REACTIVE TRANSPORT THROUGH
NANOPOROUS MATERIALS

Doctorate degree thesis by
André Morgado Lopes

Carried out at Laboratoire MADIREL - UMR7246, CNRS, Aix-Marseille Université
Proposed, financed and supervised by IFP Energies nouvelles

Thesis director: Renaud Denoyel
Thesis co-director: Véronique Wernert

Examinator: Loïc Sorbier
Examinator: Melaz Tayakout-Fayolle
Reviewer: Gert Desmet
Reviewer: Pierre Levitz

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Defended on December 17th, 2018
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ABSTRACT

Porous alumina supported catalysts are used to convert asphaltenes in hydrotreatment processes in petroleum refineries. However, asphaltenes are polydisperse and have a broad range of behaviors such as aggregation. Thus, the objective of this work is to study these complex behaviors within the catalytic porous system including transport properties and adsorption. Inverse size-exclusion chromatography (ISEC) and impedance spectroscopy are used to determine the topological characteristics of different alumina porous solids (porosity, pore size, tortuosity). The effective diffusion coefficient of polystyrenes of different sizes was also studied via chromatography in non-adsorbing conditions. Elution peaks are used to determine the effect of molecule size on the accessible pore volume and the transport properties therein: molecules of relatively small sizes penetrate further into the porous medium, thus taking more time to navigate the chromatographic setup, while larger molecules traverse much faster, through the macroporosity. The liquid chromatography technique is divided in two different methods: the dynamic method determines mass transfer limitations due to the concentration gradients between the stationary and mobile phases using the General Rate Model; and the static (“peak parking”) method, which uses Einstein’s law of diffusion. Both methods yield diffusion coefficient values which are modelled, predicting the behavior of molecules of any size. Columns were assembled manually from alumina powders or monoliths. A synthesized asphaltene model molecule was used and its adsorption behavior was determined and compared to an asphaltene fraction recovered from crude oil. The asphaltene model molecule shows a dimerization behavior as well as extremely strong interactions with the alumina surface. Dynamic method was attempted in short alumina columns at saturation conditions and an apparent influence of the flow rate on the extent and mechanics of adsorption was observed.

Keywords: porous media; porosity; tortuosity; asphaltenes; alumina; inverse size-exclusion chromatography; transport; diffusion; adsorption
RÉSUMÉ

Des catalyseurs à base d'alumine poreuse sont utilisés pour convertir des asphaltènes dans des procédés d'hydrotraitement utilisés au sein des raffineries de pétrole. Cependant, les asphaltènes ont une large gamme de comportements, agrégation inclus. Le but de cette thèse est donc d'étudier ces complexités, y compris les propriétés de transport et d'adsorption. La chromatographie d'exclusion stérique inverse (ISEC) ainsi que la spectroscopie d'impédance sont utilisées pour déterminer des paramètres topologiques de solides poreux d'alumine (porosité, taille de pores, tortuosité). Des coefficients de diffusion effectifs de polystyrènes de différentes tailles sont aussi étudiés par chromatographie liquide en conditions non-adsorbantes. A partir des pics chromatographiques il est possible de déterminer le volume poreux accessible par des molécules de différentes tailles et d'étudier leurs propriétés de transport : les molécules de petites tailles pénètrent plus profondément dans le milieu poreux donc elles prennent plus de temps pour traverser la colonne, tandis que les molécules ayant une taille supérieure à la taille du pore ne sondent que la macroporosité. Les expériences en conditions dynamiques sont utilisées pour déterminer la limitation de transfert de masse à l'intérieur de la colonne chromatographique en tenant compte des gradients de concentration entre les phases stationnaires et mobiles en utilisant l’équation de van Deemter et le modèle GRM (General Rate Model). La méthode statique (ou « peak parking ») utilise la loi de la diffusion d'Einstein afin de calculer le terme d'auto-diffusion de l'équation de van Deemter. Avec l'utilisation des deux méthodes, il est possible de modéliser le transport des molécules de différentes tailles, et cela aidera à prédire le comportement de molécules d'une taille quelconque. Les colonnes ont été assemblées au laboratoire à partir de poudres et de monolithes d'alumine. Les caractéristiques d'adsorption des asphaltènes modèles sont déterminées et comparées avec une fraction d'asphaltènes extraite d'un brut. Un phénomène de dimérisation ainsi qu'une très forte adsorption sur la surface de l'alumine sont observés avec la molécule modèle. La méthode dynamique a été utilisée avec des colonnes courtes dans des conditions de saturation. Une influence apparente du débit dans l’importance et le mécanisme d’adsorption a pu être constatée.

Mots clés: milieu poreux; porosité; tortuosité; asphaltènes; alumine; chromatographie d'exclusion stérique inverse; monolithes; transport; diffusion; adsorption
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It is my firm belief that there could be no better place for this project to take place than the MADIREL laboratory, where I was welcomed with open arms by many great people, most of whom this text will regrettfully fail to mention, but to all of whom I owe a great debt. It is with great pains that I even relegate those mentioned to paragraph two... Case in point, Renaud Denoyel, whose patience and wisdom are beyond human and for whom I have the utmost respect and admiration. His tireless curiosity and curious tirelessness have been an inspiration, above and beyond his role as thesis director. Likewise, I must thank Véronique Wernert whose expertise and care were quite literally instrumental over the course of the last three years. Thank you for the second chance, and for the third and fourth ones, too.

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### NOTATION AND GLOSSARY

**Equation variables and their units**

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<tr>
<td>(r_e)</td>
<td>Electrode radius</td>
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</tr>
<tr>
<td>(r_D)</td>
<td>Pore radius</td>
<td>m</td>
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**Equation variables and their units (continued)**

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<tr>
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<td>Molecule hydrodynamic radius</td>
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<td>$r_s$</td>
<td>Skeleton radius</td>
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<tr>
<td>$S_d$</td>
<td>Entropy of dissociation</td>
<td>J.mol$^{-1}$.K$^{-1}$</td>
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<td>$S_{BET}$</td>
<td>BET specific surface area</td>
<td>m$^2$.g$^{-1}$</td>
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<td>$T$</td>
<td>Temperature</td>
<td>K</td>
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<tr>
<td>$t$</td>
<td>Time</td>
<td>s</td>
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<tr>
<td>$t'$</td>
<td>Residence time</td>
<td>s</td>
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<td>$t_0$</td>
<td>Retention time with a non-adsorbing compound</td>
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<td>Characteristic diffusion time</td>
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<td>Mean retention time without column</td>
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<td>Parking time</td>
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<td>Linear velocity</td>
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<td>Interstitial velocity</td>
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<tr>
<td>$x$</td>
<td>Distance</td>
<td>m</td>
</tr>
<tr>
<td>$x'$</td>
<td>Distance traveled</td>
<td>m</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
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</tr>
<tr>
<td>$V_i$</td>
<td>Initial volume</td>
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<td>$V_{inj}$</td>
<td>Injection volume</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_f$</td>
<td>Final volume</td>
<td>m$^3$</td>
</tr>
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<td>$V_p$</td>
<td>Volume of pores</td>
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<td>$V_t$</td>
<td>Total volume</td>
<td>m$^3$</td>
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<tr>
<td>$V_v$</td>
<td>Volume of voids</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_{macro}$</td>
<td>Specific volume of macropores</td>
<td>m$^3$.g$^{-1}$</td>
</tr>
<tr>
<td>$V_{meso}$</td>
<td>Specific volume of mesopores</td>
<td>m$^3$.g$^{-1}$</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Specific volume</td>
<td>m$^3$</td>
</tr>
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<td>$\gamma$</td>
<td>Obstruction factor</td>
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<td>$\gamma'$</td>
<td>Gyromagnetic ratio (PFG-NMR)</td>
<td>C.kg$^{-1}$</td>
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<tr>
<td>$\delta$</td>
<td>Eddy diffusion coefficient</td>
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<tr>
<td>$\delta'$</td>
<td>Pulse duration (PFG-NMR)</td>
<td>ms</td>
</tr>
<tr>
<td>$\Delta'$</td>
<td>Time between two gradient pulses (PFG-NMR)</td>
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<tr>
<td>$\epsilon$</td>
<td>Porosity</td>
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</tr>
<tr>
<td>$\epsilon_e$</td>
<td>Interparticle porosity</td>
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</tr>
<tr>
<td>$\epsilon_p$</td>
<td>Particle porosity</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_{sus}$</td>
<td>Suspension porosity</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_t$</td>
<td>Total porosity</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
<td>Pa.s</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Ratio of molecule to pore radius</td>
<td></td>
</tr>
<tr>
<td>$\xi_2$</td>
<td>Three-point parameter in the Torquato equation</td>
<td></td>
</tr>
<tr>
<td>$f_{ads}$</td>
<td>Amount adsorbed</td>
<td>g.m$^{-2}$</td>
</tr>
<tr>
<td>$f_{max}$</td>
<td>Maximum adsorption capacity</td>
<td>g.m$^{-2}$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity</td>
<td>(\Omega.m)</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>Electrolyte resistivity</td>
<td>(\Omega.m)</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Monolith resistivity</td>
<td>(\Omega.m)</td>
</tr>
<tr>
<td>$\rho_t$</td>
<td>True density</td>
<td>g.L$^{-1}$</td>
</tr>
<tr>
<td>$\mu_1$</td>
<td>First moment</td>
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</tr>
<tr>
<td>$\mu_2$</td>
<td>Second moment</td>
<td>s$^2$</td>
</tr>
<tr>
<td>$\sigma^0$</td>
<td>Electrolyte conductivity</td>
<td>S.m$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{eff}$</td>
<td>Effective conductivity</td>
<td>S.m$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_i^2$</td>
<td>Peak variance without column</td>
<td>s$^2$</td>
</tr>
<tr>
<td>$\sigma_p$</td>
<td>Conductivity within the particle</td>
<td>S.m$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{eff}^2$</td>
<td>Peak variance</td>
<td>s$^2$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Tortuosity</td>
<td></td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>External tortuosity</td>
<td></td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>Particle tortuosity</td>
<td></td>
</tr>
<tr>
<td>$\tau_{sus}$</td>
<td>Suspension tortuosity</td>
<td></td>
</tr>
<tr>
<td>$\tau_t$</td>
<td>Total bed tortuosity</td>
<td></td>
</tr>
<tr>
<td>$\tau'$</td>
<td>Pulse separation (PFG-NMR)</td>
<td>ms</td>
</tr>
</tbody>
</table>
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BHT</td>
<td>Butylated hydroxytoluene</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>EMT</td>
<td>Effective medium theory</td>
</tr>
<tr>
<td>GRM</td>
<td>General rate model</td>
</tr>
<tr>
<td>HDT</td>
<td>Hydrotreatment</td>
</tr>
<tr>
<td>HDM</td>
<td>Hydrodemetalization</td>
</tr>
<tr>
<td>HDS</td>
<td>Hydrodesulfurization</td>
</tr>
<tr>
<td>HDN</td>
<td>Hydrodeazotation</td>
</tr>
<tr>
<td>HETP</td>
<td>Height equivalent to a theoretical plate</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>ISEC</td>
<td>Inverse size-exclusion chromatography</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NMR DOSY</td>
<td>Nuclear magnetic resonance - diffusion ordered spectroscopy</td>
</tr>
<tr>
<td>PFG-NMR</td>
<td>Pulsed field gradient nuclear magnetic resonance</td>
</tr>
<tr>
<td>PP</td>
<td>Peak parking</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RTW</td>
<td>Residence time weighted</td>
</tr>
<tr>
<td>SANS</td>
<td>Small angle neutron scattering</td>
</tr>
<tr>
<td>SARA</td>
<td>Saturate, aromatic, resin and asphaltene</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small angle X-ray scattering</td>
</tr>
<tr>
<td>SEC</td>
<td>Size-exclusion chromatography</td>
</tr>
<tr>
<td>SRXTM</td>
<td>Synchrotron-based X-ray tomographic microscopy</td>
</tr>
<tr>
<td>TDA</td>
<td>Taylor dispersion analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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</table>
1 INTRODUCTION

1.1 Description of the institution

This project was proposed, funded and supervised by IFP Energies nouvelles (IFPEN). IFPEN is a public research and training institution. It has an international scope, covering the fields of energy, transport and the environment. From research to industry, technological innovation is central to all its activities. As part of the public-interest mission with which it has been tasked by the public authorities, IFPEN focuses on providing solutions to take up the challenges facing society in terms of energy and the climate by promoting the emergence of a sustainable energy mix as well as creating wealth and jobs by supporting French and European economic activity, and the competitiveness of related industrial sectors.

The project was developed at the MADIREL laboratory in Marseille, France, which is incorporated in the Aix-Marseille University, and part of the Centre National de la Recherche Scientifique (CNRS). The MADIREL laboratory is focused on areas of work involving high surface areas and large interfaces between phases of the materials in study: the capture and separation of gas using metal-organic frameworks, adsorption at the liquid-solid interface, the study of transport within condensed matter and electrochemistry.

1.2 Framing of the project

Porous materials are ubiquitous in modern society. They can be found everywhere from the aerospace industry to the household kitchen sponge. Porous media are generally comprised of a matrix, typically a solid material (though liquids can be considered as well such as in the case of foams) which surrounds empty pockets - or voids - which can be filled by a gas or liquid. Intuitively, it is possible to characterize these materials according to their porosity, that is, the ratio of void volume to the total volume, that is, the volume of both the matrix and the voids. Another important characteristic of a porous material is its surface area per unit of mass (henceforth referred to as specific surface area). This factor is the key to their prevalence and practicality in several chemical applications, the most relevant to the matter at hand being their use as catalyst supports. High specific surface area in a catalyst support translates to an abundance of active sites coupled with an economy in volume.

In the realm of heterogeneous catalysis, a reagent is first introduced to the porous network where it will be carried (by diffusion and advection processes) to the active site, where it is adsorbed and transformed. The products of the reaction are released, then exiting the porous network. The steps of this process which are of greatest interest to this thesis are the ones entailing the transport of the molecules through the porous network and their subsequent
adsorption. These two processes are paramount toward process optimization given the thorough understanding of the reaction taking place.

The optimization of parameters related the aforementioned steps is the key to increases in profitability for certain industrial processes. The catalytic conversion of asphaltenes is one such process and its improvement is the greater goal of this study. Asphaltenes are hydrocarbons recovered from heavy cuts of the crude oil distillation process. These molecules have low market value and must be converted into lighter, more useful hydrocarbons. To this end, asphaltenes must go through a conversion stage - hydrotreatment (HDT) - in which they must traverse a porous catalyst. This means that there are diffusional resistances to overcome, not only because asphaltenes are large molecules, but also because they tend to form aggregates. This further decreases the efficiency of this process by blocking the access of other molecules to the active sites where they would be converted. All these difficulties mean that it is imperative to study the diffusion and transport through catalysts in order to optimize the hydrotreatment and conversion processes.

1.3 Project objective and contributions

Over the course of this work the topology of several porous materials was characterized and the transport of relevant molecules within them was thoroughly studied. This was done with the objective of potentially modeling the transport of these molecules and its influence on their adsorption and reactivity inside these porous media. The ultimate goal of this project is, therefore, the development of a simple and accurate predictive method that allows for easier optimization and successful integration of such porous materials in production processes. Essentially, the objective is the in-depth understanding of asphaltene diffusion and adsorption properties within alumina-based catalysts in order to ease the challenges faced in the asphaltene conversion into useful hydrocarbons which is currently extremely difficult due to their large diversity in composition, presence of heteroatoms and the formation of aggregates and micelles. Asphaltenes comprise a sizeable percentage of the molecules in some of the heavier crude oils, which means that their recovery and conversion would not only mitigate the waste of these potentially valuable molecules, it would also increase overall profits in refineries.

1.4 Document structure

Including this introductory chapter, this document is divided into six different sections. Immediately succeeding the current chapter there will be a bibliographic review section detailing the state of the art of the current asphaltene treatment processes, the existing knowledge of these molecules’ behavior and, more specifically, studies on their diffusion and
transport within porous media presently in use as well as a study on the porous media themselves and their features. Following this, a chapter will be dedicated to the basic concepts regarding porous materials and how they can be characterized by Inverse Size-Exclusion Chromatography. The ISEC technique and its intricacies will also be fully explored within this chapter as well as previous results obtained within or around this topic. Next, a chapter devoted to a summary of all the techniques used and the specifics of the experimental procedures. The subsequent unit is devoted to the presentation of the results obtained in this thesis, wherein they are rationalized and scrutinized. The results section contains four parts: the first three subsections deal with the characterization of different solid frameworks and the study of transport in non-adsorbing conditions therein. The fourth subsection contains all the work performed using the asphaltenes. The final chapter contains the conclusions and perspectives and will end this document with a short reiteration of the objectives, a summary of the steps taken toward the achievement of these objectives and the proposal of possible future experimental pathways. Also attached are a list of the bibliographic references used and appendices containing extra data and supplementary info.
2 CONTEXT - THE ASPHALTENE PROBLEM

Market tendencies within the oil industry are fickle but current predictions estimate a much higher proportion of demand for lighter hydrocarbons than heavy hydrocarbons. This is mainly due to their use in the transportation industry, where gasolines and diesel are used at a seemingly ever-increasing rate, as well a great contribution of natural gas. Unfortunately, oil reserves tend to have much heavier hydrocarbon compositions than what the market demands, which means that these heavy products must be transformed or, in the absence of such an option, utilized in different, less productive, less profitable ways. Figure 2.1 shows the relative compositions of crude oils of several origins as well as the market demand for the different fractions in the USA.

![Figure 2.1 - Weight fractions of crude oils from several origins and comparison with market demand in the United States (IFPEN data)](image)

Refining crude oil is enormously elaborate. The first step is atmospheric distillation, where compounds are separated into several fractions by their molecular weight. A second distillation, called vacuum distillation (performed at a pressure below 5 kPa) separates the heaviest, least volatile products without thermal cracking. Asphaltenes are heavy hydrocarbons concentrated in the vacuum distillation residue. They have very high molecular weights and are usually rich in heteroatoms (nitrogen, sulfur and oxygen) and metals. This means that they require several stages of treatment. Depending on the origin of the crude oil, the percentage in volume of asphaltenes can range from as low as 2.6 % (Arab Light - Saudi Arabia) to as high as 7.2 % (Tia Juana Heavy - Venezuela).
2.1 Asphaltene origin, composition and structure

As previously stated, asphaltenes are products from the heaviest cuts of the atmospheric and vacuum distillation, appropriately called atmospheric and vacuum residue respectively. The formal definition of what is considered an asphaltene has been subject of debate but the current SARA (“saturate, aromatic, resin and asphaltene”) classification of heavy hydrocarbons defines asphaltenes as molecules which are insoluble in a normal paraffin (n-Cx with x between 3 and 12) but soluble in toluene (J. G. Speight 2007). This distinguishes them from all the other hydrocarbons groups present in these heavy fractions, which are soluble in normal paraffins. As such, asphaltenes usually precipitate in these solvents and can be easily separated from the remaining molecule groups.

Chemically, the molecular weight of asphaltenes ranges from 500 to 1500 g.mol\(^{-1}\) and they are the group within the heavy fractions of petroleum richest in heteroatoms such as a sulfur, nitrogen, oxygen and metals. Nitrogen can make up a significant fraction of the total asphaltene mass, reaching percentages of 1.23 % (w/w). Sulfur is a major contributor, sometimes reaching values as high as 8% (w/w). Metals such as iron, nickel, vanadium, zinc, among others also make up a fair amount of the asphaltene total mass, together reaching values of 200 mg/kg (Adebiyi and Thoss 2014).

Structurally, asphaltenes have been divided into two groups: “continental” (also called “island”) asphaltenes and “archipelago” asphaltenes. Continental asphaltenes are characterized by a large central mass of aromatic rings with small alkali chains connected to this central structure. Archipelago asphaltenes are constituted by small groups of aromatic rings loosely connected by alkali chains. Figure 2.2 shows the differences between these two proposed types of asphaltene structure.

