol were eluted in BPX5 capillary column.

### Table A. 1 Average Distribution Constant ($K_s$) and Diffusion Coefficient in the Stationary Phase ($D_s$)

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>$log K_s \pm SD$</th>
<th>$D_s \times 10^8$ (cm$^2$/s) $\pm SD$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.32 $\pm$ 0.04</td>
<td>4.50 $\pm$ 0.30</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2.85 $\pm$ 0.40</td>
<td>5.73 $\pm$ 0.46</td>
</tr>
</tbody>
</table>

* Reported $K_s$ and $D_s$ are the average values obtained from various tested solute concentrations ($c_o$): from $0.75\times10^{-2}$, $1.00\times10^{-2}$, $1.50\times10^{-2}$, $2.00\times10^{-2}$, $2.50\times10^{-2}$ and $5.00\times10^{-2}$ mg/cm$^3$. Values were calculated with Eqs (5.11) and (5.12). Each concentration was performed in triplicate. $T_c=343$ K for toluene and 393K for naphthalene. General experimental conditions of the GC/MS equipment are as Chapter 4 reports.

On the other hand, the two models proposed in this PhD dissertation for a BPX5 capillary column, consider that carrier gas linear velocity in the column (cm/s), using an average value represented as $\bar{u}$. This is described in Eqs (B.1) to (B.3) in the upcoming Appendix B.

In this respect, one should notice that modelling capillary columns requires careful assessment of the potential effect of total pressure change along the capillary column. In order to address this matter, independent experiments were performed in the present study injecting peaks of air. Air does not display adsorption interaction with the capillary column. As documented in Figure A.1, the $M_{I,exp}/t_M$ ratio, can be calculated using the measured first statistical moment and the “$t_M$” contact time or hold up retention time of a tracer compound ($t_M = L / \bar{u}$). It can be observed that for all the experiments developed at
isotherm conditions, the $M_{1,\text{exp}}/t_M$ ratio remains very close to 1 in all cases. Standard deviation was between 0.5 and 1%. This means that changes of total pressure (depressurization) can be neglected and Eqs (5.1), (5.2), (6.1) and (6.2) are fully applicable in the context of describing elution GC peaks of the present study.

![Figure A.1](image)

**Figure A.1** $M_{1,\text{exp}}/t_M$ Ratio of Air in BPX5 Capillary Column at Three Different Temperatures. Note: Each of the reported symbols is an average value of 3 experimental points. Standard deviations for repeats are 1%.

Another evaluation made for the linear isotherm model at the equilibrium, was the influence of the average linear velocity $\bar{u}$ or the equivalent hold up time ($t_M$) in the axial dispersion term. This is described in Eqs (5.15) and (5.16), where the power of “$n$” affecting the axial dispersion term can be either “0” for the diffusionaly controlled regime and “2” for the convective controlled regime. Figure 11 shows that the $(M_2^*/t_M)$ coefficient remains essentially constant at various $\bar{u}$ values. In this respect, Chapter 5 discussed that the value selected for “$n$” is consistent with the expected dimensionless Bodenstein numbers ($Bo=2r_c\bar{u}/D_G$).

Figure A.2 reports Bodenstein numbers for the elution of toluene and naphthalene in a BPX5 capillary. One can observe that the calculated dimensionless numbers are in a transition zone of the flow control regime in an open tube (Levenspiel, 1999). This could explain the typical standard deviations of ± 20% in Figure 11. Also, it can justified for a
"n=2" or a "-n+2=0" exponents in Eqs (5.15) and (5.16). Therefore, it has been suggested on this Ph.D dissertation that under these conditions, the flow regime in a BPX5 capillary column remains in the convective or near convective flow regime.

The quantification of peak asymmetry is determined by Skewness \( S=M_3/M_2^{3/2} \). Thus, values of skewness \( S \) for toluene, phenol, naphthalene and 2-naphthol are reported in Table A.2. One can observe that aromatic compounds have \( S<1 \). Symmetric peaks are

Figure A. 2 Axial Dispersion Correlation of Toluene and Naphthalene in a BPX5 Capillary Column. Note: Axial dispersion coefficients \( (D_G) \) were approximated with molecular diffusion coefficient \( (D_{12}) \) as Eq (3.4). Values of \( D_{12} \) were calculated with values of experimental column temperature \( (T_c) \). Toluene \( T_c \) values: 313, 323, 343 and 353K. Naphthalene \( T_c \) values: 353, 373, 393 and 433K. Average linear velocity \( (\bar{u}) \) values at each temperature were 37, 52 and 69 cm/s.