![Figure 2.2](image-url)

**Figure 2.2** – The two proposed structures for asphaltenes A) Continental asphaltene; B) Archipelago asphaltene (Santos et al. 2016). Heteroatoms and metals are not pictured but may be present in real fractions.
While these proposed models were in competition for some time, recent works using atomic force microscopy and scanning tunneling microscopy (Schuler et al. 2015) have shown that both models are valid and coexist within asphaltene fractions, as well as molecules with hybrid combinations of both models (large aromatic cores connected to smaller aromatic formations by alkali chains).

2.2 Asphaltene aggregation

It is widely known that asphaltenes tend to form colloidal aggregates in solution. These aggregates tend to be problematic since their size and can be great enough to have severe effects when it comes to diffusion inside hydrotreatment catalysts (Barbier et al. 2014). The model proposed for these aggregation phenomena is divided into two phases: on a first phase, there is a stacking of the asphaltene aromatic cores on top of each other due to the polarity of the delocalized electrons in the p-orbitals (aromaticity) on a large scale due to the presence of many aromatic rings. These are known as nanoaggregates. During the second aggregation phase, the nanoaggregates come together to form clusters. These two processes are described in what’s known as the “Yen-Mullins model” and they are succinctly represented in Figure 2.3.

![Figure 2.3 – The Yen-Mullins model of asphaltene aggregation (Mullins et al. 2012); sizes are representative of the longest axis for all cases](image)

As previously stated, the nanoaggregate phase is a simple piling of aromatic cores due to induced dipole moments. The alkali chains surrounding these cores are, conversely, a hindrance to the aggregation phenomenon. In 2011, Eyssautier et al. set the limit for the maximum number of asphaltene molecules found in these nanoaggregates to a number between 5 and 8. The nanoaggregates present in that same study had a molecular weight around 16 000 g.mol⁻¹. According to experiments made with SAXS (Oh et al. 2003) nanoaggregates can form at concentrations as low as 50 to 200 ppm, depending on the asphaltenes present and which solvent they are in. The formation of clusters has been observed to happen at much higher concentrations, usually more than 3 g.L⁻¹. However, because asphaltenes have such a wide variety of compositions and behaviors, clusters in different solvents may form at different...
concentrations. Size-wise, Eyssautier et al. (2012) measured radii of gyration of clusters between 5 and 8 nm using SAXS and SANS as well as molecular weights of up to 200 000 g.mol\(^{-1}\). The more complex nature of these clusters makes it so that they are much more polydisperse in terms of size and, once again, many of their characteristics will depend on their geological origin and extraction method.

2.3 Hydrotreatment and catalysts

Hydrotreatment has as its objective the removal of heteroatoms and metals from the hydrocarbon charges by hydrodesulphurization (HDS), hydrodeazotation (HDN) and hydrodemetalization (HDM). This is done by hydrogenolysis of C-N, C-S and C-M bonds at high hydrogen partial pressure. Adding to this is the cracking process (hydroconversion) which also necessitates a relative abundance of hydrogen at high pressures and temperatures in order to break the bonds within the hydrocarbons as well as delaying the formation of coke deposits which would accelerate catalyst deactivation. There are several different ways to perform hydrotreatment, however they all share a couple of aspects (Toulhoat and Raybaud 2013). In all these processes, the vacuum residue to be treated is pumped into a reactor with extremely high hydrogen pressures (around 200 bar), temperatures in the order of 400 °C and they require large amounts of catalyst. The catalysts have a high residence time due to the low space velocities. These processes can be divided into three categories depending on the type of reactor they use: fixed bed, bubbling bed and slurry bed. Bubbling and slurry bed reactors are suitable for charges with higher concentration of metals.

![HYVAHL-S hydrotreatment process](Kressmann et al. 1998)

*Figure 2.4 – HYVAHL-S hydrotreatment process (Kressmann et al. 1998)*
Figure 2.4 shows the HYVAHL-S process proposed by Axens, an example of a process which uses a combination of fixed beds. In this process, the vacuum residue is pumped into one reactor while the other reactor’s catalyst is regenerated. Once the catalyst in the first reactor is poisoned, the flow is switched to the second reactor. Bubbling and slurry bed reactors are in constant use. Catalyst is introduced into the system and recovered continuously. In bubbling reactors, the catalyst is dispersed within the fluid phase and constantly mixed due to the hydrogen being pumped from the bottom, forming the bubbling effect this type of reactor is named after. An example of bubbling reactors in an HDT process is given in Figure 2.5.

Figure 2.5 – Example of a process using a series of three bubbling reactors (IFPEN data)

The catalysts used in hydrotreatment reactors are commonly comprised of an alumina support usually in the form of spherical particles or extrudates. The active sites are metallic sulfides using molybdenum and either nickel or cobalt. The alumina supports currently used have rather well-defined specifications when it comes to their pore size distribution (Figure 2.6).

Figure 2.6 – Specifications for the pore size distributions of alumina catalyst supports for the different hydrotreatment processes (Toulhoat and Raybaud 2013)
Unfortunately, hydrotreatment catalysts don’t last very long - only a couple of months - due to poisoning. This happens in various ways: deposition of coke is by far the quickest way in which catalysts are deactivated. The metals removed through hydrogenation are also deposited in the active sites. Concomitantly, both coke and heavy metals tend to plug or otherwise obstruct the porous network of the catalysts inside the reactors, quickly rendering the active sites inaccessible (Marafi et al. 2009). Likewise, at high temperatures, the asphaltene clusters in these highly concentrated fractions also tend to block the catalyst pores over time. At the high operational temperatures of the reactors, the aggregates formed are smaller than the ones observed at room temperature (Eyssautier et al. 2012), meaning that the more complex cluster formations are divided back into nanoaggregates. Furthermore, at such high temperatures, conversion and cracking tend to break down some of the large asphaltenes into smaller hydrocarbons. Cracking produces coke as well as light hydrocarbons by breaking alkali chains from the aromatic cores of the asphaltene molecules while hydroconversion saturates some aromatic rings into naphthenes. This has, of course, an impact on the diffusion inside the catalysts as well.
3 TRANSPORT THROUGH POROUS MEDIA - STATE OF THE ART

The most important advantage of porous over non-porous materials is their high surface area in relation to their volume and mass. As such, they are extremely important in fields like heterogeneous catalysis, separation and many others (Volfkovich et al. 2014). Molecular sieves, for example, are porous materials with a well-defined pore size. These materials adsorb smaller molecules within their pores, while leaving larger molecules out, thus effectively segregating these small molecules from large ones. In this case, evaluating the details of molecular transport is not essential; it is much more important to assure that the correct pore size is achieved and that there is a very small distribution of pore sizes.

Focusing instead on the use of porous materials as catalysts and separation columns, there is a much greater interest in how molecules traverse through these materials. In fact, when employing these materials, a thorough study of the transport of molecules through the porous medium is paramount so as to optimize parameters like separation efficiency in the case of separation columns or reaction yield for fixed and fluidized particle and pellet beds.

3.1 Advection and diffusion

There are two main mechanisms through which molecules move: convection (more precisely called advection) and diffusion. The phenomenon of advection is simply the transport of molecules due to the existence of a flow of carrier fluid, essentially “pushing” the molecules along a flow path. Diffusion, however, happens without any outside influence from fluid flow.

Temperature is a measure of the kinetic energy of particles (be they atoms or molecules), therefore, particles with temperatures above absolute zero have some degree of inherent motion or vibration. This is called “Brownian motion” and it is the sole motivator for molecular diffusion. If there is a concentration gradient, molecular diffusion will, through the random collisions of the Brownian motion mechanism, evolve toward the elimination of this gradient. Over a large enough period of time, a dynamic equilibrium will be reached wherein the molecules will be evenly distributed. Molecular motion still exists, however, it has does not spontaneously create concentration gradients - this is called self-diffusion. Figure 3.1 illustrates this phenomenon. In an attempt to describe the macroscopic evolution of this molecular diffusion process, Adolf Fick developed his laws of diffusion.

\[ J = -D \frac{\partial C}{\partial x} \]
Equation 1 is called Fick’s first law of diffusion. Assuming a steady state, it relates the diffusion flux, $J$ (given in mol.m$^{-2}$.s$^{-1}$), with the diffusion coefficient, $D$ (m$^2$.s$^{-1}$), and the gradient of the concentration, $C$, in a given space, $x$. The diffusion coefficient can take many forms, usually depending on the diffusing compound as well as the medium through which it is diffusing.

![Figure 3.1 – Evolution of the concentration gradient over time through molecular diffusion](image)

In the end, both advection and diffusion contribute to transport the molecules through porous media and onto their surface, where they may or may not be adsorbed.

### 3.2 Adsorption and surface diffusion

Adsorption is a surface phenomenon in which molecules interact with the interface between two media. This process can occur through two general mechanisms: chemisorption and physisorption. The chemisorption process requires reactivity between the adsorbed species and an active site, which means that this is a chemically selective process involving a much higher binding energy between the species and the surface. Physisorption, however, is much less specific and requires only a small interaction between the surface and the molecule in question. It is intuitive as well that chemisorption should only occur in a single layer due to the chemical bonds that are created, as opposed to physisorption, which can follow multi-layer models under certain conditions.

The study of adsorption of different molecules onto surfaces is of great interest as the phenomenon is highly versatile and can be applied in myriad different ways. Surfaces can be tuned for specific purposes such as separation or catalysis, each of those fields branching out into an innumerable amount of specific applications. Conversely, the adsorbent itself may be selected to have an interaction such that reliable characterization of the surface and topological properties of solid materials is possible. Gas adsorption in particular is extremely useful in such studies, so much so that it has become a standard measurement in material science.

From this arises the concept of an adsorption isotherm, a way to plot the amount adsorbed on a surface against bulk concentration (in the case of liquid adsorption) or partial pressure (for gases) at a fixed temperature. Intuitively, higher concentrations in the fluid phase mean that
higher quantities of molecules are adsorbed in the surface. Most materials loosely follow a certain set of behaviors, the modelling of which has been achieved using adsorption isotherms. IUPAC’s isotherm classification is widely used to characterize materials which follow these patterns.

**Figure 3.2 – IUPAC adsorption isotherm classification (Thommes et al. 2015)**

Figure 3.2 shows the different adsorption isotherms, each of them corresponding to materials with different characteristics or exhibiting different adsorption mechanisms. One of the most important features of a material - and one of the most relevant when interpreting adsorption isotherms - is its pore size. IUPAC divides pores into three categories based on their size: micropores have a size of 2 nm or less, mesopores range between 2 and 50 nm and macropores have diameters greater than 50 nm. Isotherms I(a) and I(b) are both typical of a microporous material, I(a) with micropores of 1 nm or less and I(b) with slightly larger micropores, up to 2.5 nm. Isotherms II and III represent adsorption on a solid, non-porous material, or a material with macropores large enough to be indistinguishable from the outer surface area. Samples with isotherms IV(a) and IV(b) are mesoporous and the presence of hysteresis depends on the pore shapes and sizes. Isotherms III and V show weak adsorbent-adsorbate interaction such as what is observed in the case of water adsorption on a hydrophobic microporous material. Isotherm VI is the adsorption layer by layer on well-organized surfaces (e.g. argon or krypton).
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on graphite). This isotherm classification is generally applicable to gas adsorption below critical temperature. It is worth noting that these six isotherms encompass only some of the most common types of isotherm and it is not uncommon for isotherms of more exotic materials to have different shapes and behaviors, which, again, must be interpreted considering factors such as surface chemistry, crystalline arrangement, topology, among others. On separate note, an idiosyncrasy of the “pore size” concept is that “size” has a malleable definition depending on the pore geometry. In the case of slab-type pores, size is the distance between the walls while for cylindrical and spherical pores, pore size refers to the diameter. The term becomes more nebulous when complex pore shapes (such as bottle-shaped pores) are involved.

Adsorption from liquid solution shares many aspects with gas adsorption as detailed above such as the utility of the isotherm as a description of the adsorption mechanics but brings with it complications such as possible changes of behavior of the adsorbent when immersed in a liquid medium. Adsorption from dilute solutions often reduces the complexity of the measurements by assuming a base state of a solid immersed in a solvent and a solute at small concentrations which displaces the solvent from the surface of the solid when introduced to the system. Thus, complex interactions between two solutes and the competition for adsorption between these solutes and the solid phase are reduced to a single displacement mechanism.

The adsorption isotherm models used for such simple cases are not unlike the ones previously suggested IUPAC for characterization via gas adsorption. Commonly in dilute solutions with simple interactions, Henry and Langmuir isotherm models are applicable. The Henry adsorption model is a constant linear isotherm model, depending on one factor, often called the Henry constant, corresponding to the slope. This model is usually only applicable at very low concentrations, ergo, very low surface coverage.

At higher coverages, more options start to appear such as the Langmuir, BET (Brunauer-Emmet-Teller) and a myriad others suited to specific cases with unique interactions, however these specialized cases lie beyond the scope of this thesis. Another commonly discussed, the Freundlich isotherm, for example, is an entirely empirical isotherm fit, rather than a theoretically based one, and, as such, should be used with caution.

The Langmuir isotherm (Langmuir 1918) extends the isotherm beyond the linearity regime of the Henry model by limiting the availability of adsorption sites, leading to a maximum surface coverage which can never be overcome. It also assumes that only a single layer of molecules adsorbs in the surface of the solid with one molecule per adsorption site. The Langmuir isotherm is analogous to isotherms I (a) and I (b) in the IUPAC classification shown in Figure 3.2. Multilayer adsorption, in turn, can be described by the BET theory (Brunauer et al. 1938 - analogous to isotherm II in the IUPAC classification), with the first layer having a specific interaction with
the surface and the subsequent layers interacting with the adsorbed molecules in the previous layer. Neither BET nor Langmuir consider side interactions between adsorbed molecules.

In order to exclusively study the molecular diffusion, neither adsorption nor reaction should be allowed to happen as they interfere with the bulk transport properties, by respectively halting said transport and transforming the molecules in question. Surface diffusion effects can be seen only when adsorption is present, so experiments in adsorbing conditions are also necessary to completely model the transport properties.

Surface diffusion is a phenomenon intrinsically related to adsorption in which an adsorbed molecule moves along a surface, from one adsorption site to another. This happens when the adsorbed molecule is given an amount of energy which is too small to make it desorb. This phenomenon is controlled by a surface diffusion parameter, $D_s$. Figure 3.3 is a graphical representation of the phenomenon.

![Figure 3.3 – Surface diffusion phenomenon (Q$_{st}$ – heat of adsorption; $E_s$ – surface diffusion activation energy) (Miyabe 2007)](image)

**3.3 Porosity and tortuosity**

The term ‘porosity’, when used in the field of material sciences, can have several meanings. In its classical definition, porosity refers to the ratio between the volume of the void space in a material and its total volume. However, using common measurements such as mercury intrusion, the porosity value obtained does not take into account the pores that are inaccessible or isolated, as such giving us a different porosity value. The definition of interest for molecular transport thus becomes the ratio of the volume of accessible pores over the total volume (for heat transfer, the total porous volume including non-accessible pores, must be taken into account).

The concept of porosity is visualized in Figure 3.4 and its value can be calculated using Equation 2, in which $\varepsilon$ is the porosity, $V_v$ is the volume of the accessible voids (or pores) and $V_t$ is the
total volume, the sum of the volume of solid as well as the voids. This porosity concept can be further refined towards the preferred convenience. When working with a particle bed, one must be able to distinguish the porosity of the particles from the porosity of the bed packing and how they relate to the total porosity. In the same sense, when working with materials with multimodal pore size distributions it can be useful to discriminate between the porosity of the smaller and larger pores.

\[ \varepsilon = \frac{V_v}{V_t} \]

**Figure 3.4** – Example of a porous material: brown – solid phase; blue – voids/pores

Most porous materials do not have uniformly sized and straight pores, so when studying the diffusion of molecules through these porous media, the concept of tortuosity is introduced. Like porosity, tortuosity has been defined in several different ways but the overarching concept attempts to quantify the difficulty with which a molecule traverses a path with some sort of obstacle, curvature or roughness when compared to a straight line. Figure 3.5 illustrates this concept. The most common definition is the geometric one which takes a single path into account as detailed in Equation 3.

\[ \tau = \frac{x'}{x} \]

**Figure 3.5** – In red: possible tortuous flow path through the porous material

Tortuosity, \( \tau \), in this definition, is the ratio of the distance actually traveled, \( x' \), over the distance in the horizontal dimension, between the starting and ending points, \( x \).

Along the years, this unidimensional definition has proven lacking in the modeling of diffusion and transport within three-dimensional, complex and interconnected paths because of its simplistic nature. Not properly describing most practical applications, its use as a parameter in
calculations has been phased out and substituted by more encompassing flow hindrance parameters which are, themselves, a measurement of the tortuosity. \( \tau \) as defined through Equation 3 also fails to take into account dead volumes in the flow path. Even so, it remains a reliable starting point which facilitates the basic understanding of the concept.

Measurements of tortuosity for three-dimensional networks are done nowadays using a variety of methods depending on the application in question.

### 3.3.1 Direct measurements of tortuosity

In 1956, Carman proposed the use of electrical conductivity measurements (first attempted by Schofield and Dakshinamurti 1948) as a way to measure tortuosity. This tortuosity, however, is not a simple ratio of the real and ideal paths but a quantification of the resistance to the transfer of an electrical current and, by analogy, the transfer of mass. To better comprehend the foundation for this analogy, the experimental basis must be explained. The conductivity measurements are performed by filling the porous material with an electrolyte for which the bulk conductivity is \( \sigma^0 \). The measurement of electrical conductivity for the electrolyte/porous material system will, in turn, produce a value of conductivity that is lower than the conductivity of the bulk electrolyte - the effective conductivity, \( \sigma_{\text{eff}} \). Equation 4 describes the relation between the conductivity measurements and the achieved tortuosity value.

\[
\sigma_{\text{eff}} = \sigma^0 \frac{\varepsilon}{\tau}
\]

According to this equation, the effective conductivity is nothing more than the bulk electrolyte conductivity within the pore volume with a delay factor equal to the reciprocal of the tortuosity. The fact that this interpretation of tortuosity has an experimental basis means its applicability is much greater in the study of diffusion, since the process by which electrical conduction is delayed is analogous to happens to the molecular diffusion of particles within the material.

In particular, the method proposed by Barrande et al. (2007) is useful for the characterization of porous particles. In this method, porous particles are added to an electrolyte solution and the resistivity of the solution is measured. For small masses of added solid, it is assumed that there is no interaction between particles, often called “infinite dilution” conditions (Kim and Chen 2006). This method proves immaterial when assessing the tortuosity of monolithic structures. The measurement for these sorts of materials would require some sort of milling process which would not only destroy the material but also possibly alter its topological features, which might generate in an unreliable result.

Other methods of tortuosity evaluation revolve around the same principle yet evaluating the diffusion of probe particles rather than conductivity. The diffusion coefficient of the probes
through the porous material can be obtained by various techniques such as size-exclusion chromatography peak evaluation (Athalye et al. 1992), Wicke-Kallenbach diffusion cells (Kolaczkowski 2003) or pulse-field gradient NMR (Sen et al. 1994). With the exception of NMR, which uses a slightly altered version, these techniques rely on Equation 5, a parallel to Equation 4 using the bulk molecular diffusion coefficient, $D_m$, to calculate the effective diffusion coefficient, $D_{eff}$. This allows for the calculation of the tortuosity observed by a probe molecule throughout the entire accessible porosity, thus, an apparent tortuosity.

$$D_{eff} = D_m \frac{\varepsilon}{\tau} \tag{5}$$

In order to employ techniques in which probe molecules are used to evaluate the tortuosity of a porous material one must be especially prudent: if it is assumed that tortuosity is an unchanging attribute, inherent to the topology of the porous material in question, it is logical that it should not be dependent on the size of a probe molecule introduced to measure it. With this in mind, one must ensure that the probe’s size does not affect the measurements by choosing the smallest probe possible. In this aspect, conductivity measurements are usually more accurate since very small ions can be used as conductors within the electrolyte, therefore producing negligible effects on the measurement of tortuosity.