Moreover, it is described in Chapter 5 and 6 that chromatograms in GC/MS of analyzed chemical species deviate from Gaussian peaks. Figure 6 shows typical chromatograms for toluene and naphthalene while Figure 14 reports chromatograms for phenol and 2-naphthol. It is observed that oxygenated aromatic compounds such as phenol and 2-naphthol, have a strong tailing in the chromatographic band. This tailing or the deviation of a Gaussian peak, is also called asymmetry.
originated if similar adsorption/desorption phenomena \((k_{\text{ads}} = k_{\text{des}})\) occur between the solute and the stationary phase. Therefore, symmetric peaks could be modeling with a linear isotherm model with adsorption at the equilibrium.

On the other hand, oxygenated species with a \(S>1\) corresponds to asymmetric peaks. This asymmetric peaks such is the case for phenol and 2-naphthol chromatograms could be explained by non-equilibrium adsorption where adsorption/desorption phenomena are not in dynamic equilibrium.

Table A. 2 Skewness (S) Values of Chromatographic Peaks of Toluene, Phenol, Naphthalene and 2-naphthol in GC/MS Analysis with BPX5 Capillary Column

<table>
<thead>
<tr>
<th>Toluene</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_c (K))</td>
<td>(M_3/M_2^{3/2} \pm SD)</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>313</td>
<td>0.78 ± 0.09</td>
</tr>
<tr>
<td>323</td>
<td>0.33 ± 0.03</td>
</tr>
<tr>
<td>343</td>
<td>0.24 ± 0.01</td>
</tr>
<tr>
<td>353</td>
<td>0.77 ± 0.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Naphthalene</th>
<th>2-Naphthol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_c (K))</td>
<td>(M_3/M_2^{3/2} \pm SD)</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>353</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>373</td>
<td>0.30 ± 0.03</td>
</tr>
<tr>
<td>393</td>
<td>0.43 ± 0.03</td>
</tr>
<tr>
<td>433</td>
<td>1.32 ± 0.01</td>
</tr>
<tr>
<td>453</td>
<td>0.87 ± 0.05</td>
</tr>
</tbody>
</table>

\(^a\) Skewness \((S=M_3/M_2^{3/2})\) values were obtained from chromatograms at \(\bar{u}=69\) cm/s. Skewness are average values from a triplicate at each temperature.
Appendix B: First and Second Statistical Moments for an Adsorption Equilibrium Model in a Capillary Column

This study considers aromatic species evolution in capillary columns. With this end, equations and assumptions, as originally considered by Pawlisch et al. (1987) (Pawlisch et al., 1987) for packed beds, are used. These equations, involve an average linear velocity ($\bar{u}$) of the carrier. Eq. (B.1) defines this $\bar{u}$ average velocity as:

$$uA\rho = \left[ \frac{1}{A} \int_0^r 2\pi ru \, dr \right] A\rho$$  \hspace{1cm} (B.1)

where $A$ is the total area (cm$^2$) of the capillary column, $\rho$ is the density (mg/cm$^3$) of the flow, $2\pi r$ is the cross-sectional area, $r_c$ is the ratio, and $u$ is the velocity of the carrier gas at $r$.

Linear velocity, $u$, can be described in terms of the maximum velocity of the carrier gas as follows:

$$u = u_{\text{max}} \left[ 1 - \left( \frac{r}{r_c} \right)^2 \right]$$  \hspace{1cm} (B.2)

Thus, from Eq (B.1) and (B.2), the average linear velocity of the carrier gas $\bar{u}$ can be represented as shown in the following Eq (B.3):

$$\bar{u} = \frac{u_{\text{max}}}{2}$$  \hspace{1cm} (B.3)