Barrande et al. proposed a generic equation, applicable to different sorts of measurements, that would yield a tortuosity value.

$$\left( \frac{J}{DFG} \right)^{eff} = \left( \frac{J}{DFG} \right)^0 \frac{\varepsilon}{\tau} \tag{6}$$

In Equation 6, $J/DFG$ is a ratio that can be replaced by any transport flux, $J$, with a driving force gradient, $DFG$. This equation posits that tortuosity measurements can be done using any sort of transport parameter, be it flow of matter (which leads to diffusion measurements), electrical current (the basis for the conductivity measurements) and possibly others. As previously, the “$^{eff}$” and “$^0$” superscripts pertain to measurements with and without the porous medium respectively.

Much work has been done throughout the years to associate tortuosity directly to topological parameters. Weissberg (1963) related the void fraction (porosity) of a solid spherical particle bed to a parameter which was to be later called tortuosity. This parameter quantified the reduction in the diffusion due to confinement. Comiti and Renaud (1989) generalized this expression into what would become Equation 7, valid for fixed beds of non-spherical particles, dependent on a parameter, $p$, which would represent the particular physical arrangement of the particles giving the material its structure and its effect of this arrangement on molecular transport (for example, $p = 0.5$ for a collection of solid spheres, as stated by Weissberg). Equation 7 was later experimentally used (Barrande et al. 2007) to analyze the internal particle
topology, $\tau_p$ (Equation 8) by using the Maxwell equation relating $\sigma_{eff}$ and $\sigma_p$ - the conductivity within the particle. The allowed for the separation of the contribution of different porous domains to the total tortuosity of a multiscale system (a concept further explored in section 5.1.5). Later still (Wernert et al. 2010), the viability of the equation was further extended to include studies for larger probe sizes with non-negligible effects on transport, ergo, the particle porosity accessed by these molecules was smaller thus influencing the experienced tortuosity, $\tau_p[r_m]$ (Equation 9).

$$\tau = 1 - p \ln(\varepsilon)$$  \hspace{1cm} 7
$$\tau_p = 1 - p \ln(\varepsilon_p)$$ \hspace{1cm} 8
$$\tau_p[r_m] = 1 - p \ln(\varepsilon_p[r_m])$$ \hspace{1cm} 9

The intraparticle porosity, $\varepsilon_p$, is, in turn, a function of the total bed porosity, $\varepsilon_t$, and the external (also referred to as interparticle) porosity, $\varepsilon_e$, according to Equation 10.

$$\varepsilon_t = \varepsilon_e + \varepsilon_p(1 - \varepsilon_e)$$ \hspace{1cm} 10

These equations provide a model in which tortuosity is a function of the shape factor and the porosity of a given dimension, be it the bed porosity, the particle porosity or the accessible particle porosity.

### 3.3.2 Geometric reconstruction of the pore network via tomography

Tomography is an imaging technique which aims at visualizing the three-dimensional geometry of a material. A versatile technique, tomography can be performed using beams of several types of waves (or wave-like particles) which penetrate the material and are then detected after passing through it. The attenuation of these beams is what leads to an image by the end. Depending on the beam, resolution can range from angstrom to millimeters, however, field of view is often limited to a thousand times the resolution.

It is possible to deconstruct a tomographic image of a porous network, algorithmically delineating the shape and interconnectivity of pores to achieve a value of tortuosity via geometrical considerations, random walk simulations or numerical resolution of mass transfer equations.

Tomography can provide a clear and highly accurate view of the porous network and its topological intricacies. However, in spite of this method’s interesting development and results, it requires very expensive equipment and extensive calculation and processing resources. In addition, results are often not representative of the real sample. (Schlüter et al. 2014).
3.4 Determination of diffusion coefficients via liquid chromatography

Size Exclusion Chromatography (SEC) is a liquid chromatography technique which has the objective of separating molecules of different hydrodynamic volumes or sizes based on their diffusion through a porous medium (Katz et al. 1998). A liquid sample is introduced into a column packed with a material with a known and well-defined pore size. As the several components in the sample make their way through the column, some of them are too large to fit inside the pores and quickly make their way through the chromatographic setup. Smaller and smaller molecules will penetrate within the porous medium more and more and be further delayed by the tortuosity of the pores.

Fundamentally, SEC is simply an analytical chemistry separation technique and, as such, involves a stationary phase with known characteristics. Halász and Martin (1978) introduced Inverse Size-exclusion Chromatography (ISEC), a technique which allowed them to, rather than analyze a solute, characterize the stationary phase, determining the pore size distribution of particles in a packed column. In ISEC, therefore, the characterization centers on the column packing material rather than what is injected. As mentioned in section 3.3.1, this is a method that uses probe molecules which are introduced into the porous system. By analysis of the chromatographic peak one can study the transport properties of the probe molecules. This is especially interesting when one wants to learn about the diffusion of molecules that do not have negligible hydrodynamic radii compared to the pore dimensions.

More specifically, when a molecule has a size that is large enough to be comparable to the pore radius, it will be more difficult for it to percolate through the porous material. This is due to three main mechanisms which affect the tortuosity experienced by a large molecule as shown in Figure 3.7.
Figure 3.7 – Three delay mechanisms in the flow of large molecules through porous media: i) steric hindrance; ii) size-dependent tortuosity; iii) friction (Wernert et al. 2010)

In case i), the volume of the pore can be occupied entirely by the edges of molecule but not by its center, which is excluded from a certain volume of the pore equivalent to the volume of a cylindrical shell (assuming a cylindrical pore). This could also be equated to a constriction of the pore for a zero radius particle. In essence, however, the molecule still can occupy the entire porosity of the particle. Case ii) differs precisely in this sense: the large molecule cannot occupy any of the volume in the small pore. The large particle is therefore forced into a specific flow path and will explore only a fraction of the total pore volume. As the figure depicts, this causes the larger molecule to take a different path and therefore experience a different tortuosity as well. Situation iii) is a particularity of hydrodynamic flow and the definition of tortuosity. Defined as an impedance to flow, tortuosity increases along with the drag caused by laminar flow. The larger the molecule, the larger this friction will be and, consequently, the higher the tortuosity value measured. For smaller molecules, eluting closer to the pore walls will be another delay factor. As such, it is more descriptive to call this an “apparent tortuosity” when talking about probes of significant sizes relative to the pore size.

As previously stated, the extent of all these contributions depends on the size of the probe molecule, $r_m$, relative to the size of the pores, $r_p$ – the ratio $\lambda = r_m/r_p$. The use of chromatography to quantify these contributions is readily apparent over any of the techniques mentioned above. There are two methods used to achieve the characterization of transport in a porous medium using chromatography: the dynamic and static (or “peak parking”) methods. Both of these methods require a few parameters to be previously known, mainly the structural parameters of the particle/particle bed (or column) such as its dimensions as well as the mean pore size of the particles. Parameters related to the probe molecules such as their hydrodynamic radius and their molecular self-diffusion coefficient must also be specified.

The dynamic method is the simplest and relies solely on the injection of the sample in the chromatographic system at different flow rates. Using the shape of the chromatographic peaks in conjunction with the van Deemter equation and the General Rate Model (GRM), it is possible to calculate the effective internal diffusion coefficient for each probe size directly from the variance of the peaks.
The static method involves the injection of the probe at a fixed flow rate until the probe reaches approximately the longitudinal center of the column/particle bed. At this point, the flow rate is stopped and the probe is left to diffuse through the porous network. After the given parking time, the pump is reinitiated, at which point the chromatogram is retrieved and the variance of each peak is used to calculate the effective total diffusion coefficient. Models are then used to relate this value to the effective internal diffusion coefficient.

### 3.4.1 Dynamic method fundamentals

For non-adsorbing conditions, the dynamic method is ideal for the study of the transport properties of molecules in a porous system. It is relatively simple and much less time consuming from a practical standpoint (though there is usually more data to analyze, depending on the number of data points required for a proper correlation to arise).

Martin and Synge (1941) introduced the concept of “height of an equivalent theoretical plate” (or HETP) to characterize the mass transfer limitations in a packed bed of porous particles. This concept denotes the separation ability of a chromatographic column and is given as a relationship between the mean retention time, $t_R$, and variance, $\sigma_R$, of the chromatographic elution peak as shown in Equation 11.

$$ HETP = L \frac{\sigma_R^2}{t_R^2} \tag{11} $$

In this situation, $L$, is the length of the chromatographic column. In a distillation column, more plates equate to a more efficient distillation. Likewise, the lower the value of the HETP, the more efficient the separation is inside chromatographic column. All else being equal, smaller HETP values result in thinner elution peaks. This is essential in the dynamic method as wider peaks yield less reliable results when it comes to the HETP calculation, as will be expanded upon later. There are two ways of extracting the valuable data (variance and mean retention time) from a chromatographic peak: one can either fit the peak to a Gaussian curve or use the method of the moments (Miyabe et al. 2007). In the case of a perfectly Gaussian peak (no tailing or fronting), both calculations should yield the same results, however, when peaks are skewed or display either tailing or fronting, this sub-optimal appearance has an effect on the results obtained for the peak characteristics. In this case, the use of the method of the moments is recommended as it takes into account the non-Gaussian shape of the peak. The method of the moments requires a cut-off point at the base of the peak and the choice of this cut-off point may influence the values obtained for the mean and variance values. With this in mind, the Gaussian fit, while less rigorous than the method of the moments, suffices in most cases. Figure 3.8 shows a typical elution peak and the Gaussian fit approximation.
The Gaussian fit on the elution peak through the column is not enough for an accurate representation of what is truly happening inside the column. This is because the molecule elutes through the extra-column volume as well: from the injector and through the capillaries connecting the injector to the column, as well as the capillaries connecting the column to the detector. This volume, although small, has a large effect on the variance of the peaks for both ends of the spectrum of molecular masses. For relatively small molecules, the extra-column volume is relatively significant when compared to the intraparticle diffusion (which is the sole objective of the ISEC analysis). The same happens for molecules with hydrodynamic radii bigger than the mean pore radius. As these polymers do not enter the particles, the effect of the extra-column volume is in the same order of magnitude as what happens inside the column (but still outside the particles). For molecules in the mid-range of sizes, intraparticle diffusion is a much bigger contributor to the variance of the peak, though the extra-column dispersion’s effect is still not negligible. These effects are independent from each other as they occur in different zones of the flow path. Therefore, it is possible to expand Equation 11 into Equation 12, adding mean retention time and variance without a column, $t_i$, and, $\sigma_i$, respectively.

$$HETP = L \frac{\sigma_R^2 - \sigma_i^2}{(t_R - t_i)^2}$$

This extra-column dispersion effect is more and more relevant when working at higher flow rates. At low flow rates, the molecules spend a much longer time diffusing within the column than they do in the extra-column volume which means that the impact of the extra-column diffusion in the variance of the peak is much smaller than the diffusion happening inside the column. As flow rates increase, the amount of time that molecules spend inside the column...
becomes a lot smaller, meaning that a more significant value of variance is due to the extra-column contribution.

The height of an equivalent theoretical plate for chromatography is usually also calculated using the van Deemter equation, introduced in 1956. This equation attempts to quantify every contribution to the diffusional and transport behavior inside a chromatographic column thus helping to predict the final shape of the chromatographic elution peak. The van Deemter equation (Equation 13) can be reduced to three general terms:

$$HETP = A + \frac{B}{u} + Cu$$

As each of the terms $A$, $B$ or $C$ increases, so does the HETP, which results in a loss of efficiency.

Term $A$, called the “eddy diffusion” term, is classically assumed to remain constant regardless of linear velocity, $u$. This is because eddy diffusion is dependent only on the physical characteristics of the flow path, such as packing and particle size. The extent of this parameter is due to solely convective processes: the sinuosity of independent flow paths causes turbulent behavior when routes merge and split along the column. These interactions between uneven flow paths end up increasing the band broadening in the elution peak regardless of diffusional effects.

Term $B$ is the self-diffusion term and contributes greatly to the peak broadening at low velocities. Self-diffusion, as has been explained in section 3.1, occurs naturally due to the erratic motion of molecules (the aforementioned Brownian motion). The more time the molecules spend inside the column, the higher the contribution of the $B$ term, therefore, it is considered that its influence decreases in an inversely proportional relationship with linear velocity. This term will be discussed and analyzed in more detail in section 3.4.2, since it becomes much more relevant in the peak parking method. For very high velocities, $B/u$ is considered negligible, particularly when compared to $C \cdot u$.

$C$ is the term that takes into account the concentration gradients between the stationary and mobile phases. This mass transfer limitation is evident at higher velocities, where it is harder to achieve equilibrium due to the existence of a greater convective force. This causes a delay between the mobile phase and the solute which results in a broadening of the peak. $C$ quantifies the transfer on the particle film, an adsorption term and the intraparticle diffusion, the latter of which is of particular interest to this study. Inside particles, the main motivator for movement is molecular diffusion (rather than advection, which is negligible within the particles’ porous network). With an increase in velocity, molecules that spend more time inside the particles will have spent a significantly higher time in the column (since molecular diffusion is independent from the convective forces imposed by the higher flow rate) than molecules
which stay only on the extra-particle porosity. The latter percolate much faster through the column. This, again, causes a significant broadening of the peak.

Using the GRM developed by Kučera (1965), which takes into account most contributions to the mass transfer resistance and from it, the HETP curve can be written as such for non-adsorbing conditions:

\[
HETP = 2\delta d'_p + \frac{2\gamma D_m}{u} + 2 \left( \frac{1 - \varepsilon_e}{\varepsilon_t} \right) \varepsilon_p \left( \frac{d'_p}{6k_m} + \frac{d'_p^2}{60D_p^{eff}[r_m]} \right) \cdot u \tag{14}
\]

Equation 14 develops constants A, B and C in terms of the physical characteristics of the porous material and the solution therein. This involves a constant eddy diffusion coefficient, \(\delta\), the particle diameter, \(d'_p\), the obstruction factor, \(\gamma\), the mobile phase mass transfer coefficient, \(k_m\), the different porosity domain volumes and \(D_p^{eff}[r_m]\), the effective intraparticle diffusion coefficient for probes of radius \(r_m\). Equation 14 is derived from the two mass balances within a packed bed and inside the particles as well as the transfer rate at the interface between both the extra-particle and intra-particle volumes.

Both the A and B factors are related since both eddy diffusion and dispersion happen in parallel as axial diffusion, \(D_{ax}\), in a packed bed (Equation 15).

\[
D_{ax} = \delta d'_p u + \gamma D_m \tag{15}
\]

The eddy diffusion coefficient, \(\delta\), is mostly determined experimentally and tends to vary between 0.5 and 1. For the obstruction factor, \(\gamma\), Gritti and Guiochon (2007) suggested that it is inversely proportional to the tortuosity of flow path in the absence of friction. This conclusion can also be achieved altering Equation 6 so that \(D_{eff}\) corresponds to \(D_{ax}\), thus giving us Equation 16.

\[
D_{eff} = \frac{\varepsilon D_m}{\tau} \tag{16}
\]

Wernert, et al. (2010) proposed a way to calculate the obstruction factor based on this which is applicable as a function of the size of the probes and the portion of the porosity that is accessed by the probe which is verifiable in static conditions (see section 3.4.2).

\[
\gamma = \frac{\varepsilon_t[r_m]}{\varepsilon_e\tau_t[r_m]} \tag{17}
\]

For high velocity, the term \(C\) dominates and thus becomes equal to the slope of the HETP curve.

It is comprised of two different contributions: the intraparticle effective diffusion and the mobile phase mass transport coefficient, the latter of which can be approximately estimated using Equation 18 (Wilson and Geankoplis 1966).
\[ k_m = \frac{1.09D_m}{d_p^\epsilon e/\epsilon_p} \left( \frac{u\epsilon_p d_p'}{D_m} \right)^{1/3} \]

Whether or not the C term has an influence on the HETP at high velocities depends on the ratio \( \lambda = \frac{r_m}{r_p} \), between the probe’s size (by definition, their hydrodynamic radii, \( r_m \)) and the mean pore size, \( r_p \). For very small probes (\( \lambda < 0.1 \)) and very large (\( \lambda > 1 \)) at low interstitial velocities, transport is mostly regulated by longitudinal dispersion as has been stated before but at large velocities, eddy diffusion dominates. This can be seen in their HETP curves (Wernert et al. 2010), which tend toward a constant value, rather than an ascending slope. This makes sense for large probes, as they do not enter the particle porosity, which means that convective forces (eddy diffusion) are the only contributors to dispersion. For very small molecules, it is expected that the C term would have a higher effect, however, measurements are not precise enough to detect it reliably.

The transport of intermediate sized molecules (0.1 < \( \lambda < 1 \)) is governed almost exclusively by the C term and its calculation is the objective of the dynamic conditions experiments. With A and B out of the picture, the HETP becomes proportional to the velocity, \( u \), by a factor of C (different for each probe size). Combining Equations 12, 13 and 14, makes the method very clear.

\[ HETP = L \left( \frac{\sigma_R^2 - \sigma_i^2}{(t_R - t_i)^2} \right) \approx 2 \left( 1 - \epsilon_e \right) \epsilon_p [r_m]^2 \epsilon_e \left[ \frac{d_p'}{6k_m} + \frac{d_p'^2}{60D_p^{e f f} [r_m]} \right] \cdot u \]

Equation 19 allows us to have the particle diffusion coefficient for each probe as an output with the variances and retention times as input, all else being the physical characteristics of the bed and material, as well as the mobile phase mass transport coefficient calculated by Equation 18. This equation (as a consequence of the GRM) assumes intraparticle diffusion and bulk diffusion as parallel phenomena. Injecting molecules in the intermediate range of relative sizes in a variety of flow rates (with and without column) results in a linear plot from which the diffusion coefficient can be determined using a linear regression.

In adsorbing conditions, in the linear domain of the isotherm, the GRM equation sharply increases in complexity to accommodate for all the interactions, including the surface diffusion coefficient, \( D_s \), the equilibrium Henry’s constant, \( K \), and the kinetic adsorption-desorption parameter, \( k_a \). At high enough speeds, the HETP will be given by Equation 20. (Gritti and Guiochon 2012)

\[ HETP \approx 2 \frac{\epsilon_e}{1 - \epsilon_e} \left( \frac{k_1}{1 - k_1} \right)^2 \left[ \frac{d_p'}{6k_m} + \frac{d_p'^2}{60D_p^{e f f} [r_m]} + \frac{k_2}{k_a} \right] \cdot u \]
This equation depends on two topological terms, \( k_1 \) and \( k_2 \), as well as substituting the individual contribution of the particle diffusion, \( D_{p,\text{eff}} \), with an adsorbing conditions parameter, \( D_{a,\text{eff}} \), including both particle and surface diffusion. Expansions of \( k_1, k_2, D_{a,\text{eff}} \) and \( K \) are shown in Equations 21, 22, 23 and 24.

\[
k_1 = \frac{1 - \varepsilon_e}{\varepsilon_e} \left[ \varepsilon_p[r_m] + K(1 - \varepsilon_p[r_m]) \right]
\]

\[
k_2 = \frac{1}{1 - \varepsilon_p[r_m]} \left[ \frac{K(1 - \varepsilon_p[r_m])}{\varepsilon_p[r_m] + K(1 - \varepsilon_p[r_m])} \right]^2
\]

\[
D_{a,\text{eff}}[r_m] = D_{p,\text{eff}}[r_m] + K(1 - \varepsilon_p[r_m])D_s[r_m]
\]

\[
K = \frac{(t_R - t_0)/t_0}{(1 - \varepsilon_t[r_m])/\varepsilon_e[r_m]}
\]

A new term is introduced in Equation 24, \( t_0 \), the retention time with a non-retained compound. Equation 20 assumes intraparticle diffusion and surface diffusion are independent phenomena. The particle diffusion coefficient, having been determined with non-adsorbing conditions, allows now for the calculation of the surface diffusion coefficient. It also treats adsorption kinetics as parallel to both the film and particle diffusion parameters.

### 3.4.2 Static or peak parking method fundamentals

Peak parking refers to the practice of injecting the probes into the column and stopping the flow rate. Molecules are left to diffuse through the column on their own for a certain period of time, dubbed “parking time”, \( t_p \), after which they are flushed, typically resulting in a less intense and wider peak than the one resulting from experiments with a constant flow rate (or \( t_p = 0 \text{ min} \)). The extent of the broadening of a parked peak compared to a non-parked peak is linked to the diffusion of the molecule within the porous network.

As referred to in section 3.4.1, the static method makes use of the \( B \) term, in order to achieve a better understanding of the diffusion characteristics of the probe inside the column at very low flow rates. Equations 13 through 17 already give us an idea of how this is to come about but to put it more explicitly, Equation 25 discretizes the \( B \) term of the equation.

\[
B = 2 \, D_{\text{eff}} \frac{\varepsilon_t[r_m]}{\varepsilon_e}
\]

The \( D_{\text{eff}} \) term refers to the contribution of the longitudinal diffusion across the entire column, including intra and interparticle contributions. Along with the porous volumes, the effective diffusion coefficient is necessary to calculate the total influence of the \( B \) parameter. Using Einstein’s law of diffusion (Knox and Scott 1983), it is possible to relate the unidimensional...
effective diffusion coefficient with the elution peaks obtained through the peak parking experiments:

\[ \Delta \sigma_z^2 = 2 D_{\text{eff}} t_p \]

It’s worth noting that any result obtained through peak parking is relative to an experiment conducted in the same conditions but with no parking time. In Equation 26, \( \Delta \sigma_z^2 \) is the difference between the variance obtained in the peak parking experiment and the variance obtained with no parking time.

This global effective diffusion coefficient is not the final objective of the analysis, as it considers the entire bed (intra and interparticle) diffusion. Luckily, there are several predictive models which allow for an estimation of the intraparticle diffusion, based on a few other parameters, to varying degrees of accuracy and applicability. The Residence Time Weighted model or RTW (also called the “time-averaged” model) a was originally proposed by Knox and Scott (1983) but was later found to be inaccurate since it assumes that the diffusion processes through the bed’s external porosity and the particle’s internal porosity occur in parallel (Desmet et al. 2008).

Later, several other models were developed using the Effective Medium Theory (EMT). These models are more accurate but require different parameters and are more or less applicable depending on the element of study. The equations share their purpose of relating the ratio of total effective diffusion and molecular diffusion - often written as \( D_{\text{eff}} / D_m \) - with the ratio of intraparticle effective diffusion and molecular diffusion, abbreviated in the equations as a parameter \( \Omega = D_{p_{\text{eff}}(PP)} / D_m \). Table 3.1 sums up the different models and their required equations.

The several data points for different parking times are then fitted to each of the different models, facilitating the prediction of the diffusion solely within the particles from the diffusion in the entire bed porosity by finding the most appropriate model. Experimentally, peak parking is a longer, more arduous process. Experiments of columns with very high tortuosity (more difficult transport) can have parking times of several days for a single data point. When performed using a wide range of molecule sizes, this can be a very time-consuming process. However, one advantage peak parking has over dynamic conditions experiments, is that it does not require very thin chromatographic peaks to retain its accuracy. This means that columns with less than perfect packing or any other issues that may cause systematic band broadening, the peak parking method is still valid, even if the results obtained may be of more difficult interpretation.
Table 3.1 – Total versus intraparticle effective diffusion models for assemblies of spheres

<table>
<thead>
<tr>
<th>Governing and associated equations</th>
<th>Theoretical basis and applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knox (RTW):</td>
<td>Based on the parallel mass density fluxes in intra and extraparticle volume</td>
</tr>
<tr>
<td>$\frac{D^{\text{eff}}}{D_m} = \frac{\varepsilon_e/\tau_e + (1 - \varepsilon_e)\Omega}{\varepsilon_t[r_m]}$</td>
<td>27</td>
</tr>
<tr>
<td>Maxwell (EMT):</td>
<td>The original EMT model; usually exact for dilute suspensions of spherical particles</td>
</tr>
<tr>
<td>$\frac{D^{\text{eff}}}{D_m} = \frac{1}{\varepsilon_t[r_m]} \left[ \frac{1 + 2(1 - \varepsilon_e)\beta}{1 - (1 - \varepsilon_e)\beta} \right]$</td>
<td>28</td>
</tr>
<tr>
<td>$\beta = \frac{\Omega - 1}{\Omega + 2}$</td>
<td>28b</td>
</tr>
<tr>
<td>Torquato (EMT):</td>
<td>Adds to the Maxwell model by considering the exact microstructural details of the fixed bed using a second order parameter ($\xi_2 = 0.3277$ for packed particle columns)</td>
</tr>
<tr>
<td>$\frac{D^{\text{eff}}}{D_m} = \frac{1}{\varepsilon_t[r_m]} \left[ \frac{1 + 2(1 - \varepsilon_e)\beta - 2\varepsilon_e\xi_2\beta^2}{1 - (1 - \varepsilon_e)\beta - 2\varepsilon_e\xi_2\beta^2} \right]$</td>
<td>29</td>
</tr>
<tr>
<td>Garnett (EMT):</td>
<td>Ignores contact between particles and assumes the different phases as cores in an overarching homogeneous phase</td>
</tr>
<tr>
<td>$\frac{D^{\text{eff}}}{D_m} = \frac{2\varepsilon_e + (3 - 2\varepsilon_e)\Omega}{\varepsilon_t[r_m] 2(3 - 2\varepsilon_e) + 2\varepsilon_e\Omega}$</td>
<td>30</td>
</tr>
<tr>
<td>Landauer (EMT):</td>
<td>Used to calculate electrical conductivity in composite materials; assumes some order in the dispersion on the different phases</td>
</tr>
<tr>
<td>$\frac{D^{\text{eff}}}{D_m} = \frac{a + \sqrt{a^2 + 0.5\Omega}}{\varepsilon_t[r_m]}$</td>
<td>31</td>
</tr>
<tr>
<td>$a = \frac{1}{4}[3\varepsilon_e - 1 + \Omega(2 - 3\varepsilon_e)]$</td>
<td>31b</td>
</tr>
</tbody>
</table>

3.5 Previous experiments on asphaltene diffusion

3.5.1 Alumina topology results

As previously stated, porous alumina is widely used in industrial applications, most notably as a catalyst support. As such, with project optimization in mind, the topological properties of alumina have been studied and scrutinized. As mesoporous γ-alumina will be used in the upcoming study, this section focuses on the results obtained with this crystalline arrangement.

Apart from its main use as a catalyst support, alumina has also been used in membranes. Roy Chowdhury et al. (2004) used a nanofiltration cells to perform steady state flux experiments on 3 µm membranes of purely mesoporous γ-alumina deposited on an α-alumina support. The
probes used were toluene and hexane with different hydration levels to perform solvent permeation experiments. Due to the low porosities of the γ-alumina as well as their purely mesoporous nature, the tortuosity values observed were extremely high, ranging from 6.4 for a structure with a pore diameter of 5.9 nm to as high as 16 for a pore size of 3.5 nm.

Similarly, Mottern et al. (2008) use a different technique (permeation porometry) to perform experiments on an identical membrane in which the γ-alumina has a thickness ranging from 0.75 to 2 µm and a pore size of 2 nm along with a secondary distribution of pores at 12 nm originating from defects in the layers. The tortuosity was measured was slightly lower, ranging from 4 to 4.2.

Mesnier (2008) studied the diffusion of a three polystyrene samples of different polymerization degree (thus different sizes) on γ-alumina with a bimodal distribution of pores, using PFG-NMR to effectively separate the diffusional contributions within the two different-sized porosities. Tortuosities near 1 were found in the macroporous network (with pore diameters of 315 and 540 nm) and as high as 7 within the mesopores (diameter around 10 nm). These results were confirmed by simulation models of adsorption-diffusion kinetics.

D’Agostino et al. (2012) performed PFG-NMR measurements on γ-alumina pellets with a pore size of 15 nm using several alkanes, alcohols and other organic molecules as probes. The tortuosity measured with alkanes, 1.70, was the most representative of the true tortuosity as many of the other probes contain functional groups which interact with the oxide surface. Of special note is the behaviour of polyols, which presented a higher rate of apparent diffusion within the pores than in the bulk solution. According to the authors this is caused by disruption of the hydrogen-bond self-interactions between the polyol molecules by the oxide surface. PFG-NMR was also used by Weiland et al. (2016) to study the topology of γ-alumina extrudates with porosities around 0.7 and pore sizes ranging from 6 to 11 nm. With n-hexane as a probe, their tortuosities ranged from 1.4 to 1.9.

Likewise, Gaulier (2016), this time using toluene as a probe, studied a range of extrudates with both monomodal and bimodal pore size distributions but similar mesoporous volumes. Among the purely mesoporous samples, the tortuosity of the extrudate with the smallest pores (9 nm) was the highest at a value of 3.4, while the value obtained with the largest pore size sample (17 nm) was 1.6. Interestingly, even with the presence of macropores, the bimodal sample’s tortuosity was still higher (1.97) than that of the mesoporous sample with the largest mesopore size. For comparison, one of the purely mesoporous samples had a similar mesopore size and its tortuosity was nearly identical to the one measured on the bimodal sample (2.01).

PFG-NMR results were compared to numerical simulations in the work of Wang et al. (2017), where alumina structures were randomly generated by iteration of the basic crystalline
structure of $\gamma$-alumina. Diffusion within these simulated structures was compared to PFG-NMR results with extrudates with monomodal pore size distributions (pore diameters around 11 nm) and porosities of 0.7. A model was achieved whose tortuosity was similar to the one obtained by PFG-NMR, both of them at around 2.3.

Kolitcheff et al. (2017) ventured to explain the high values of tortuosity observed in previous $\gamma$-alumina studies, relating these values with the specific structural arrangement of the alumina crystals and crystal aggregates. Heptane, methylcyclohexane and squalane were used to probe five extrudates with similar porous volume but different pore size distributions. Using inverse size-exclusion chromatography, the tortuosities observed were much higher than anticipated using typical models when using the porosities associated with the entire porosity range. Instead it was determined that the nitrogen physisorption pore size distributions were composed of two overlapping distributions of pore sizes corresponding to intra-aggregate and inter-aggregate porosities with very similar pore sizes. This structural complexity and hierarchical organization are deemed to be responsible for the elevated tortuosity values (2 - 3) compared to networks with similarly sized pores but made from different materials such as silica, whose tortuosity usually sits around 1.4 (Barrande et al. 2007).

Additionally, Zhang and Kolaczkowski (2017) used gas chromatography to determine the tortuosity of alumina pellets and arrived at a value of 2.2 - 3.5.

3.5.2 Asphaltene diffusion

Most of the work done so far when it comes to the diffusion of asphaltenes has been performed either on diffusion cells or using nuclear magnetic resonance using asphaltenes from real cuts of vacuum residue. Membrane diffusion cells have been used by several authors to study the diffusion of asphaltenes. These involve two stirred compartments separated by a membrane of well-defined pore size, usually below 5 $\mu$m to limit mass transfer due to convection caused by stirring.

In 1983, Baltus and Anderson analyzed a fraction of vacuum residue from Kuwait. Using SEC, the molecular weight range of the fraction was further reduced to an interval between 3 000 and 48 000 g.mol$^{-1}$, and diluted in toluene. Using the Stefan-Maxwell relation, they determined that at 25 $^\circ$C, the molecular diffusion coefficient of these asphaltenes was on the order of magnitude of 3 to $20 \times 10^{-11}$ m$^2$.s$^{-1}$ and their effective diffusion coefficient within the $4 \times 10^{-12}$ to $10 \times 10^{-11}$ range when traversing a membrane with a pore size of 20 nm, a large interval, which is to be expected with such a polydisperse solution. They have also observed a marked difference in the behavior of the membrane as asphaltenes had adsorbed on it, reducing its effective diffusion coefficient by at least 5%.
In 2011, Dechaine and Gray used cellulosic membranes with a pore size of 20 nm to analyze asphaltenes of several different origins, once again diluted in toluene to fractions of 0.1 to 0.01% in weight. They followed the evolution of the concentration of asphaltenes over time through the solutions’ absorbance in UV-Vis. They also used Fick’s molecular diffusion relationship as well as a configurational diffusion model (Deen 1987). Regardless of their origin and concentration, the asphaltenes post-separation have been shown to have a molecular diffusion coefficient of $2 \times 10^{-10}$ m$^2$.s$^{-1}$ and an effective diffusion coefficient of around $1.6 \times 10^{-10}$ m$^2$.s$^{-1}$ at 25 °C. This means the asphaltenes used were probably lighter and less polydisperse than the ones used by Baltus and Anderson, likely due to the improvement of separation technique or a difference in concentration. They also performed tests at 70 °C, yielding an effective diffusion coefficient of $4 \times 10^{-10}$ m$^2$.s$^{-1}$, an increase which is to be expected given the higher temperature.

Also in 2011, Chen et al. have used polycarbonate membranes of pore size of 1 µm to characterize a Canadian vacuum residue fraction, using supercritical extraction to separate the asphaltenes. Using a solution of 1% in weight in toluene, and replicating Baltus and Anderson’s methods, they determined the molecular diffusion value to be $2 \times 10^{-10}$ m$^2$.s$^{-1}$.

Diffusion cells with catalyst supports have also been tested. These cells have only one compartment in which a certain mass of catalyst is introduced. The concentration in the bulk solution is then followed across time. Mieville et al. (1989) used this technique to study the diffusion of asphaltenes from Maya, Hondo and Jobo crude samples within hydrotreatment alumina supports with a pore size between 4 and 30 nm. The effective diffusion of the asphaltene fraction used was determined to be between $4 \times 10^{-11}$ and $11 \times 10^{-11}$ m$^2$.s$^{-1}$. In 1998, Yang and Guin studied Boscan and California Valley crude asphaltenes diluted in THF at a concentration of 0.01% (w/w) within NiMo/Al$_2$O$_3$ catalysts with a particle size of 1 mm and pore size of 12.5 nm at 35 °C. Using the Stefan-Maxwell model the molecular diffusion coefficient was found to be between $1 \times 10^{-9}$ and $9 \times 10^{-10}$ m$^2$.s$^{-1}$ and an effective diffusion coefficient between $1 \times 10^{-10}$ and $5 \times 10^{-14}$ m$^2$.s$^{-1}$. The size of asphaltenes used was given by SEC to be between 300 and 22 000 g.mol$^{-1}$. They have observed that the larger asphaltenes have lower diffusion coefficients and adsorption isotherm tests showed that the affinity of asphaltenes increases as their molecular weight increases.

In 2009, Liu et al. studied a vacuum residue from Dagang crude, from which the asphaltenes were recovered by supercritical extraction. Once again, higher molecular weight asphaltenes were showed to have lower diffusion coefficients. Within SiO$_2$ catalysts with a pore size of 23 nm, the effective diffusion coefficient achieved was on the order of $10^{-10}$ to $10^{-11}$ m$^2$.s$^{-1}$.

Tayakout et al. (2010) used Safaniya asphaltenes with solutions from 0.1 to 5% (wt) in toluene within NiMo/Al$_2$O$_3$ catalysts at 25 °C. It was noted that mesopore size has a larger impact on
the diffusion than macropore size, which is likely to mean that diffusion through mesopores is the limiting step in the overall transport of asphaltenes through catalysts. Using a modified version of the Stefan-Maxwell model which takes into account the evolution of the size of the mesopores in time, along with the adsorption of asphaltenes, the molecular diffusion coefficient was determined to be approximately $1.1 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$ and the effective diffusion coefficient ranged from 4 to $8 \times 10^{-12} \text{m}^2 \cdot \text{s}^{-1}$, decreasing slightly as the concentration increased.

Using the same procedure and the same crude origin, Marchal et al. (2010) took samples from several stages of the hydrotreatment process and noted that asphaltenes taken from further in the hydrotreatment were smaller and more aromatic (due to the cracking of the alkali chains). Therefore, while the asphaltenes in the inlet of the process showed effective diffusion coefficient values of $8 \times 10^{-12} \text{m}^2 \cdot \text{s}^{-1}$, at the outlet, this value had increased by one order of magnitude, to $6 \times 10^{-11} \text{m}^2 \cdot \text{s}^{-1}$.

It is also possible to achieve diffusion values using nuclear magnetic resonance (NMR), particularly using a pulsed field gradient (PFG-NMR). This technique forces a magnetic spin onto the molecules and subsequently sends a pulse disrupting this magnetic field. Measuring the way in which the magnetic field of the molecules is affected, one can zero in on their diffusion behavior (Callaghan 1994).

In 2001, Östlund et al. used PFG-NMR to study a Venezuelan asphaltene sample. They used solutions in toluene with different concentrations ranging from 0.04 to 5% (wt) and arrived at values of the diffusion coefficient in the order of $2 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$. Lisitza et al. (2009) performed the same experiments on a different asphaltene sample and arrived at a similar value of $3 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$ for concentrations of 0.01% (wt) with a decrease toward $1 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$ for 0.2%, which can be explained by the formation of nanoaggregates.

Using Diffusion Ordered Spectroscopy (NMR DOSY) Korb et al. (2013) studied vacuum residue with a weight percentage of 9% (wt) and measured diffusion coefficients between 0.5 and $3 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$ at 20 °C. Durand et al. (2009) performed a wide study, encompassing crude oil from different geological origins in different solvents, showing their effect on the formation of aggregates, namely deuterated toluene, deuterated THF and deuterated chloroform. In toluene particularly, the diffusion coefficients varied from 0.4 to $6.9 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$.

Gaulier (2016) expanded on the work done by Durand et al. by studying vacuum residue from Safaniya crude oil samples to recover asphaltenes and extracted them using n-heptane. Using toluene as a solvent, the diffusion coefficients measured ranged from orders of magnitude of $10^{-9}$ to $10^{-10} \text{m}^2 \cdot \text{s}^{-1}$. This work also exposed some of the drawbacks NMR, mainly the difficulty in the discrimination of the origin of the signals measured due to the presence of toluene as a solvent, and the short relaxation times of asphaltenes being detrimental to the precise measurement of the NMR signal attenuation of protons belonging to asphaltenes.
Table 3.2 presents a summary of all the results discussed previously pertaining to the diffusion coefficient of asphaltenes.