Furthermore, under the conditions and assumptions mentioned in section 5.1 of this Ph.D thesis, the equation of continuity for both, mobile and stationary phases can be written as follows:

$$\frac{\partial c_m}{\partial t} + 2u \left[ 1 - \left( \frac{r}{r_c} \right)^2 \right] \frac{\partial c_m}{\partial z} = D_G \left( \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c_m}{\partial r} + \frac{\partial^2 c_m}{\partial z^2} \right)$$  \hspace{1cm} (B.4)
\[
\frac{\partial c_s}{\partial t} = D_s \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_s}{\partial r} \right)
\]  \hspace{1cm} (B.5)

The continuity equation can be further simplified, by accounting for radial concentration changes in the gas phase using an average species concentration as follows:

\[
c_{\text{mean}} = \frac{\int_0^r r c_m \, dr}{\int_0^r r \, dr}
\]  \hspace{1cm} (B.6)

\[
\frac{\partial c_{\text{mean}}}{\partial t} + \frac{1}{\pi r_c^2} 2 u \int_0^r \left( 1 - \left( \frac{r}{r_c} \right)^2 \right) \frac{\partial c_{\text{mean}}}{\partial z} \, 2 \pi r \, dr = \frac{1}{\pi r_c^2} D_g \int_0^r \left( \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c_{\text{mean}}}{\partial r} + \frac{\partial^2 c_{\text{mean}}}{\partial z^2} \right) 2 \pi r \, dr
\]  \hspace{1cm} (B.7)

On the other hand, the variation of the local concentration for the mean concentration \( c_{\text{mean}} \) is defined by \( \Delta c_m \) as follows: \( c_m(r,z,t) = c_{\text{mean}}(z,t) + \Delta c_m(r,z,t) \). Pawlisch et al. (1987) argues that if the chromatographic peak is well dispersed, \( \Delta c_m \ll c_{\text{mean}} \). Thus, to consider \( \Delta c = 0 \), appears to be adequate, with this meaning that the radial mobile phase concentration gradients are small enough to be equated as follows \( c_m(r,z,t) = c_{\text{mean}}(z,t) \).

Thus, considering the \( c_{\text{mean}} \) as defined in Eq (B.6) and Eq (B.7), these results in Eq (B.8). This applies, given the \( c_{\text{mean}} \) approximation and the boundary condition reported in section 1.1 with \( D_g (\partial c_m / \partial r) = D_s (\partial c_s / \partial r) \) at \( r = r_c \). Thus, this leads to a gas phase tracer continuity equation in a capillary column as follows:

\[
\frac{\partial c_{\text{mean}}}{\partial t} + u \frac{\partial c_{\text{mean}}}{\partial z} = D_g \frac{\partial^2 c_{\text{mean}}}{\partial z^2} + \frac{2 D_s}{R} \frac{\partial c_s(r = r_c)}{\partial r}
\]  \hspace{1cm} (B.8)

As described in Eqs (4) and (5) of the manuscript, the equations (B.8) and (B.9) for the stationary phase can be represented in terms of dimensionless variables. These variables are provided in the nomenclature section of this Ph.D thesis:

\[
\frac{\partial y}{\partial E} + \frac{\partial y}{\partial x} = \gamma \frac{\partial^2 y}{\partial x^2} + 2 \frac{\partial q(0)}{\partial \xi}
\]  \hspace{1cm} (B.9a) and \[
\frac{\partial q}{\partial E} = \frac{1}{\kappa^2} \frac{\partial^2 q}{\partial \xi^2}
\]  \hspace{1cm} (B.9b)
Applying the Laplace Transformation to Eq (B.9b), leads to the following differential equation for the stationary phase:

\[ s q(s, \zeta, x) + \bar{q}(0) = \frac{1}{\kappa^2} \frac{d^2 \bar{q}(s, \zeta, x)}{d\zeta^2} \]  \hspace{1cm} (B.10)

with \( x \) being \( z/L \) and \( \zeta \) being the dimensionless radial axis or dimensionless film thickness \( \zeta = (r - r_c) / d_f \).

The general solution of a homogeneous differential equation can be expressed as:

\[ \bar{q}(s, \zeta, x) = A e^{-r_1 \zeta} + B e^{r_2 \zeta} \]  \hspace{1cm} (B.11)

where \( r_1 \) and \( r_2 \) are roots of the quadratic equation: \( ax^2 + bx + c = 0 \) and have the following values \( r_1 = r_2 = r_{i2} = \pm \kappa \sqrt{s} \).