**Table 3.2 – Summary of the diffusion coefficient values obtained for asphaltenes**

<table>
<thead>
<tr>
<th>Author</th>
<th>Method; temperature; % (wt); solvent</th>
<th>Asphaltene Origin</th>
<th>Diffusion coefficient / m².s⁻¹</th>
<th>Effective Diffusion coefficient / m².s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baltus and Anderson (1983)</td>
<td>Membrane cell; 25 °C; -%; toluene</td>
<td>Kuwait</td>
<td>3 to 20 × 10⁻¹¹</td>
<td>0.4 to 10 × 10⁻¹¹</td>
</tr>
<tr>
<td>Dechaine and Gray (2011)</td>
<td>Membrane cell; 25 °C; 0.01 to 0.1%; toluene</td>
<td>Several</td>
<td>2 × 10⁻¹⁰</td>
<td>1.6 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Dechaine and Gray (2011)</td>
<td>Membrane cell; 70 °C; 0.01 to 0.1%; toluene</td>
<td>Several</td>
<td>--</td>
<td>4 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Chen et al. (2011)</td>
<td>Membrane cell; --; 1%; toluene</td>
<td>Canada</td>
<td>2 × 10⁻¹⁰</td>
<td>--</td>
</tr>
<tr>
<td>Mieville et al. (1989)</td>
<td>Catalyst cell; --; --; toluene</td>
<td>Maya</td>
<td>--</td>
<td>4 to 11 × 10⁻¹¹</td>
</tr>
<tr>
<td>Yang and Guin (1998)</td>
<td>Catalyst cell; 35 °C; 0.01%; THF</td>
<td>Boscan and California</td>
<td>9 to 10 × 10⁻¹⁰</td>
<td>0.005 to 1 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Liu et al. (2009)</td>
<td>Catalyst cell; --; --; --</td>
<td>Dagang</td>
<td>--</td>
<td>1 to 10 × 10⁻¹¹</td>
</tr>
<tr>
<td>Tayakout et al. (2010)</td>
<td>Catalyst cell; 25 °C; 0.1 to 0.5%; toluene</td>
<td>Safaniya</td>
<td>1.1 × 10⁻¹⁰</td>
<td>4 to 8 × 10⁻¹²</td>
</tr>
<tr>
<td>Marchal et al. (2010)</td>
<td>Catalyst cell; 25 °C; --; toluene</td>
<td>HDT inlet</td>
<td>--</td>
<td>8 × 10⁻¹²</td>
</tr>
<tr>
<td>Marchal et al. (2010)</td>
<td>Catalyst cell; 25 °C; --; toluene</td>
<td>HDT outlet</td>
<td>--</td>
<td>6 × 10⁻¹¹</td>
</tr>
<tr>
<td>Östund et al. (2001)</td>
<td>PFG NMR; --; 0.04 to 5%; toluene</td>
<td>Venezuela</td>
<td>2 × 10⁻¹⁰</td>
<td>--</td>
</tr>
<tr>
<td>Lisitza et al. (2009)</td>
<td>PFG NMR; --; 0.01 to 0.2%; toluene</td>
<td>--</td>
<td>1 to 3 × 10⁻¹⁰</td>
<td>--</td>
</tr>
<tr>
<td>Korb et al. (2013)</td>
<td>NMR DOSY; 20 °C; 9%; --</td>
<td>Vacuum residue</td>
<td>0.5 to 3 × 10⁻¹⁰</td>
<td>--</td>
</tr>
<tr>
<td>Durand et al. (2009)</td>
<td>NMR DOSY; --; --; deuterated solvents</td>
<td>Several</td>
<td>0.4 to 6.9 × 10⁻¹⁰</td>
<td>--</td>
</tr>
<tr>
<td>Gaulier (2016)</td>
<td>NMR DOSY; 25 °C; 2-5%; toluene</td>
<td>Safaniya</td>
<td>1 to 10 × 10⁻¹⁰</td>
<td>--</td>
</tr>
</tbody>
</table>
3.5.3 Asphaltene adsorption

Adsorption isotherms in solution are usually traced by the solution depletion method. This consists in preparing solutions with precise concentrations, introducing the adsorbing material (a porous solid with a known specific surface area) and measuring the final concentration of the solution at equilibrium. Asphaltenes have particularly strong affinities for mineral surfaces and usually follow Langmuir-type isotherms.

Franco et al. (2013) studied the adsorption of asphaltene/toluene solutions (0.015 to 0.2% wt) in NiO/Al₂O₃ (0 to 15% wt) particles 35 nm in diameter. Isotherms were drawn at 25, 40, 55 and 70 °C with a 10-hour equilibrium.

![Figure 3.9 - Adsorption isotherms of asphaltenes from toluene on alumina nanoparticles impregnated with different percentages of nickel (Franco et al. 2013)](image)

As shown in Figure 3.9, the presence of a higher number of Ni active sites encourages adsorption. Isotherms are nearly identical at different temperatures, showing only a 10% variation in affinity. Impregnation and active site chemistry are, thus, big factors in the adsorption behavior of asphaltenes.

In 2016, Gaulier performed asphaltene adsorption tests on alumina powder at 25 °C and atmospheric pressure and near process conditions (250 °C and 50 bar). Operational temperature and pressure conditions were avoided to prevent thermal cracking processes. The results showed similar isotherm curves but a marked increase of the amount adsorbed plateau (approx. 20%) when near process conditions. This result is surprising not only because it is opposite to what the trend in the work of Franco et al., but also because adsorption is in most cases an exothermal process, which was confirmed recently by calorimetry for the case of...
asphaltene adsorption on various surfaces (Pradilla et al. 2016/1). This can be explained however by the dissociation of aggregates at very high temperatures, which in itself, completely alters the adsorbing system.

Pradilla et al. (2016/1) performed experiments with synthesized asphaltene molecules on several different materials. These will be further discussed in the experimental section, as these model asphaltenes have been used in the development of this project.

Given the extensive amount of work performed within diffusion cells and by NMR, the reason for using chromatography to study the diffusion properties of asphaltenes must be addressed. In fact, it is much easier and more intuitive to use the chromatographic method than either of the previously mentioned ones. The injection of a solution of asphaltenes in a chromatographic column is more analogous to the industrial process of injecting vacuum residue into a reactor and the study of diffusion thus becomes more similar. It is much simpler to observe the kinetics and the process of diffusion in a chromatographic column than in a diffusion cell given that the latter would require many experiments, which would be much more time consuming. Diffusion cells are also more susceptible to external conditions of temperature and to the evaporation of solvent which can disrupt the experiment or otherwise alter the results obtained while chromatography eliminates any outside interference. On the other hand, using PFG-NMR to perform measurements on large molecules confined in mesopores is difficult due to short relaxation times and weak solubility.
4 MATERIALS AND EXPERIMENTAL METHODS

4.1 Chemicals

Two chemicals have been used as mobile phases in chromatography and as solvents for adsorption from liquid phase. Tetrahydrofuran (THF) and toluene were purchased from Carlo Erba Reagents, Peypin, France and used as received. Toluene was also used as a probe molecule along with twelve polystyrenes. These polymers were purchased from Polymers Standards Service, Mainz, Germany. Dynamic Light Scattering (DLS) and Taylor Dispersion Analysis (TDA) experiments on these polymers have been performed to determine their bulk molecular diffusion coefficient and their hydrodynamic radii, were calculated with the Stokes-Einstein equation (Wernert et al. 2010). The characteristics of the probes used are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Probe reference</th>
<th>Molecular weight - $M_w$ / g.mol$^{-1}$</th>
<th>Polydispersity index - PDI</th>
<th>Molecular diffusion coefficient - $D_m$ / m$^2$.s$^{-1}$</th>
<th>Probe radius - $r_m$ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>92</td>
<td></td>
<td>2.15×10$^{-9}$</td>
<td>0.22</td>
</tr>
<tr>
<td>P1</td>
<td>162</td>
<td>1.00</td>
<td>1.51×10$^{-9}$</td>
<td>0.31</td>
</tr>
<tr>
<td>P2</td>
<td>690</td>
<td>1.09</td>
<td>7.10×10$^{-10}$</td>
<td>0.67</td>
</tr>
<tr>
<td>P3</td>
<td>1380</td>
<td>1.05</td>
<td>5.00×10$^{-10}$</td>
<td>0.95</td>
</tr>
<tr>
<td>P4</td>
<td>3250</td>
<td>1.05</td>
<td>3.19×10$^{-10}$</td>
<td>1.43</td>
</tr>
<tr>
<td>P5</td>
<td>8900</td>
<td>1.03</td>
<td>2.04×10$^{-10}$</td>
<td>2.36</td>
</tr>
<tr>
<td>P6</td>
<td>19100</td>
<td>1.03</td>
<td>1.33×10$^{-10}$</td>
<td>3.62</td>
</tr>
<tr>
<td>P7</td>
<td>33500</td>
<td>1.03</td>
<td>8.73×10$^{-11}$</td>
<td>5.50</td>
</tr>
<tr>
<td>P8</td>
<td>96000</td>
<td>1.04</td>
<td>5.08×10$^{-11}$</td>
<td>9.44</td>
</tr>
<tr>
<td>P9</td>
<td>243000</td>
<td>1.03</td>
<td>3.19×10$^{-11}$</td>
<td>15.02</td>
</tr>
<tr>
<td>P10</td>
<td>546000</td>
<td>1.02</td>
<td>2.10×10$^{-11}$</td>
<td>22.84</td>
</tr>
<tr>
<td>P11</td>
<td>827000</td>
<td>1.08</td>
<td>1.65×10$^{-11}$</td>
<td>29.09</td>
</tr>
<tr>
<td>P12</td>
<td>1850000</td>
<td>1.05</td>
<td>1.12×10$^{-11}$</td>
<td>42.90</td>
</tr>
</tbody>
</table>

A model asphaltene molecule has been used to simulate the behavior of asphaltenes through the alumina supports. This model molecule (henceforth referred to as C5PeC11) has been synthesized at the Ugelstad Laboratory, Norwegian University of Science and Technology. This
molecule has a molecular weight of 829.13 g.mol\(^{-1}\), has a carboxyl acid functional group and is a continental-type asphaltene.

![Structure of model asphaltene C5PeC11](image)

**Figure 4.1 – Structure of model asphaltene C5PeC11 (Pradilla et al. 2016/1)**

Asphaltenes extracted from a heavy cut of petroleum were also used as a point of comparison. These asphaltenes were extracted from Safaniya (Saudi Arabia) crude with n-heptane (henceforth referred to as RC7), following a process based on norm NF T60-115.

### 4.2 Porous Materials

#### 4.2.1 Alumina commercial columns

The Chromegasphere Alumina columns, manufactured and purchased from ES Industries (henceforth referred to as ESI-1 and ESI-2), have been the only commercially available chromatographic columns used in the project and their characteristics are available in Table 4.2.

<table>
<thead>
<tr>
<th>Length - L / cm</th>
<th>Diameter - d(_i) / cm</th>
<th>Particle diameter - d(_p) / μm</th>
<th>Mean pore radius - r(_p) / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.46</td>
<td>5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The column was connected to the HPLC system using capillary tubes of 0.17 mm in internal diameter with a length of 90 mm purchased from Agilent.

#### 4.2.2 Alumina powders and powder column assembly

Chromatographic columns were assembled manually using alumina powder samples. Powder was inserted into column shells of the same dimensions as the commercial column (L = 15 cm; d\(_i\) = 0.46 cm) with frits of 2 μm porosity from Supelco. The columns were connected to the HPLC system using the same capillary tubes as the commercial column. The powder chosen to pack the column is introduced inside the column shell in small portions. After each portion of powder is inserted, the column is put under high pressure (between 200 and 300 bar) in THF to compress and pack the powder. After the column is completely full and properly packed, the whole assembly is set to dry in a vacuum chamber at 50 °C overnight. Table 4.3 presents a list of the alumina powders which have been used to fill columns and their basic characteristics.
**Table 4.3 – Characteristics of the powders used to make columns**

<table>
<thead>
<tr>
<th>Powder name</th>
<th>M161</th>
<th>540B</th>
<th>700B</th>
<th>540G</th>
<th>700G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>Merck</td>
<td>IFPEN</td>
<td>IFPEN</td>
<td>IFPEN</td>
<td>IFPEN</td>
</tr>
<tr>
<td>Description</td>
<td>Neutral pH</td>
<td>Gel, treated @ 540 °C 4h</td>
<td>Gel, treated @ 700 °C 2h</td>
<td>“MEF”, treated @ 540 °C 4h</td>
<td>“MEF”, treated @ 700 °C 2h</td>
</tr>
<tr>
<td>Particle size / μm</td>
<td>63-200</td>
<td>32-50</td>
<td>32-50</td>
<td>25</td>
<td>50</td>
</tr>
</tbody>
</table>

The “gel” and “MEF” descriptors for the IFPEN powders described in table refer to the stage of production from which these alumina powders were recovered. The gel sample is retrieved after synthesis by precipitation of the aluminium salts, washed, dried, sieved and then calcinated at the treatment temperature denoted in the table. The “MEF” powders are subjected to additional kneading and extrusion processes before calcination, crushing and sieving. The kneading process involves the mixing of the gel inside rotating jaws which slightly alters its structure, eliminating the macroporosity and narrowing its mesopore size distribution.

**4.2.3 Alumina monoliths**

In addition to powders, columns were also made out of alumina monoliths. As a significant part of the time invested in this project was spent on research and testing of proper assembly methods for monoliths, a section will be dedicated to it in results and discussion section (Chapter 5). Table 4.4 presents the monoliths used and their characteristics.

**Table 4.4 - Characteristics of the monoliths used to make columns**

<table>
<thead>
<tr>
<th>Monolith name</th>
<th>FG Mono</th>
<th>360 Mono</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>IFPEN</td>
<td>IFPEN</td>
</tr>
<tr>
<td>Description</td>
<td>Used in Gaulier (2016)</td>
<td>Treated @ 700 °C 2h;</td>
</tr>
<tr>
<td>Monolith radius, r_c / mm</td>
<td>1.37</td>
<td>0.94</td>
</tr>
</tbody>
</table>

**4.3 Liquid chromatography experiments**

The project has been developed using two HPLC setups. Firstly, an Agilent 1200 series modular HPLC equipped with a high-performance degasser, a quaternary gradient pump, an automatic liquid sampler with a 100 μL injection loop and a column compartment with thermostat. This setup includes a diode-array detector which is able to record the light absorbed between 190
and 950 nm. The overall extra-column volume in this system is $63 \pm 3 \mu L$ from injector to detector. An Agilent 1260 Infinity series HPLC was also used, it is similarly equipped with a high-performance degasser, a quaternary gradient pump, an automatic liquid sampler and a column compartment with thermostat. This setup has two detectors: a variable wavelength detector and a refractive index detector. The total extra-column volume in this system is $87 \pm 2 \mu L$.

Solutions of the different probes were prepared at a concentration of $1 \text{ mg.mL}^{-1}$ in THF, a solvent which ensures the experiments with polystyrenes are performed in non-adsorbing conditions (Mori 1993). The concentration and injection volume are chosen so as to generate an absorbance of around 100 mAU at the maximum of the peak.

The temperature in the column compartments is fixed at 25 °C (unless stated otherwise in Chapter 5) and the UV detectors were set to record the absorbance at 262 nm in the case of toluene and polystyrene samples, at 526 nm in the case of the C5PeC11 asphaltene model molecule and at 290 nm for the RC7 fraction. Analytical conditions such as flow rate, parking time (if applicable) and column tested are described along with the results in Chapter 5.

- Dynamic conditions experiments

In dynamic conditions, the probe solutions are injected into the system at $2 \mu L$ (toluene/polystyrenes) or $5 \mu L$ (asphaltenes) at a series of flow rates, and made to pass through either a chromatographic or a bypass (for extra-column corrections). The flow rates used depend on the column in question and are chosen such that the working pressure of the system doesn’t exceed 150 bar.

- Peak parking experiments

Peak parking experiments are performed at a flow rate of $0.5 \text{ ml.min}^{-1}$ (powder columns), $0.2 \text{ ml.min}^{-1}$ (wide monolith column) and $0.1 \text{ ml.min}^{-1}$ (thin monolith columns). The probe solutions are injected into the system at $2 \mu L$ (toluene/polystyrenes) or $5 \mu L$ (asphaltenes). The procedure follows as such: the compound is injected into the system, and after a given time (called “stop time”) the flow within the column is stopped by changing the flow of the HPLC from the column position to the bypass position (via the six-way valve). During parking time, the pump and detector lamp may be stopped to avoid unnecessarily wasting solvent and the lamp’s working lifespan, though they must be switched on before the end of parking time to ensure a stable baseline. After parking time is elapsed, the valve is switched back to the column position and the peak is left to elute. “Stop time” is usually half the typical retention time of the probe, when the probe is approximately at the midpoint of the column.
- Taylor dispersion analysis (TDA)

Taylor dispersion analysis is used to determine the molecular diffusion of asphaltenes in toluene by studying the widening of the peak due to radial diffusion (Taylor 1954). 10 µL of a C5PeC11 solution at 0.08 g·L⁻¹ in toluene were injected into short (5 cm) and long (150 cm) polytetrafluoroethylene capillaries with an internal diameter of 0.7 mm at flow rates of 0.5, 0.1 and 0.01 mL·min⁻¹. To have valid results, TDA experiments are ensured to be in proper conditions: a residence time, $t'$, in great excess of what is necessary to let molecules diffuse radially from the center of the capillary to its edges; and a negligible contribution of the axial dispersion on the mass transfer (measured using the Péclet number - $Pe$). These conditions are specified in Equations 32 and 33, $t_0$ is the residence time of the system, $r_c$ is the radius of the capillary and $u$ is the linear velocity of the fluid.

$$t' = \frac{D_m t_i}{r_c^2} > 1.4$$ \hspace{1cm} (32)

$$Pe = \frac{ur_c}{D_m} > 70$$ \hspace{1cm} (33)

Equation 34 is used to calculate $D_m$, based on the differences in retention times and variances of peaks with a short capillary (subscript $i$) and long capillary (subscript $r$).

$$D_m = \frac{r_c^2(t_r - t_i)}{24(\sigma_r^2 - \sigma_i^2)}$$ \hspace{1cm} (34)

### 4.4 Electrical tortuosity measurements

Impedance spectroscopy measurements were performed by imposing an alternating current with a frequency range from 1 kHz to 1 MHz at a fixed voltage (30 mV). For all cases the signal coming from the electrodes was processed with a Solartron Analytical Modulab XM ECS.

- Dilution method

Dilution method tortuosity experiments were performed with a specially designed jacketed beaker (Figure 4.2) with conical inner walls to allow for the least possible amount of poorly mixed volume. The cell was kept fluidized by a magnetic stirrer. The design also allowed for experiments to be conducted with a small volume of electrolyte. The electrolyte used was a 1 mol·L⁻¹ solution of sodium chloride purchased from Sigma-Aldrich. It is crucial that this concentration is high enough to mitigate electrical double layer effects. This also ensures that conductivity within the pores is equal to the bulk electrolyte. Powder is progressively added to the beaker in increments of 0.1 to 0.2 g and the resistance is measured at each step. After each measurement, the stirring is stopped, the powder is left to settle for 10 min and the
resistance of the bulk fluid is verified to be consistent throughout the experiment. More powder is added for the next step and stirring is reinitiated.

**Figure 4.2 – Experimental setup used in the electrical tortuosity dilution method experiments: 1 – electrode; 2 – electrolyte/particle suspension; 3 – magnetic stirrer**

- **Column method**

For monolithic columns, the tortuosity was measured electrically using a different method. Monolithic chromatographic columns are assembled and saturated with a solution of potassium nitrate (1 mol.L\(^{-1}\)) and electrodes are clamped to either end of the columns’ metal fittings, from which the resistance is measured. A blank column (with no monoliths) is used as a reference. More details on the assembly of the monolithic and blank columns are given in section 5.3.3. Equation 35 gives us the total resistance, \( R \), within a cylinder in the longitudinal direction, which is proportional to its length, \( L \), and resistivity, \( \rho \), and inversely proportional to its cross-sectional area, \( A \).

\[
R = \frac{\rho L}{A}
\]  

Equation 35

The blank column used had a smaller internal diameter than the monolithic column to ensure a snug fit of the capillary connectors. Measuring the resistance of the blank column, and knowing its geometrical characteristics, one can calculate the resistivity of the blank system. It is possible, then, to calculate the resistance of a blank with a cross-sectional area equal to the cross-sectional area of the monoliths. Given that resistivity is the reciprocal of conductivity, Equation 4 is easily adapted to the measurement of resistance.

\[
\tau = \frac{R}{R_0} \varepsilon
\]  

Equation 36

- **Tortumeter method**

In individual monoliths, tortuosity was measured with an apparatus designed and built in-house designated “tortumeter” (Figure 4.3). This apparatus has a chamber designed to hold the
electrolyte and the sample. On either side of the chamber, cylindrical electrodes are axially centered and opposite each other. The distance between these electrodes can be adjusted with two micrometric control knobs to a precision of 0.001 mm. The sample is kept in place with a PMMA plastic piece specifically designed to keep the monolith aligned with the center of the electrode within the electrolyte.