Regarding the \( A \) and \( B \) constants in Eq (B.11), they can be defined considering that at \( \zeta = 0 \), at \( q(s, \zeta) = 1 \) and at \( \zeta = 1 \), \( (d\bar{q}/d\zeta) = 0 \).

\[ A = \frac{\bar{q}(s,0,x)}{2} \left( \frac{1}{\cosh r} \right) e^{r_{i2}} \]  \hspace{1cm} (B.12)

\[ B = \frac{\bar{q}(s,0,x)}{2} \left( \frac{1}{\cosh r} \right) e^{-r_{i2}} \]  \hspace{1cm} (B.13)

The \( A \) and \( B \) constants as reported in Eqs. (B.12) and (B.13), can be replaced in Eq (B.11), providing a dimensionless concentration change of solute in the capillary column stationary phase that can be described as follows:

\[ \frac{d\bar{q}(s,0,x)}{d\zeta} = \bar{q}(s,0,x) \kappa \sqrt{s} \tanh(\kappa \sqrt{s}) \]  \hspace{1cm} (B.14)

Moreover, applying the Laplace Transformation to Eq (B.9a) or Eq (5.4) in Chapter 5 results in:
Another suitable assumption is to consider that at \( E=0 \), with all chemical species from a previous experiment eluted. Thus, \( \bar{q}(s,0,x) = \bar{Y}(s,x) = 0 \). Applying this condition to Eq (B.15), yields a homogeneous differential equation as follows:

\[
\gamma \frac{d^2 \bar{Y}(s,x)}{dx^2} - \frac{d \bar{Y}(s,x)}{dx} - s \bar{Y}(s,x) - \frac{2}{\omega \kappa} \left[ \bar{q}(s,0,x) \sqrt{s} \tanh(\kappa \sqrt{s}) \right] = 0
\]  

(B.15)

where \( \psi(s) = s + \frac{2}{\omega \kappa} \sqrt{s} \cdot \tanh(\kappa \sqrt{s}) \)

As a result, the general solution of Eq (B.16) is given by:

\[
\bar{Y}(s,x) = A e^{r_1 x} + B e^{r_2 x}
\]  

(B.17)

where \( r_1 \) and \( r_2 \) are the roots of the general equation \( ax^2 + bx + c = 0 \):

\[
r_1 = \frac{1+\sqrt{1+4\gamma\psi s}}{2\gamma} \quad \text{and} \quad r_2 = \frac{1-\sqrt{1+4\gamma\psi s}}{2\gamma}
\]

Given that a meaningful physical solution using Eq (B.17) requires that at \( x=1 \) and in all cases, \( \bar{Y} \) remain always bounded, then, the \( A \) parameter has to be zero. Furthermore, if Eq (B.17) is considered with its second term only and \( B=1 \). This is consistent with the conditions that at \( x=0, y = \delta(\theta) \) or \( y(s,0) = 1 \). Thus \( B \) has to be 1.

Thus, the solution for \( \bar{Y}(s,x) \) can be expressed as in Eq (5.6) of Chapter 5 as follows:

\[
\bar{Y}(s,x) = e^{(1/2)\gamma x} e^{-\frac{1}{4\gamma}(4\gamma \psi(s))^{1/2} x}
\]  

(B.18)

Where:

\[
\Psi(s) = s + (2s^{1/2} / \omega \kappa) \tanh(\kappa s^{1/2})
\]
As a result this yields:

\[ \bar{Y}(s,1) = e^{1/2\gamma} e^{-1/2(1+4\gamma\psi(s))^{1/2}} \]  

(B.19)

One should mention that the \( e^{1/2\gamma} \) term in Eq (B.19) is different from the term \( e^{1/2\gamma} \) reported by Pawlish, et al. (1989), with the equation at the exit of the column or \( x=1 \), being given by Eq (5.7).

Statistical moments of different order can be derived from the first and second derivatives of \( \bar{Y}(s,1) \) as follows:

\[
\frac{d\bar{Y}(s,1)}{ds} = \exp(1/2\gamma) \cdot \exp\left[-1/2(1+4\gamma\psi(s))^{1/2}\right] \cdot 1/2 \left[-1/2(1+4\gamma\psi(s))^{-1/2}\right] \cdot 4\gamma \frac{d\psi(s)}{ds} \]  

(B.20)

with

\[
\frac{d\psi(s)}{ds} = 1 + \frac{1}{\omega K} s^{1/2} \cdot \tanh(\kappa \sqrt{s}) + \frac{1}{\omega} \cdot \frac{1}{\cos^2 h(\kappa \sqrt{s})} \]

One should notice that at \( s \to 0 \), the Eq (B.20) becomes:

\[
-\frac{d\bar{Y}(0,1)}{ds} = M_1 = \left(1 + \frac{2}{\omega}\right) \]  

(B.21)

Eq (B.21) describes the first statistical moment of the chemical species distribution or \( M_1 \). \( M_1 \) as per Eq (B.21) is in the same order of magnitude. However, it is not identical to that previously reported in (Pawlish, et al., 1987), where \( M_1 = (1+1/\omega) \). The addition of the “2” factor in Eq (B.21) is critical given that it affects the absolute magnitude of \( K_x \) by as much as 100%. In fact, a 100% error in \( \omega \), propagates proportionally to the \( \omega = r_e / K_x d_f \) parameter.

In addition, the second derivative of \( \bar{Y}(s,1) \) yields:

\[
\frac{d^2\bar{Y}(s,1)}{ds^2} = \frac{d\bar{Y}(s,1)}{ds} \cdot \left(-\frac{d\bar{Y}(s,1)}{ds} \left(1+4\gamma\psi(s)\right)^{-1/2}\right) \]
\[ + \bar{Y}(s,1) \left( -\frac{1}{2} \frac{4\gamma(1+4\gamma \psi(s))^{-3/2}}{ds} \left( \frac{d\psi(s,1)}{ds} \right)^2 - (1+4\gamma \psi(s))^{-1/2} \frac{d^2\psi(s,1)}{ds^2} \right) \] (B.22)

With:

\[ \frac{d^2\psi(s)}{ds^2} = -\frac{1}{2\omega\kappa} s^{-3/2} \cdot \tanh(\kappa \sqrt{s}) + \frac{s^{-1}}{\omega \kappa} \cdot \frac{1}{\cos^2 h(\kappa \sqrt{s})} - \frac{\kappa}{\omega} \cdot s^{-1/2} \sinh(\kappa \sqrt{s}) \]

Eq (B.22) can be evaluated at \( s \to 0 \) yielding:

\[ \frac{d^2\bar{Y}(0,1)}{ds^2} = \left( 1 + \frac{2}{\omega} \right)^2 \left( 1 + 2\gamma \right) + \frac{\kappa^2}{\omega} \] (B.23)

Thus, considering the first and second derivatives of \( \bar{Y} \) evaluated at \( s \to 0 \) as in Eq (B.23), the variance of the distribution can be established:

\[ \Delta \sigma^2 = M_2^* = \frac{d^2\bar{Y}(0,1)}{ds^2} - \left( \frac{d\bar{Y}(0,1)}{ds} \right)^2 \] (B.24)

\[ M_2^* = \left( 1 + \frac{2}{\omega} \right)^2 2\gamma + \frac{\kappa^2}{\omega} \] (B.25)

One should notice that the variance of the distribution obtained, differs with respect to

\[ M_2^* = \left( 1 + \frac{1}{\omega} \right)^2 2\gamma + \frac{4\kappa^2}{3\omega} \] variance published in (Pawlisch, et al., 1987). Given the importance of \( \gamma = D_u / \bar{u}L \) and \( \kappa^2 = d_f^2 \bar{u} / D_s L \) groups for adsorption parameter definition, one can understand the significance of using Eq (B.25) in its correct mathematical form.
Appendix C: Numerical Solution of the Adsorption Non-equilibrium Model

This Appendix describes the numerical solution method of Eqs (6.1) and (6.2) used in Chapter 6 or Eqs (C.1) and (C.2). These equations correspond to a linear isotherm with adsorption at non-equilibrium.

In order to develop the numerical solution the Finite Volume Method was employed. Thus, given the following adsorption at non-equilibrium model partial differential equations:

**Gas Phase (Mobile Phase) Chemical Species Balance**

\[
\frac{\partial c_m}{\partial t} = -u \frac{\partial c_m}{\partial z} + D_G \frac{\partial^2 c_m}{\partial z^2} + 2D_s \frac{\partial c_s(r = r_c)}{\partial r} \tag{C.1}
\]

**Solid Phase (Stationary Phase) Chemical Species Balance**

\[
\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial r^2} \tag{C.2}
\]

the following step was to establish using the Finite Volume Method (FVM) method discrete finite difference equations for elution chromatography.