**Figure 4.3** – Top: photograph of the tortuometer with circular window monolith holder (white); Bottom: cross sectional diagram of the tortuometer (a – micrometric control display; b – micrometric control knob; c – electrode connector; d – fixing lever; e – electrolyte chamber; f – electrodes)

Two different pieces were used to fix the monoliths in place: a circular window and a slit window piece. Measurements were performed with and without monolith in the holder to verify the resistivity of the liquid. The complete derivation of the mathematical equations used to calculate the resistance of the system and the tortuosity of the monolith are presented in Appendix IV.

### 4.5 Asphaltene batch adsorption tests

- Depletion experiments

Both isotherms and kinetics of adsorption tests were carried out on the asphaltene model molecule C5PeC11 as well as RC7 asphaltene sample using the solution depletion method. Tests were done on both untreated alumina (which had been exposed to the atmospheric moisture) and treated alumina (from which this moisture was partially removed). To treat the alumina,
it was set under a helium atmosphere and heated to 150 °C using a sand bath. Asphaltene solutions were then injected into the vials containing the alumina solids as shown in Figure 4.4.

**Figure 4.4 – Experimental setup for the heat treatment and adsorption isotherm/kinetics measurements (sand bath in yellow)**

All isotherms and kinetics experiments were performed at 25 °C. The vial with the solution/solid mixture is kept in a rotating mixer. After the exposure, solution samples were taken from the vials and their concentrations were measured via UV-Vis spectroscopy. Equation 37 was used to calculate the amount adsorbed per unit area, $\Gamma_{ads}$, in which $m_s$ is the mass of solid, $n_i$ and $n_f$ are the initial and final amount of solute in the liquid phase, $C_i$ and $C_f$ are the initial and final concentrations and $V_i$ and $V_f$ are the initial and final volumes (volume can change due to solvent evaporation through the pierced septum).

$$\Gamma_{ads} = \frac{n_i - n_f}{m_s} = \frac{C_i V_i - C_f V_f}{m_s}$$

The mass of solid used for both powder and monoliths was around 10 mg in a volume of 1 mL. In the experiments performed with heat treatment, the septa of the vials used was pierced twice to allow the helium to flow. This causes a small volume of toluene to evaporate over the course of the experiment. As such, the mass of the vial was measured before and after exposure to ascertain the amount of toluene evaporated.

- **Microcalorimetry**

Microcalorimetry experiments were performed using a TA Instruments TAM III Tian-Calvet microcalorimeter. A stock solution of C5PeC11 was injected in increments of 2 μL into a sample cell with alumina solid. Experiments were performed in isothermal conditions at 25 °C. The solution was well mixed, thanks to a gold propeller. The heat for each injection step was measured by thermopiles surrounding both the sample and reference cells. The experimental apparatus is shown in Figure 4.5: on the right, the reference side has pure solvent. On the left, the sample side has solid (brown) and stock solution in incrementally injected from the syringe.
at the top. The heat sink (teal - middle) keeps the temperature in the system constant, a gold propeller stirs the solution and the thermopile (in purple) measures the heat flow. The electrical resistance (red) is used to calibrate the calorimeter via the Joule effect.

**Figure 4.5 – Schematic of a Tian-Calvet differential microcalorimeter**

The experiments are divided into three steps: an initial blank experiment is performed where both the sample and reference cell contain only the solvent (toluene). Solvent is then injected into the sample cell in the same increments as experiments with the solution. The heat measured during this experiment corresponds to the heat caused by injection-related perturbations. These include the potential energy of the solvent falling into the cell, viscous effects, the compression of the vapor phase (given the addition of liquid into an otherwise closed system) which causes some condensation and any possible temperature gradients between the solvent in the syringe and the solvent in the cell, all of which are observed as a release of heat. This heat of injection is exothermal and must be subtracted from the experiments performed with asphaltene stock solution, both dilution and adsorption.

A dilution experiment where asphaltene stock solution is introduced to the sample cell with no adsorbent must be performed as well. The heat measured is equivalent to the enthalpy of dilution at each step, $\Delta h_{\text{dil}}$, of the asphaltenes from the stock solution concentration into pure toluene during the injections, as well as the heat of self-association of asphaltenes, which, again, are parallel effects to adsorption. Thus, in the adsorption experiment, where adsorbent
is present inside the sample cell, the heat measured at each step of the titration is a convolution of the heat consumed by the dissociation and dilution as well as the heat released by the process of adsorption onto the surface. As such, the dilution enthalpy must be subtracted from the experimental heat measured at each injection in the adsorption experiments, \( Q_{\text{exp}} \), which are performed with powder in the sample cell, in order to isolate the enthalpy of adsorption, \( \Delta h_{\text{ads}} \) (Equation 38).

\[
Q_{\text{exp}} = \Delta h_{\text{ads}} + \Delta h_{\text{dil}}
\]

The adsorption experiments were performed in the high affinity range of the adsorption isotherm - the initial concentration and amount of sample have been calculated such that equilibrium points fall in the high affinity region of the isotherm. The initial concentration of the mother solution was 2 g.L\(^{-1}\) and the amount of solid in the reference cell during the adsorption experiments was 10 mg. The calculations were performed via the method described by Denoyel et al. (1990), which involves the concept of Gibbs excess surface concentration.

\[
\Delta h_{\text{ads}} = \sum \Delta h_{\text{ads}}^{n_i} / n_i^a
\]

Equation 39 allows us to calculate the enthalpy of adsorption, \( \Delta H_{\text{ads}} \), in which \( n_i^a \) is the adsorbed molar quantity present in the cell at each step \( i \). As the solution is injected into the sample cell, it is assumed that the process of dilution occurs to completion and is only then followed by the process of adsorption from batch. This simplifies the calculation of what quantity is adsorbed based on the isotherm of adsorption. To this end an isotherm model is used to fit the experimental data, given by Equation 40.

\[
\Gamma_{\text{ads}} = x_0 + \frac{x_1}{1 + (C/x_2)^x_3} + x_4 e^{-C/x_5}
\]

Parameters \( x_0 \) through \( x_5 \) are chosen such that this model fits the experimental data. From here, at each injection, the amount injected is calculated. The heat from dilution already subtracted, what remains is the heat of adsorption per mole of substance.

### 4.6 Adsorption vs. flow rate tests

The apparent influence of flow rate on the adsorption was tested on monolithic columns previously saturated with C5PeC11 asphaltenes. A Gilson 302-303 HPLC pump sends the asphaltene solution into the column. The flow continues through to an Agilent Cary 60 UV-Vis spectrophotometer detector set to continuously detect at a wavelength of 526 nm using the Cary WinUV Kinetics software module. After detection, the outgoing solution loops back to the original vial to be recirculated. The concentration of the solution is chosen such that the UV-detector is not saturated (in the case of C5PeC11, below 0.4 g.L\(^{-1}\)). The cell used was a flow-
through cell with an optical path length of 10 mm. Figure 4.6 presents a simplified schematic of the setup.

*Figure 4.6 – Spectrophotometry setup; column may or may not be in use*

### 4.7 Characterization tests

- **Mercury porosimetry**

Mercury porosimetry was performed in order to characterize the porosity and pore size distribution of the different alumina samples and compare the values obtained by the different methods. Mercury intrusion and extrusion was performed on the Quantachrome Poremaster. The Laplace-Washburn equation is used to relate the volume of mercury intruded at a given pressure to pore size assuming a contact angle of 130°.

#### Table 4.5 – Mercury porosimetry characterization data

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Powders</th>
<th>Monoliths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample name</td>
<td>ESI-1</td>
<td>M161</td>
</tr>
<tr>
<td>$v_v$ / mL.g$^{-1}$</td>
<td>0.30</td>
<td>0.27</td>
</tr>
<tr>
<td>$v_{meso}$ / mL.g$^{-1}$</td>
<td>0.30</td>
<td>0.27</td>
</tr>
<tr>
<td>$v_{macro}$ / mL.g$^{-1}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$d_{meso}$ /nm</td>
<td>12.5</td>
<td>5.1</td>
</tr>
<tr>
<td>$d_{macro}$ /nm</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- **Nitrogen physisorption**

Nitrogen physisorption was performed in order to characterize the specific surface area and mesopore size distribution of the different alumina samples and compare the values obtained
by the different methods. Experiments were performed at 77 K on a Micromeritics ASAP2010 as well as a Micromeritics 3Flex. Around 200 mg of solid were outgassed at 150 °C overnight to a pressure below 1 Pa. After outgassing, nitrogen was injected into the sample and the amount adsorbed at a given partial pressure of nitrogen is measured. The BET theory is used to calculate the specific surface area of the samples. The Barrett-Joyner-Halenda (BJH) model is used to calculate the porous volume and pore diameter from the desorption branch of the isotherm (Barrett et al. 1951).

Table 4.6 – Nitrogen physisorption characterization data

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Powders</th>
<th>Monoliths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample name</td>
<td>ESI-1</td>
<td>M161</td>
</tr>
<tr>
<td></td>
<td>M540B</td>
<td>700B</td>
</tr>
<tr>
<td></td>
<td>540G</td>
<td>700G</td>
</tr>
<tr>
<td></td>
<td>FG Mono</td>
<td>360 Mono</td>
</tr>
<tr>
<td>( S_{\text{BET}} ) / ( \text{m}^2.\text{g}^{-1} )</td>
<td>110</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>281</td>
<td>251</td>
</tr>
<tr>
<td></td>
<td>286</td>
<td>232</td>
</tr>
<tr>
<td></td>
<td>194</td>
<td>180</td>
</tr>
<tr>
<td>( v_{\text{meso}} ) / ( \text{mL.g}^{-1} )</td>
<td>0.44</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>1.09</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>0.84</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>0.67</td>
</tr>
<tr>
<td>( d_{\text{meso}} ) / nm</td>
<td>13.7</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>10.3</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>13.0</td>
</tr>
</tbody>
</table>

- Thermogravimetry

The affinity of water and alumina was studied by thermogravimetry using the TA Instruments TGA Q500. Around 10 mg of sample are placed in a platinum crucible and lowered into a temperature-controlled oven under a 100 ml.min\(^{-1}\) flow rate. The evolution of the mass of the sample was measured under argon atmosphere and temperature ramp from 25 to 700 °C at different heating rates.

- Pulse-field gradient nuclear magnetic resonance (PFG-NMR)

PFG-NMR was performed to measure the longitudinal tortuosity of monolith samples. The effective self-diffusion coefficient of toluene in an extrudate, \( D_{\text{eff}} \), was measured as well as the molecular diffusion coefficient, \( D_m \), of toluene. Tortuosity \( \tau \) is calculated via a slightly modified version of Equation 5 (Hollewand and Gladden 1995) where, since the diffusion is measured directly within the pores, the porosity is not taken into account as seen in Equation 41.

\[
\tau = \frac{D_m}{D_{\text{eff}}}
\]

The molecular diffusion coefficient measurement was done on a tube filled with 10\% deuterated toluene. The deuterated fraction has the purpose of locking the NMR probe on the deuterium resonance frequency. For effective diffusion coefficient, the measure was repeated on three extrudates to take into account the batch heterogeneity. Straight extrudates were fully
immersed overnight in 10% deuterated toluene. Before measurement, one extrudate was removed from the vial, wiped with soft tissue to remove external toluene and placed vertically in a 3 mm diameter tube that was sealed. Measurements were performed with a Bruker Avance 600 spectrometer (600 MHz resonance frequency for proton). Temperature was controlled during the experiments at 295 K. The echo attenuation coefficients were measured using the Bipolar Pulse Pairs Longitudinal-Eddy-current Delay STimulated Echo (BPP-LED-STE) sequence (Wu et al. 1995) with a pulse duration, $\delta' = 2.5$ ms, a time between pulses, $\Delta' = 140$ ms and pulse separation, $\tau' = 0.05$ μs. Magnetization wave vector space is probed by varying the intensity of the gradient $g$ (from about $7 \times 10^{-3}$ Tm$^{-1}$ to $3 \times 10^{-1}$ Tm$^{-1}$), in order to obtain 16 values of attenuation from 2% to 95%. The magnetic field gradient is on the vertical direction, thus the spin displacements are probed in the vertical and the transport along the longitudinal axis of the extrudate is measured. Plotting the logarithm of the attenuation versus $g'^2\gamma'^2(\Delta'\cdot\tau'/3\cdot\tau'^2/2)$, where $\gamma'$ is the gyromagnetic ratio of the nucleus, yields a line for small $g'$ whose slope is the additive inverse of the diffusion coefficient.

- Gas pycnometry

The true density of some of the solids used was determined via gas pycnometry measurements with helium. A MicrotracBEL Belsorp-max was used to measure the difference in volume capacity of an empty cell versus a cell with 0.3 g of solid. Both blank and sample experiments were repeated ten times at a temperature of 40 °C at a range of pressures from 55 kPa to 110 kPa. All samples were pretreated at 150 °C under vacuum prior to the experiment.
5 RESULTS AND DISCUSSION

5.1 Spherical alumina powder column

A commercially available alumina powder column, column ESI-1, was chosen as the initial subject of study, as it should provide a stable and proven base to experiment with.

5.1.1 Porosity via liquid chromatography

The first step of characterization for a given bed of porous material is to determine the porosity observed by polymers of different sizes in non-adsorbing conditions. Figure 5.1 shows that the retention times decrease as the size of the molecule increases, as expected. Molecules larger than the pore size are completely excluded from the particle porosity and elute quickly through the interparticle volume.

![Figure 5.1 – Chromatographic peaks of all the probes at a fixed flow rate of 0.5 mL.min⁻¹; y-axis is the normalized peak height, A/A_max](image)

Between 3.6 and 3.9 min, there is a small and consistent perturbation of the signal. When THF (the solvent and mobile phase) is injected, the same sort of profile appears, with a small fluctuation of the baseline occurs at that same time (corresponding to the typical residence time in the column for a small molecule). This fluctuation is accounted and corrected for in each elution peak.

In chromatography, the volume of voids, \( V_v \), is given by the volume of the porous network seen by the molecule. The porosity is therefore calculated using the flow rate, \( Q \), the retention
times with and without column, $t_R$ and $t_i$, and dividing it by the total column volume, $V_t$, as given in Equation 42, a slightly altered version of Equation 2. No matter the flow rate used, the values of total porosity, $\varepsilon_t$, should be identical, if slightly smaller at higher flow rates (due to smaller residence time which grants less time to diffuse into the smaller pores), barring experimental errors.

$$
\varepsilon_t = \frac{V_v}{V_t} = \frac{Q(t_R - t_i)}{V_t}
$$

42

Adding the molecule radius modifier, $[r_m]$, adapts this to encompass all probe sizes (Equation 43). The porosity experienced by each probe is present in Figure 5.2.

$$
\varepsilon_t[r_m] = \frac{V_v[r_m]}{V_t} = \frac{Q(t_R[r_m] - t_i[r_m])}{V_t}
$$

43

![Figure 5.2](image)

**Figure 5.2** – Total porosity seen by a molecule versus the polymer/pore size ratio

To discriminate the particle porosity, it is necessary to determine the external porosity, $\varepsilon_e$. Interestingly, P8 through P12 do not observe the same volume of total porosity which is due to steric hindrance, therefore the external porosity must be determined in a different way than simply picking the porosity of the largest polymer. As proposed by Gritti and Guiochon (2007), the external (or interparticle) porosity is deduced by plotting the porosity vs the cube root of the molecular weight for the largest polymers and computing a linear regression. The value at $r_m = 0$ (y-axis intersection) of this regression is equal to $\varepsilon_e$ as shown in Figure 5.3. The value obtained is $\varepsilon_e = 0.44$.

The particle porosity, $\varepsilon_p$, can now be calculated using Equation 10 adapted, in the same way as before, to include all probe sizes (Equation 44).

$$
\varepsilon_t[r_m] = \varepsilon_e + \varepsilon_p[r_m](1 - \varepsilon_e)
$$

44
Figure 5.3 – Linear extrapolation of the porosity vs molecular weight; y-intercept is the external porosity of the material

The results of these experiments were confirmed on a second column, ESI-2, provided by the same manufacturer and produced to have the exact same characteristics and the discrimination of the two porous domains for both columns is given in Figure 5.4.

Figure 5.4 – Total and particle porosities for columns ESI-1 (O) and ESI-2 (X)

As Figure 5.4 shows, toluene and polystyrenes P1 to P7 enter the particle porosity while P8 through P12 do not. The reason the particle porosities calculated for the larger polymers are negative has to do with the fact that these very large polymers are excluded, not only from the mesopores but also, through steric hindrance, from a small fraction of the macroporosity.

From ISEC measurements of the accessible particle volume fraction, it is possible to extract the pore size distribution and an average pore size of the particles. DePhillips and Lenhoff (2000) propose the term $K'_d$ as the ratio of the section of the pore than can be occupied by a molecule of a given size and the total section of the pore (see Figure 3.7 - i), as given by Equation 45.
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\[ K_d = \frac{\varepsilon_p[r_m]}{\varepsilon_p[0]} = \frac{\int_{r_m}^{\infty} f(r) \left(1 - \frac{r_m}{r}\right)^2 \, dr}{\int_{0}^{\infty} f(r) \, dr} \]

It is customary to take the porosity of the smallest probe as \( \varepsilon_p[0] \), however, the smallest probe used, toluene is not a point-like particle and, as such, is still excluded from some of the porous network due to its size. There is an empirical relationship between external porosity and probe size relative to molecule size, detailed in Equation 46, where \( \varepsilon_p[0] \) is the porosity accessible to a probe of negligible size. This can be seen as the value of porosity accessible to the center of the molecule only (assuming spherical molecules) or to a point like molecule. As the molecule radii become more and more comparable to the pore size, the steric hindrance phenomenon takes over, as was shown in Figure 3.7.

\[ \varepsilon_p[r_m] = \varepsilon_p[0] \ast (1 - \lambda)^2 \]

As such \( \varepsilon_p[0] \) is calculated by fitting the results obtained with the different probes with Equation 46 and calculating the value at \( \lambda = 0 \). Thus, while \( \varepsilon_p[\text{Toluene}] = 0.512 \), the true value of particle porosity is \( \varepsilon_p[0] = 0.553 \). This value can be compared to the one obtained by nitrogen adsorption experiments. Equation 47 allows for the calculation of the particle porosity using the total adsorbed porous volume per unit mass, \( v_p \), and the true skeletal density, \( \rho_t \).

\[ \varepsilon_p = \frac{v_p}{v_t} = \frac{v_p}{v_p + \frac{1}{\rho_t}} \]

Using helium pycnometry it was determined that the true skeletal density of the ESI powder was \( \rho_t = 3.52 \pm 0.16 \, \text{g.cm}^{-3} \). Thus, the value of the particle porosity via nitrogen adsorption obtained was \( \varepsilon_p = 0.61 \), slightly higher than the one obtained by ISEC. The values of the pore size distribution, \( f(r) \), can thus be calculated as a function of each of probe size. This calculation is performed numerically, by minimizing the difference between the experimental \( K'_d \) and a \( K'_d \) calculated by varying the values of \( f(r)dr \) for each probe size.