One can notice that the FVM involves the following procedural steps (Hong, 2004):

a) A finite difference model is established for the capillary column using control volumes (CV) and their related nodes. Summation of all control volumes yields the entire capillary column domain.

b) This finite difference model approach yields analyte concentration values and concentration derivatives calculated by interpolation in between nodal values.

c) This finite difference model gives an array of linear algebraic equations, with a suitable numerical solution.
Regarding the control volume (CV) of the chromatographic system, one should consider that the mass balance occurs in a narrow bore capillary column with a thin film coating its surface.

One should also notice that the control volume (CV) described in this Ph.D dissertation is based on a cell center method where there is a control node centered in the corresponding CV. Also, the CV gives in a Cartesian axysymmetrical coordinate system an analyte transfer area of $2\pi (r_c + d_f)$.

Figure C.1 reports an axial and radial view of the CV defined for the system. Also the axial view illustrates a CV with a $\Delta z$ width.

Furthermore, a radial cross-section of the capillary column shows a control node centered in the established control volume. Then, Figures C.1(a), C.1(b) and C.1(c) represent the control volume in Cartesian coordinates for the mobile phase, the stationary phase and the interface, respectively. Nodes in the axial direction are designated as $ns$, nodes in the time domain are identified as $nt$ while nodes in radial direction are named $nr$. Thus, the position of a given node is described with the $i,j,k$ coordinates with $i$ being the position in the time domain, $j$ the location in the axial direction and $k$ is the radial position.

It has to be emphasized that once the control volume and control nodes of the chromatographic system established, one can apply the discretization approach to accumulation, convection and diffusion terms in the partial differential equations (C.1) and (C.2). One should notice however that the discretization used differs for various terms in the partial differential equations. For instance, accumulation discretized in the time domain involves an implicit scheme. Convection on the other hand includes a first order upwind scheme while diffusion in mobile and stationary phases centered difference (CDS).
Figure C. 1 Control Volume Defined for the Elution of Analytes in a Capillary Column Using an Adsorption Non-equilibrium Model.
Regarding this various approaches for the different terms of the partial differential equations, the implicit discretization in time considered for both $\frac{\partial c_m}{\partial t}$ and $\frac{\partial c_s}{\partial t}$ derivatives evaluations in the forward step. This approach can be expressed as:

$$\frac{\Delta c(i,j)^{n+1}}{\Delta t} = f(c(i))^{n+1}$$  \hspace{1cm} (C.3)

where $\Delta c(i,j)^{n+1}$ is the variation of the solute concentration of mobile or stationary phase in a forward step at $n+1$ time, function of diffusion, convection and mass transfer phenomena represented as $f(c(i))^{n+1}$. One should also notice that variations of time ($\Delta t$) can be defined as:

$$\Delta t = c_m(i-1) - c_m(i+1) = \frac{t_{exp}}{nt+1}$$  \hspace{1cm} (C.4)

where $t_{exp}$ is the total elution time in seconds in a capillary column and $nt$ is the number of time nodes.

Figure C.2 illustrates the implicit discretization scheme used in this system. It is observed that this method solves the equations generated in a time step without requiring values from past steps. One should notice that implicit discretization do not required to restrict the time step even if one like to simulate a process at high spatial resolution or number of time nodes ($nt$). Thus, even is a large time step is considered, the numerical model could still provide an accurate solution. Therefore, it is important to verify results of the equations by decreasing $\Delta t$ until the solution until a converged solution is obtained (Ren, et al., 2011). This topic is specifically covered in Chapter 6 for an adsorption with non-equilibrium model.

On the other hand, the convective flux can be approximated using variable values in the CV centers (nodes) with a first order “upwind scheme”. The “upwind scheme” designation is based on the numerical methodology with the data being used for the estimations is opposite to the direction of the flow. Thus, the convective flux is derived from the upstream node as described in Figure C.1(a). This can also be represented using Eqs (C.5) and (C.6),
where \( a_t \) is the transfer area in \( \text{cm}^2 \), \( 2\pi(r_c+d_f)^2 \) and \( V \) is the volume in \( \text{cm}^3 \), \( 2\pi(r_c+d_f)^2 \Delta z \).

One should also notice that the convective flux terms have \( \text{g/m}^2\text{s} \) units.

Furthermore and on this basis the change of convective flux \((d\text{Flux}_{\text{convection}})\) can be described using the difference between Eq (C.5) and (C.6), as given by Eq (C.7).

\[
d\text{Flux}_{\text{convection}} = \frac{u}{\Delta z} \left( C_m(j-1) - C_m(j) \right) \quad (C.7)
\]
where the width of control volume ($\Delta z$) represented as:

$$\Delta z = c_m(j - 1) - c_m(j + 1) = \frac{L}{ns + 1}$$  \hspace{1cm} (C.8)

One should also notice that the interpolation to obtain the flux difference is done using the trapezoidal rule.

Moreover, the first order “upwind scheme” may cause errors designated as “numerical diffusion” or “false diffusion”. This may be particularly relevant for systems with large mass fluxes. Therefore, it is necessary to find values of $\Delta z$ (Xu, et al., 2007; Ren, et al., 2011) small enough to be able to consider this approach. One should notice that this evaluation is reported in Section 6.2.5 in Chapter 6.

Regarding the discretization to assess diffusion fluxes in the mobile and the stationary phase, the selected discretization approach involves a Central Differencing Scheme (CDS). This method calculates the difference of fluxes by defining equidistant points around a control node (Medi and Amanullah, 2011). In other words, it considers that a diffusion flux can be divided in two equal parts and each part goes to the lateral control volume, as is shown in Figure C.1(a) and C.1(b). Thus, Eqs (C.9) and (C.10) describe the difference of diffusion flux ($g/cm^3/s$) for the mobile and stationary phases, respectively.

$$dFlux_{\text{diffusion,mobile\_phase}} = \frac{D_m}{\Delta z^2} \left( C_m(j - 1) - 2C_m(j) + C_m(j + 1) \right)$$  \hspace{1cm} (C.9)

$$dFlux_{\text{diffusion,stationary\_phase}} = \frac{D_s}{\Delta r^2} \left( C_s(k - 1) - 2C_s(k) + C_s(k + 1) \right)$$  \hspace{1cm} (C.10)

In the same way, it was considered for $\Delta z$ and $\Delta t$, one could account for a control volume in radial direction $\Delta r$ as defined in Eq (C.11).

$$\Delta r = c_s(k - 1) - c_s(k + 1) = \frac{d_j}{nr + 1}$$  \hspace{1cm} (C.11)
Once the control volumes (CV) and fluxes established one can rewrite the partial differential equations (C.1) and (C.2) using as the finite difference format as in (C.12) and (C.13). One can note in particular that second term in the right hand of Eq (C.9) represents the non-equilibrium adsorption condition at the capillary column interface.

\[
\frac{c_m(i,j) - c_m(i-1,j)}{\Delta t} = -\bar{u}\left(\frac{c_m(i,j) - c_m(i,j-1)}{\Delta z}\right)
\]

\[+
\frac{D_g}{\Delta z^2} \left(c_g(i,j-1) - 2c_g(i,j) + c_g(i,j+1)\right) - \alpha_{ads} \left(\frac{c_s(i,j,0) - c_s(i,j,0)}{K_s}\right)\] (C.12)

\[
\frac{c_s(i,j,k) - c_s(i-1,j,k)}{\Delta t} = \frac{D_s}{\Delta r^2} \left(c_s(i,j,k-1) - 2c_s(i,j,k) + c_s(i,j,k+1)\right)\] (C.13)

Besides, the boundary condition at the interface must be approximated as in Eq (C.14). In this position of the capillary column, the node zero in the radial coordinate is defined as \(k=1\) (refer to Figure C.1 displaying a radial cross section of CV). Thus, the diffusion flux at the interface being equal to the mass transfer at non-equilibrium and Eq (C.10) can be expressed as:

\[
\frac{c_s(i,j,1) - c_s(i-1,j,1)}{\Delta t} = \frac{k_{ads} \left(\frac{c_s(i,j,1) - c_s(i,j,1)}{K_s}\right) + \frac{D_s}{\Delta r} \left(c_s(i,j,2) - c_s(i,j,1)\right)}{\Delta r}\] (C.14)

Finally, one can assemble the system of discrete algebraic equations. as shown in Eqs (C.15) and (C.16).