Figure 5.5 shows an much wider measurement for the pore size distribution by ISEC than by any of the other methods. Having only 13 probes translates into a very noticeable lack of resolution, however, the results are not entirely unserviceable. The mean pore size as calculated using this distribution is 13.3 nm, which is in surprisingly accurate agreement with the value given by the manufacturer (13 nm) as well as the ones obtained by nitrogen adsorption (13.8 nm) and mercury intrusion (12.5 nm). The nitrogen adsorption isotherm as well as the mercury intrusion plot are available in Appendix I.
5.1.2 Dynamic method

The dynamic method (explained in section 3.4.1) was used to determine the effective particle diffusion coefficient in non-adsorbing conditions. Figure 5.6 shows the chromatograms from a small selection of the flow rates used with molecule P4. As the flow rates become lower, the retention time naturally increases, as does the variance of the peaks, both of them following inverse power laws. The solvent peak is still present here and behaves in much the same way as the main peak. As before, it is removed from analysis.

Using Equation 12, the HETP is calculated at each flow rate, taking into account the diffusion in the extra-column volumes.
Figure 5.7 – Effect of the extra-column volume correction of the HETP on a very small probe (Toluene) and a mid-size probe (P6)

For very small polymers as well as polymers which don’t enter the particle porosity, the extra-column volume correction is highly susceptible to experimental errors. This is because the peaks observed for both these cases are very thin (Figure 5.1), with a variance on the same order of magnitude as the peaks without column. Theoretically, the HETP curve should develop into a flat or slightly positively sloped curve as the flow rate increases. These slopes might have been usable in the diffusion coefficient calculations. Regrettably, experimental variances are not ideal for very small probes; toluene, for example (Figure 5.7), evolves into a flat HETP relationship with interstitial velocity, as expected, since its diffusion is extremely quick. The experimental curves for corrected HETP using P3 through P7 are positive, and thus, can be used to calculate the particle diffusion coefficient, $D_p^{eff}$, using the GRM (Equation 19). The HETP vs linear velocity as well as the linear regressions used for these calculations are shown in Figure 5.8.

Figure 5.8 – Dynamic conditions HETP curves for the mid-size polymers
5.1.3 Peak parking method

Peak parking experiments (discussed in section 3.4.2) were also performed on the commercial column. As stated, after injection, the observed peak variance should increase with parking time, $t_p$. Such can be seen, for example, in the experiments performed with toluene, presented in Figure 5.9, where the $A/A_{max}$ is the absorbance relative to the maximum of the curve obtained with $t_p = 0$ and $t - t_r$ is chosen as the x-axis to center the peaks at 0, as an aid in visualizing the effect of parking time on absorbance and band broadening.

![Peak parking chromatograms for toluene at different parking times](image)

**Figure 5.9** – Peak parking chromatograms for toluene at different parking times

Unlike dynamic conditions, peak parking is less susceptible to experimental errors since it does not require a measurement without column (diffusion is studied relative to the peak with no parking time). This means the effective diffusion coefficient, $D_{eff}$, can be calculated for polymers small enough to enter the particles - toluene through P7 - as well as for the polymers that don’t enter the porosity at all - P8 and larger - by using Equation 26. In actuality, the $D_{eff}$ obtained with the large polymers corresponds to the diffusion in the interparticle domain while the value obtained with the smaller probes considers both inter and intraparticle domains.

Figure 5.10 shows the results obtained after analysis of all the peaks. The largest polymer used is P9, since performing peak parking experiments becomes exponentially more time consuming with larger polymers, as their diffusion is slow, especially when compared with light molecules like toluene. Using a slightly modified version of Einstein’s law of diffusion (Equation 48) these slopes can be transformed into the total effective diffusion coefficient experienced by each polymer, with $u_i$ being the interstitial velocity ($u_i = u/\varepsilon_r$).

\[
D_{eff} = \frac{1}{2} \frac{t_p}{\Delta t} \frac{\varepsilon_r}{\varepsilon_i} \left( \frac{m}{r_i} \right)^2 u_i^2
\]
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Figure 5.10 – Peak variance vs parking time for the polymers used

Figure 5.11 shows how molecule size affects their behavior when confined within the porous network. Very small molecules behave throughout the system almost as if they were in bulk solution. As size increases, molecules expectedly lose mobility within the tortuous intraparticle porous network, however, a minimum of effective diffusion is observed soon after $\lambda = 0.35$. The effective diffusion value eventually stabilizes at a value of 0.8 for molecules which don’t diffuse within the mesopores.

Figure 5.11 – Effective diffusion as a function of relative molecule size; the black line delineates molecules small enough to enter the intraparticle porosity ($\lambda > 1$)

Many observations can be made from the data in Figure 5.11. Since P7 enters a very small amount of the intraparticle porosity and P8 and P9 do not enter at all, they can be used to calculate the external tortuosity of the particle bed. Typically, Equation 5 would be used, however, since peak parking experiments require the particles diffuse in the porous domain, without having to enter or exit it in the process, the external tortuosity can be calculated.
simply as the reciprocal of the effective/molecular diffusion ratio. Between these three polymers, on average, \( \tau_e = 1.3 \pm 0.1 \), which is a rather large uncertainty, considering the relatively small range of tortuosity values which are possible. Using the Weissberg equation (9), it is possible to translate these into values of \( p \). As previously stated, it is known that for a random arrangement of non-porous spheres, \( p = 0.5 \) (Barrande et al. 2007) and it is known that this particular column is packed with spherical particles, however, it was determined that \( p = 0.4 \pm 0.1 \), which is not far from the expected value.

While experiments were not performed, it is not unreasonable to expect molecules larger than the intraparticle pore size should have the same descending value of \( D_{eff}/D_m \) as molecule size approaches the interparticle pore size hence a maximum obtained with P8 - the diffusion of this molecule is more free in the aggregate than the \( D_{eff}/D_m \) of P5, since the latter intertwines its intra and extraparticle diffusion. This is could also explain the initial decline with P9, which sees less of the porosity than P8, and therefore could have a slightly more tortuous path through the column. Experiments with probes larger than P9 will, however, require an extremely large parking time so as to observe significant changes in the peak absorbance and variance.

The models previously shown in Table 3.1 were used to relate the total effective diffusion coefficient calculated with Equation 48 to the intraparticle diffusion coefficient. Deciding on the most appropriate correlation is a matter of suitability: the model is compared to the experimental values and the error is calculated by least squares method. Models are fitted to the experimental data using either a fixed particle tortuosity value, \( \tau_p \), or using the varying tortuosity model proposed in Equation 9 and optimizing the value of the parameter \( p \) (such that the particle tortuosity varies with molecule size). The calculation of the term \( \Omega = D_p^{eff}(PP)/D_m \) is discussed further in section 5.1.4. For now, Figure 5.12 shows the contrast between the experimental values and the best-fit models whose parameters are shown in Table 5.1.

![Figure 5.12](image)

**Figure 5.12** – Optimized RTW and EMT models and comparison with experimental \( D_{eff}/D_m \)
Table 5.1 – Parameters values used and sum of the error via the least squares method for each of the correlations

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Fixed $\tau_p$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>2.16</td>
<td>3.05</td>
<td>2.80</td>
<td>6.60</td>
<td>2.43</td>
</tr>
<tr>
<td>Error</td>
<td>7.4%</td>
<td>8.7%</td>
<td>6.5%</td>
<td>19.5%</td>
<td>11.9%</td>
</tr>
<tr>
<td>Variable $\tau_p$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>1.40</td>
<td>2.41</td>
<td>2.16</td>
<td>5.82</td>
<td>1.66</td>
</tr>
<tr>
<td>Error</td>
<td>3.9%</td>
<td>4.3%</td>
<td>3.4%</td>
<td>14.2%</td>
<td>18.7%</td>
</tr>
</tbody>
</table>

As Figure 5.12 reveals, none of the models predict the experimental results with complete accuracy. Particularly, fixed tortuosity models completely fail to take into account the shape of the experimental curve, with their profile being much too linear and shallow to account for the minimum of the $D_{\text{eff}}/D_m$ curve. Variable tortuosity models follow the shape more accurately but still do not go deep enough to fully encompass the both the smallest and largest molecules. The Garnett and Landauer methods seem to be useful only in a small range of relative molecule sizes (small molecules for Landauer, large for Garnett). The Torquato effective medium theory with variable tortuosity parameter has a slight edge over the Maxwell and RTW models. This is to be expected, as the Torquato model is usually seen as an improvement on the Maxwell model, since, unlike the latter, it accounts for precise microstructural details, with the addition of a second order parameter (Torquato 1985). As such, it was chosen to calculate the values of $D_{p\text{eff}}$ from the experimental $D_{\text{eff}}$ values obtained.

5.1.4 Modelling of $D_{p\text{eff}}[r_m]$

In creating an encompassing predictive model of the intraparticle diffusion as a function of probe size, it is useful to begin by assuming infinitely small probes ($\lambda \to 0$). This reasoning allows for a frictionless, unhindered particle to traverse the entire porosity. In this case, the governing equation should be identical to Equation 16 adapted from an entire bed to a single particle.

$$D_{p\text{eff}} = \frac{\varepsilon_p D_m}{\tau_p}$$

Equation 49 is widely used and valid for probes with negligible $\lambda$. The conversion to include larger relative size probes via Equations 44 and 46 was discussed above at the beginning of section 5.1.1.
The accessible particle porosity $\varepsilon_p[r_m]$ is also necessary in order to calculate the particle tortuosity, $\tau_p[r_m]$, using Equation 9. This equation also requires the constant term, $p$, which is a form factor, depending on the shape and characteristics of the porous material. It has been determined experimentally for rigid as well as porous spheres, generally, through the methods detailed in section 3.3.1.

The last term is the molecular diffusion inside the porous structure. Due to the delay caused by friction, the bulk molecular diffusion value cannot be employed as is. To quantify this friction, the Renkin model is used, which simplifies the system to calculate the friction of a sphere percolating through a cylindrical pore. Renkin’s equation takes into account the drag due to laminar flow and the steric hindrance (as discussed in section 3.4). The friction factor, $k_f[r_m]$, is a constant that relates the molecular diffusion in bulk and in the porous medium and it is given by Equation 50.

$$k_f[r_m] = \frac{D_m[r_m]}{D_m} = 1 - 2.104\lambda + 2.09\lambda^3 - 0.956\lambda^5$$  

Finally, the effective intraparticle diffusion coefficient in non-adsorbing conditions can be fully quantified by adapting Equation 49.

$$D_p^{eff}[r_m] = \frac{\varepsilon_p[r_m]k_f[r_m]D_m}{\tau_p[r_m]}$$  

Equation 51 is valid for estimating $D_p^{eff}$ in dynamic conditions. For use in the RTW and EMT models used in peak parking, a similar term is used in which the particle porosity does not appear. To use this with the term from the RTW/EMT equations, Equation 52 is used.

$$D_p^{eff}[r_m](PP) = \frac{k_f[r_m]D_m}{\tau_p[r_m]}$$  

This happens due to the difference in the basis of the methods: the dynamic method uses the $C$ term - a measure of the transfer of the probes between the inter and interparticle fluids as mentioned previously. In peak parking, the analysis is done on the probes diffusing inside the particles ($B$ term), therefore, it is not necessary to take the porosity into account. The diffusion as stated in Equation 52 is the one used to calculate the $\Omega$ term (one of the inputs in the RTW/EMT models). To compare the peak parking results to the results in dynamic conditions, it is therefore necessary to multiply $D_p^{eff}(PP)$ by the particle porosity.

An expanded version of Equation 51 follows as Equation 53, with the particle tortuosity given by the Weissberg equation.

$$\frac{D_p^{eff}[r_m]}{D_m} = \frac{\varepsilon_p[0](1 - \lambda)^2 \ast (1 - 2.104\lambda + 2.09\lambda^3 - 0.956\lambda^5)}{1 - p \ln(\varepsilon_p[0](1 - \lambda)^2)}$$
The topological parameter, $p$, is calculated as a best fit for the results obtained with peak parking. The results of the dynamic experiments as well as the models can be seen in Figure 5.13.

![Figure 5.13](image)

**Figure 5.13** – Intraparticle diffusion coefficient experimental values for the ESI-1 commercial column and comparison with models

As before, using a fixed tortuosity value, the model fails to line up the experimental results of either the peak parking or dynamic experimental values. The variable tortuosity model with $p = 1.8$ follows a very similar trend to the peak parking experiments but can deviate quite starkly from some of the experimental points. It also lines up quite well with the experimental results obtained with the dynamic method for larger molecules but loses predictive power for molecules of lower size. The dynamic method results seem, in fact, to follow a much shallower curve than the peak parking method results. Naturally, this new value of $p$ value is different to the one optimized for in section 5.1.3. That value was an input to the Torquato model while this time, $p$ is an output of the $D_p^{eff}/D_m$ model.

Peak parking results are especially useful, as they provide particle diffusion coefficient values for toluene. Since this molecule can permeate through close to the totality of the particle porosity, utilizing Equation 52, one can calculate the total tortuosity of the particles within the commercial column, via the peak parking method. The value of $\tau_p = 1.87$ is not surprising, given that the model using a fixed tortuosity value of 2 comes very close to the toluene point in Figure 5.13.

### 5.1.5 Electrical tortuosity experiments via dilution method

It is possible, then, to confirm this value with a direct tortuosity measurement using the dilution method, described by in section 4.4. Figure 5.14 shows a cluster of points taken from three
measurements. As previously stated, Maxwell (1873) offered a quantification of the conductivity of a fluidized bed.

\[
\frac{\sigma_{\text{eff}}}{\sigma^0} = \frac{2\sigma^0 + \sigma_p - 2(1 - \varepsilon_e)(\sigma^0 - \sigma_p)}{2\sigma^0 + \sigma_p + (1 - \varepsilon_e)(\sigma^0 - \sigma_p)}
\]

Combining Maxwell’s theory (Equation 54) and the proposed relationship between tortuosity and porosity given in Equation 4 shows a linear relationship between the tortuosity of the suspension and the porosity of the suspension as the porosity of the suspension, \(\varepsilon_{\text{sus}}\), tends toward unity (“infinite dilution”). The tortuosity value given by electrical measurements is given by Equation 55. This equation is solved for the conductivity ratio parameter, \(\sigma_p/\sigma^0\). As made explicit by Equation 4, this ratio is directly related to the tortuosity of the particles in the suspension.

\[
\tau_{\text{sus}} = \varepsilon_{\text{sus}} \frac{2 + \frac{\sigma_p}{\sigma^0} + (1 - \varepsilon_e)\left(1 - \frac{\sigma_p}{\sigma^0}\right)2 + \frac{\sigma_p}{\sigma^0} - 2(1 - \varepsilon_e)\left(1 - \frac{\sigma_p}{\sigma^0}\right)}{2 + \frac{\sigma_p}{\sigma^0} - 2(1 - \varepsilon_e)\left(1 - \frac{\sigma_p}{\sigma^0}\right)}
\]

**Figure 5.14** – Cluster of points obtained by three measurements by the dilution method on ESI-1 powder (orange) compared to Equation 55 (blue)

The final value of tortuosity obtained for the ESI particles was \(\tau_p = 1.78\), which corroborates the value obtained by ISEC measurements. Using the particle porosity, \(\varepsilon_p[0]\), the value of \(p\) from electrical measurements is 1.32.

The results for tortuosity and the \(p\) value from the different methods are compiled in Table 5.2.
### Table 5.2 – Tortuosity results for column ESI-1

<table>
<thead>
<tr>
<th></th>
<th>Torquato $D_{\text{eff}}/D_{\text{m}}$ fit</th>
<th>Peak parking experimental values</th>
<th>Peak parking $D_p,\tau_p$</th>
<th>Dilution method</th>
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<tr>
<td>$\tau_t$</td>
<td>1.18</td>
<td>1.05 (w/ toluene)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>2.44</td>
<td>1.87 (w/ toluene)</td>
<td>2.04</td>
<td>1.78</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>-</td>
<td>1.32 (w/ P7, P8 &amp; P9)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$p, \tau_e$</td>
<td>-</td>
<td>0.37</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 5.1.6 Commercial column characterization overview and assessment:

Both ISEC methods described in the literature for non-adsorbing conditions were used to characterize a commercial alumina column and yielded interesting results without any major complications.

After conversion with the Torquato EMT correlation, the peak parking experimental values for the intraparticle diffusion coefficient align well with the model proposed in Equation 51. The peak parking method has the major advantage that it directly studies the diffusion without any convective interference (since the flow is stopped). Another advantage is the higher accuracy for the diffusion of relatively very small molecules when compared to the dynamic method. Unfortunately, peak parking experiments for larger molecules can take extremely long times (up to and over 48 hours) for a single point in the linear fit. This also comes at the risk of any disturbance in the experimental setup, which can require repeating the injection, further extending the length of the analysis.

Conversely, dynamic method experiments are much faster to perform even using a large number of flow rates (about 2 hours per probe studied). Nevertheless, the values obtained with some of the probes (particularly P3) are quite different from expected if one assumes the intraparticle diffusion model to be correct. Following the trend of the points obtained, it is possible to see a much shallower curve than the model would predict. Such values would require a value of $p$ as high as 6, which is extremely high. The exact origin of this deviation is not known though it is suspected that the calculation through the General Rate Model might be to blame, as it assumes parallel and disconnected contributions from the mobile phase mass transfer and the particle diffusion, which may not strictly be the case.
The electrical tortuosity dilution method experiments yielded a very solid confirmation of the observations made via ISEC with toluene. The particle tortuosity values obtained from both experimental approaches differ by only 0.03, a relative experimental difference of less than 1.7%.
5.2 Powder-based chromatographic column filling

Home-made alumina columns were made by filling shells identical to that of the commercial column with different alumina powders. The main assembly method used was explained in section 4.2.2, however, before arriving at this specific method, others were tried. At first, the 700G alumina powder was used and the fluid applying the compacting pressure was water. This proved ineffective as the column was immediately plugged by fine particles, formed due to the alumina’s instability in water. A second approach involved the use of the non-polar n-hexane. Injecting 1 g.L\(^{-1}\) solutions of both toluene and P12 in THF into this column (labeled 700G-1) revealed a doubling of the elution peak as can be seen in Figure 5.15.

![Figure 5.15 – Double peaks in column 700G-1](image)

It was suspected that the appearance of double peaks was also related to the existence of fine particles inside the column, therefore washing tests were performed on the powders available from IFPEN with both polar and non-polar solvents, in order to determine whether this was the case. The washing tests involved small vials with about 10 mg of alumina powder. The solvent of choice was then added and the vials’ contents were then thoroughly mixed for periods of 45 to 60 minutes. Finally, the vials were left for 15 minutes while the particles settled. After each wash and settling, the supernatant (and any fine particles therein) was removed and the powder was left behind to be washed again. A sample was deemed suitable if after the third wash, no fine particles were observed (clear supernatant).

As Table 5.3 shows, the results obtained with powders 540G and 700G, which had been extruded before calcination, were far from ideal. These powders were a lot more fragile when submerged in any kind of solvent, which may be due to the kneading, crushing and sieving process necessitated by the extrusion to prepare the powder. The samples sieved directly after aggregation and calcination (540B and 700B) did not have to undergo such high stress processes.
Table 5.3 – Results of the powder washing tests; √ - pass; x – fail; ~ - unclear

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Wash nº</th>
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<th>700B</th>
<th>540G</th>
<th>700G</th>
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<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>✔</td>
<td>✔</td>
<td>x</td>
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<td>✔</td>
<td>✔</td>
<td>~</td>
<td>x</td>
</tr>
</tbody>
</table>

Figure 5.16 - SEM image of 700G powder; grain size varies greatly within the sample

The 700B powder was then used to make a chromatographic column (labeled 700B-1). Initial results showed some fronting of the peak but after drying the column under vacuum overnight, the peak became almost perfectly Gaussian.

Figure 5.17 – Toluene peak obtained with column 700B-1 before and after drying under vacuum
Drying the column in the vacuum chamber removes water that might have been adsorbed in the particles from when they were in contact with air and this may be what caused the peak abnormalities observed in the first graph in Figure 5.17. Since the peak is quite large (around 2 min wide for toluene at 0.5 mL.min⁻¹), peak parking was chosen to be performed since dynamic conditions require thin peaks to be as accurate as possible (the width of the toluene peak at the same conditions with the commercial column was 0.5 min, a quarter of the one observed in the powder column).