**Gas Phase (Mobile Phase) Chemical Species Balance**

\[
c_m(i-1,j) = -f_1(c_s(i,j,1)) - f_2(c_m(i,j-1)) + f_3(c_m(i,j)) - f_4(c_m(i,j+1))\] (C.15)

**Solid Phase (Stationary Phase) Chemical Species Balance**

\[
c_s(i-1,j,k) = -f_{s2}(c_s(i,j,k-1)) + f_{s3}(c_s(i,j,k)) - f_{s2}(c_s(i,j,k+1))\] (C.16)

where dimensionless coefficients \(f_1, f_2, f_3, f_4, f_{s2}, f_{s3}\) are as follows:
\[ f_1 = \frac{a_i k_{ads} \Delta t}{K_s} ; \quad f_2 = u \frac{\Delta t}{\Delta z} + D_g \frac{\Delta t}{\Delta z^2} ; \quad f_3 = 1 + u \frac{\Delta t}{\Delta z} + 2D_g \frac{\Delta t}{\Delta z^2} + a_i k_{ads} \Delta t ; \]

\[ f_4 = D_g \frac{\Delta t}{\Delta z^2} ; \quad f_{s2} = D_s \frac{\Delta t}{\Delta r^2} ; \quad f_{s3} = 1 + 2D_s \frac{\Delta t}{\Delta r^2} \]

One should also consider that these linear algebraic equations should also represent both the initial and boundary physical conditions of the system. In this respect, Eqs (C.17), (C.18), (C.19), (C.20) and (C.21), are established to describe these initial boundary conditions.

a) At the inlet of the column \((j=1)\), the solute concentration, \(c_{m}(i, l)\) becomes equal to the initial solute concentration \(c_{m}(i, 0)\). Therefore, Eq (C.15) can be written as follows:

\[ c_{m}(i-1, 1) = -f_1(c_s(i, 1, 1)) - (f_2 - f_2)(c_{m}(i, 1)) - f_4(c_{m}(i, 2)) \] (C.17)

b) At the outlet of the column, there is no axial diffusion phenomenon. Therefore, mobile phase solute concentration of Eq (C.15) can be expressed as:

\[ c_{m}(i-1, j) = -f_1(c_s(i, j, 1)) - f_2(c_{m}(i, j - 1)) + f_3(c_{m}(i, j)) \] (C.18)

c) At the interface \((k=1)\), there is non-equilibrium adsorption as described in Eq (6.5) in Chapter 6. Thus, the solute concentration in stationary phase is defined by Eq (C.19):

\[ c_s(i-1, j, 1) = -f_{s3a}(c_s(i, j, 1)) + f_{s1}(c_s(i, j, 0)) - f_{s2}(c_s(i, j, 2)) \] (C.19)

where:

\[ f_{s1} = \frac{k_{ads} \Delta t}{\Delta r} ; \quad f_{s3a} = 1 + 2D_s \frac{\Delta t}{\Delta r^2} + \frac{k_{ads} \Delta t}{K_s} \]

d) At the outlet of the column, there is no mass transfer phenomenon. Thus, at this radial node, \(k\), the concentrations \(c_s(i,j,k)\) and \(c_s(i,j,k+1)\) are equal. Thus, Eq
(C.20) yields the stationary phase solute at the outlet of the capillary column as follows:

\[ c_s(i-1,j,k) = -f_{s_2}(c_s(i,j,k-1)) + (f_{s_3} - f_{s_2})(c_s(i,j,k)) \]  \hspace{1cm} (C.20)

As a result, once the linear algebraic equations (C.15) and (C.16) established with Eqs (C.17)-(C.20) for boundary conditions, this system of equations was solved using Matlab and the Gauss-Siedel Iterative Method. One should notice that this method converges if the resulting matrix has entries in the dominant diagonal of a larger magnitude than in the other matrix coefficients (Ray and Gupta, 2004). Calculated \(c_m(i,j)\) and \(c_s(i,j,k)\) values were considered converged when \(\frac{(c_{\text{initial guess value}} - c_{\text{calculated value}})}{c_{\text{initial guess value}}} < 1 \times 10^{-10}\).
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