**Figure 5.18** – Total and particle porosities versus relative probe size for column 700B-1

As before, the total and particle porosities as a function of relative probe size were measured (Figure 5.18). The porosity of this powder sample is quite high ($\varepsilon_p = 0.896$ according to mercury porosimetry) so the value measured by chromatographic means ($\varepsilon_p = 0.892$) is quite accurate.

Peak parking measurements with column 700B-1 yielded peculiar results. Performed with toluene, P1 and P2, these tests were quite prolonged (unexpected due to the high porosity) and most astonishingly, peaks were thinner and taller at low parking times than with no parking time. At higher parking times, the peak width would increase and height decrease. The chromatograms obtained for toluene are shown in Figure 5.19 as well as the variances for all probes studied in Figure 5.20.

This behavior is unusual as it would mean compounds are not diffusing outwards at relatively low parking times. In fact, outward diffusion should still occur but it is likely that it is competing with another phenomenon of unknown origin.
5.2.1 Alumina powder experiments overview and assessment:

For the one semi-successful column (700B-1), a dozen had to previously fail but from all of them, vital information was retrieved: from filling with different solvents to the individual behaviors of different powders. Important spectrum information was retrieved from the experiments made with column 700G-1. A very intense absorbance peak at 215 nm was found that does not correspond to the spectrum of the toluene solution injected. This peak was also found in one of the monolithic columns discussed in section 5.3. This may be in some way connected to the increase in absorbance witnessed in column 700B-1 but fails to explain the thinning of the peak. This phenomenon is further explored in Appendix V.

A column identical to 700B-1 (with 0.5 μm frits; labeled 700B-2) was filled and washed with pure toluene rather than THF. The objective was to remove all the fine particles at once. This process caused the working pressure to continuously increase over time. The frits were changed
to the typical 2 µm yet the pressure kept increasing. The last recorded pressure with column 700B-2 was 300 bar (at 0.1 mL min⁻¹) before the column deemed unsuitable and was subsequently dismantled.
5.3 Transport in home-made monolithic columns

Given the instability of the synthesized powder samples, a different route was taken, focusing instead on the characterization and transport properties of cylindrical alumina extrudates (monoliths).

5.3.1 Column assembly development

To make columns out of monoliths it was necessary to do two things: fix them sequentially in place and connect them to the capillaries in the HPLC system. Initially, the FG Mono sample was used. Due to their large diameter, special stainless steel fittings had to be produced in order to successfully connect them to capillaries. To fix the monoliths, heat-shrink tubing made from polytetrafluoroethylene (PTFE) was used (d = 3.91 mm to d = 2.26 mm after heating). The monoliths were inserted into the tube as well as the end fittings on each side and the whole assembly was placed in a furnace with a 1 h ramp from 25 to 350 °C, then staying at this temperature for 1 h. When assembly was cooled, the PTFE tube had shrunk completely and the monoliths were secure.

![Figure 5.21 – FG Mono-1 monolithic column schematic; white – monoliths, grey – stainless steel fittings, lime green – PTFE heat-shrink tubing](image)

Column FG Mono-1 (L = 6.00 cm; m = 270.1 mg) had a working pressure of around 5 bar. The peak resulting from an injection of toluene in THF solution was an exceedingly wide peak (6 to 8 min) due to extremely prominent tailing. Nevertheless, peak parking measurements were attempted and the results can be seen in Figure 5.22.

![Figure 5.22 - Peak parking results for toluene in FG Mono-1; legend: parking time (min)](image)
It was observed that the peak variances and heights as well areas under the peak vary wildly with parking time, with no definite pattern. This erratic behavior is likely due to an abundance of dead volumes between each monolith, between the monoliths and the end fittings (since their diameter was different) and within the fittings themselves. Compatibility tests where PTFE and Monolith pieces were put into vials with THF and toluene were performed but it was determined that their presence had no effect on the absorbances measured, meaning there were no side reactions occurring. Spectral analysis of the peaks revealed that the same unexplained peak observed in the alumina powder column 700G-1 also appeared on the spectra of the peaks obtained with FGMono-1 at a similar wavelength (215 nm).

Shortly after these results were obtained, the column was dismantled and it was observed that the monoliths had disintegrated into disks due to longitudinal pressure (Figure 5.23).

**Figure 5.23** – FG Mono-1 column aftermath

Following this, the fabrication of columns using thinner 360 Mono monoliths was attempted, though under different assembly procedures. Firstly, the PTFE tube used was of smaller inner diameter (d = 1.93 mm to d = 1.17 mm after heating) to accommodate the smaller monoliths. This smaller diameter also allowed for the eschewing of the extra fittings in favor of the fittings present in the capillary connectors. The first column attempt resulted in a crooked column, due to the uneven temperature profiles within the furnace and the uneven edges of the monoliths. The solution involved introducing the column into a stainless steel tube and fixing it on both sides with Hoffman clamps. The assembly is shown in Figure 5.24.

**Figure 5.24** – Monolithic column mounting assembly and result 360 Mono-1

This assembly method proved superior yet not perfect. The low surface area of PTFE in contact with the stainless steel capillaries meant that there was not enough friction to fix the capillaries
in place. Another problem arose due to the smaller diameters – for the same flow rates, the pressure had increased (around 30 bar) which made the PTFE tube burst. To mitigate these problems, several new measures were put in place: the PTFE tube would envelope a larger section of the capillary fitting and small grooves were filed into the fittings in order to increase friction. To prevent the PTFE tube from rupturing under the elevated pressure, a second tube was wrapped around the first one. This second heat-shrink tube was lined with adhesive and shrunk at a temperature of 95 °C, which meant that the process would have to have two steps: heat up and fix the first tube in place at 350 °C, then insert the second tube and heat up the column once more, this time to 95 °C.

![Figure 5.25](image)

**Figure 5.25 – Monolithic column with second tube: 360 Mono-2**

This solution only worked temporarily. While the capillaries were no longer slipping out from the tube, after some use, another rupture occurred in the inner tube, followed by a failure of the outer tube caused by contact with the solvents. Under normal conditions, the outer tube should never be exposed to the solvents going through the column, however, since the outer tube is not rigid enough, it allows the inner tube to stretch and, eventually, burst.

The search for a solution to this problem finally ended with the use of epoxy glue as lining between the inner tube and an outer shell. The hard epoxy resin provided the necessary mechanical stability and prevented the inner tube from expanding under the pressure. Thus, a column named **360 Mono-4** (L = 8.72 cm; m_s = 0.1842 g) was assembled as shown in Figure 5.26.

![Figure 5.26](image)

**Figure 5.26 – 360 Mono-4 monolithic column**

The porosity of this monolithic column, ε_t = 0.612, determined with by ISEC, is smaller than the one given by mercury porosimetry (ε_t = 0.767). The extra-column volume adjustments have a larger impact on the results obtained since the column volume is very small and the variance of the peaks is quite large. This led to the construction of a long monolithic column, **360 Mono-7** (L = 15.98 cm; m_s = 0.3356 g), shown in Figure 5.27.
In a regular chromatographic setup, adjusting parameters like flow rate is the only way to optimize for separation quality. Making a larger column will not increase the HETP within the column but it will add to the number of theoretical plates present in the column. This will lead to a sharper peak and thus, to a more precise measurement of the porosity. This also leads to a large increase of the pressure necessary to impose a certain flow rate. Figure 5.28 shows the porosity values for the larger column.

The total porosity obtained is now comparable to the Hg porosimetry results. Bizarrely, some of the large polymers are retained for a longer time within this column and, as such seem to observe a higher porosity than some of the mid-size polymers. The pore size distribution obtained by mercury porosimetry holds some clues as to why.

Unlike the very well-defined pore domains of the commercial column pore size distribution, the monoliths display a complex array of features such as a bimodal distribution of mesopores (consistent with the intra-aggregate/inter-aggregate model proposed by Kolitcheff et al.), a large range of macropores, from 200 to 2000 nm as well as a contingent of pores between these two major features (as the volume doesn’t quite go back down to zero). Such a distribution complicates the issue further as it is not easy to define a cut-off point from the macroporosity. Molecules like P8 and P9 have hydrodynamic sizes of 19 through 30 nm and, as such, are blocked from the majority of the mesoporous network (which, from 0 to 30 nm, accounts for 60% of the porous volume of the column). Polymers larger than P8 are, therefore left to contend with what can be an assumed to be an extremely highly tortuous network of macropores while polymers
like P6 can use the mesoporosity to take “shortcuts” in between the tortuous and poorly connected macroporous domains.

\[ \varepsilon_e = \frac{v_e}{v_t} = \frac{v_e}{v_v + \frac{1}{\rho_t}} \]

Since the limit between the porous domains is not clear, the cut-off point for maximum macropore diameter was set at 50 nm - the limit per IUPAC. The value obtained for the true skeletal density of the monolith was $\rho_t = 3.43 \pm 0.17$ g.cm\(^{-3}\) and thus the macroporosity value obtained was $\varepsilon_e = 0.246$. Conversely, the value of porosity obtained by ISEC with P12 was $\varepsilon_e = 0.350$, which is almost certainly not representative of the true macroporous volume.

These tests were repeated with different columns and at a slower flow rate of 0.05 ml.min\(^{-1}\) instead of 0.1 ml.min\(^{-1}\), to ensure that enough time was afforded the molecules to explore the entire porosity, however, the same behavior was observed.

5.3.2 Dynamic method experiments

Peak parking experiments with these midsize and large polymers would be useful to confirm the shortcut hypothesis and 360Mono-7, with its sharper, thinner peaks would seem to come with this additional advantage. The wide peaks of 360 Mono-4 were unsuitable for static conditions experiments as the flow stop time overlapped with the initial detection of the peak.
With a larger column, the process of placing the molecule in the middle of the column becomes a lot less susceptible to errors. In spite of this, peak parking experiments proved unsuccessful due to two main factors: the widening and flattening of the elution peaks required parking times that were unusually long (another clue to the high tortuosity of this sample) as well as the emergence of unexpected secondary and tertiary peaks which obscured the main peak. Observing the spectra along the peak reveals, once again, a secondary absorbance peak aside from toluene with a maximum absorbance at the wavelength of around 240 nm. More information on this peak is on Appendix V.

Injections with no parking time did not generate such peaks and as such, dynamic conditions experiments were attempted. The monolithic column’s diameter is much smaller than that of ESI-1, which means that much smaller flow rates are needed to achieve the same orders of magnitude of linear velocity.

![Graph](https://via.placeholder.com/150)

**Figure 5.30** – Dynamic conditions results for polymers P4 through P7 in 360 Mono-7

As before, small probes present a challenge when it comes to the precision of the measurement and as such are not useful in the dynamic conditions experiments. The general rate model is once again used, but in a different form for monolithic columns. The different factors are the result of the different topological characteristics of the monoliths, which approximate more closely to a labyrinth of cylindrical fibers, rather than the common assembly of spheres (Miyabe and Guiochon 2002).

\[
C = 2 \frac{(1 - \varepsilon_e) \varepsilon_p [r_m]^2 \varepsilon_e}{\varepsilon_f [r_m]^2} \left[ \frac{d_s'}{4k_m} + \frac{d_s'^2}{32D_p^{eff}[r_m]} \right]
\]

Equation 57 is only marginally different from the typical GRM presented in Equation 14. Apart from a few factors, the biggest change is the swap from \(d_p'\) to \(d_s'\), this last term representing the size of the skeleton of cylinders which comprises the structure of the monolith. This is the solid porous region within which the mesopores reside and around which the macropores weave.
In the case of the monoliths used, the size of the skeleton was measured by image analysis from scanning electron microscopy (see Appendix III) as being $d'_{s} = 35.4 \mu m$. Using this value in the GRM, the diffusion coefficient within the mesopores, $D_{p_{\text{eff}}}$, for polymers of different sizes is finally calculated and compared to the different models.

Figure 5.31 – Mesopore diffusion coefficient experimental values for 360 Mono-7 and comparison with model

The value of the topological parameter, $p$, which best fits the experimental results is 3.2, as can be seen in Figure 5.31. These results should be representative of not solely of this column but be generally applicable to any column or any system using monoliths with the same topological characteristics as the ones used. Total tortuosity values cannot be calculated directly from these results as there is no value of $D_{\text{eff}}/D_{m}$ obtained for toluene via peak parking. Electrical tortuosity measurements, however, are possible.

5.3.3 Electrical tortuosity measurements on monolithic samples

The fashion with which the monolithic columns were constructed leaves them with two metal connectors, which make for convenient electrodes. The epoxy resin, the PTFE lining and the alumina itself should not be conductive, therefore, the tortuosity should be a simple ratio between the resistance measured on a column with the same cross-sectional area and length without the monolithic support and the resistance measured with the monolithic column, when both are filled with electrolyte.

Figure 5.32 – Top: Monolithic Column 360 Mono-6; Bottom: Empty mock-up/blank column
The PTFE tube in the mock-up column shown in Figure 5.32 must be a snug fit around the metal fittings, which means that it will have a smaller internal diameter than the monolithic section, whose lining is shrunk around the monoliths. Therefore, a correction was made to the resistance value obtained with the blank as stated in section 4.4. Using Equation 36 the total tortuosity of the monoliths measured was $\tau_{\text{LONG}} = 2.39 \pm 0.02$. Much like the effective diffusion coefficient, this tortuosity value should be applicable to not only the column it was measured in, 360 Mono-6, but to any column assembled with the same monoliths. PFG-NMR experiments were performed in order to confirm this value. The self-diffusion coefficient of toluene was measured at 35 °C and the tortuosity value in the mesopores in the longitudinal direction was $\tau_{\text{NMR}} = 2.54 \pm 0.02$, which while not perfectly overlapping with the value obtained by impedance measurements, implies a similar topological organization in both pore domains.

In addition to the longitudinal tortuosity measurement, the tortuosity of the monoliths was measured in the transverse direction using the tortumeter system. In the tortumeter, the monolith is set in between two electrodes using a plastic piece with an aperture. Two aperture shapes were used: circular and slit. Ideally, the different aperture geometries would have no influence on the measurement itself, only on the equation required to calculate the resistance of the monolith. The calculation has a basis in the Coulter counter method, where resistance is a function of number of particles of a specific size between the electrodes.

\[
R_2 = \int_0^{\pi} \frac{a \sin \theta \, d\theta}{c \left[ \sin^{-1}(b) + \sqrt{b^2 - b^4} \right] + d}
\]

\[
a = \frac{r_c \rho_l}{r_e^2} \quad ; \quad b = \frac{r_c}{r_e} \sin \theta \quad ; \quad c = \left( \frac{\rho_l}{\rho_c} - 1 \right) \]

\[
d_{\text{circular}} = \frac{\pi}{2} \quad ; \quad d_{\text{slit}} = \sin^{-1} \left( \frac{w_s/2}{r_e} \right) + \sqrt{\left( \frac{w_s/2}{r_e} \right)^2 - \left( \frac{w_s/2}{r_e} \right)^4} \]
Figure 5.33 depicts a schematic version of the monolith positioned within the system and the division of the system in three sets of in-series resistances. R1 and R3 are calculated using Equation 35 with an area depending on the aperture shape. R2, the resistance of the section where the monolith is positioned, is rather more complex to calculate. The relationship is given in Equation 58 (see Appendix IV for detailed derivation).

This calculation depends on the radius of the cylindrical electrode, \( r_e \), the radius the monolith, \( r_c \), the resistivity of the electrolyte, \( \rho_l \), and of the monolith, \( \rho_c \) and in the case of the slit aperture, on the width of the slit, \( w_s \). Parameter \( d \) changes with the different geometry of the aperture. R2 is obtained from the measurement. The parameter \( \rho_c \) is what the equation is solved for, since, as shown in Equation 59, it is the variable used to calculate the tortuosity in the transverse direction as a reciprocal variation of Equation 4.

\[
\tau_{\text{TRANS}} = \frac{\rho_c}{\rho_l} e^{\frac{d}{r_c}} \quad 59
\]

Experiments attempted with the circular aperture piece showed extremely high variability and low reproducibility. Given the very small volume of the monolith, all the unoccupied space at either side of the monolith necessitated a large correction which exacerbated experimental or systematic errors. Using the slit geometry, these side volumes were eliminated and, as such the sensitivity and precision were greatly increased.

<table>
<thead>
<tr>
<th>Aperture Type</th>
<th>Sample</th>
<th>N° tests (failures)</th>
<th>Tortuosity, ( \tau_{\text{TRANS}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circular</td>
<td>Monolith 1</td>
<td>3 (0)</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Monolith 2</td>
<td>5 (3)</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Monolith 3</td>
<td>2 (1)</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Monolith 4</td>
<td>3 (3)</td>
<td>-</td>
</tr>
<tr>
<td>Slit</td>
<td>Monolith 5</td>
<td>4 (0)</td>
<td>2.99 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>Monolith 6</td>
<td>3 (0)</td>
<td>3.01 ± 0.02</td>
</tr>
</tbody>
</table>

Table 5.4 – Results of transverse tortuosity measurements

All the monoliths used in the tortumeter experiments were retrieved from the same batch (360 Mono) and, as such should have the same topological characteristics. The term “failures” refers to the measurements where the tortuosity calculation diverged toward infinity; this
happens when the resistance measured is lower than what is expected from a system of parallel resistances, likely due to systematic error/lack of measurement precision. The slit aperture greatly diminishes these uncertainties as can be seen in Table 5.4. The results for tortuosity and the $p$ value from the different methods are compiled in Table 5.5.

**Table 5.5 – Tortuosity results for the 360 Mono extrudates**

<table>
<thead>
<tr>
<th></th>
<th>Dynamic $D_p^{\text{eff}}/D_m$ fit (Weissberg eq.)</th>
<th>PFG-NMR</th>
<th>Column impedance (longitudinal)</th>
<th>Tortumeter method (transverse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_t$</td>
<td>-</td>
<td>-</td>
<td>2.39</td>
<td>3.00</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>2.66</td>
<td>2.54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$p, \tau_p$</td>
<td>3.2</td>
<td>2.97</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Electrical measurements reveal a higher total tortuosity in the transverse direction than in the longitudinal direction, which implies anisotropy, that is, the sample is topologically different along different axes. SEM images of the monoliths were taken to assess this hypothesis. The images were taken from slices of the monoliths along the different planes: the top/transverse plane, as well as the side/longitudinal plane. Figure 5.34 reveals the topological anisotropy present in the monoliths.

![SEM images](image)

**Figure 5.34 – SEM images of 360 Mono slices in a) side/longitudinal plane; b) top/transverse plane**

Along the longitudinal direction, macroporous channels span the entirety of the monolith. The entrances of these macropore highways can be seen in the top view, as large dark spots. The images also show that these channels are embedded in a mesoporous network and not very well
connected, which would give credence to the hypothesis that large molecules cannot avoid traversing preferred paths through the highly tortuous and poorly connected macropores, which effectively delays their percolation through the porous network. Supplemental images can be found in Appendix VI.

5.3.4 Monolithic column characterization overview and assessment:

After much persistence, the assembly of reliable monolithic columns was developed and streamlined. This allowed for myriad tests to be performed on the monoliths, including electrical longitudinal tortuosity tests and ISEC, along with everything that can be done with individual monoliths such as every surface and topological characterization test. This versatility, of course, proved to be even more of an asset when performing tests with asphaltenes.

360 Mono-4 was the first column on which chromatography was performed successfully, though the results were lacking. The low column volume coupled with leaks in the assembly spelled the end for this column. Its successors fared significantly better: 360 Mono-6 provided accurate results for the longitudinal tortuosity, comparable to the values obtained by a tried and tested technique, PFG-NMR. It is worth noting that even the 360 Mono-6 column suffered from increases in pressure, particularly during the longitudinal tortuosity tests, when it was flushed with water and electrolyte. Much like what happened with the powder columns, the alumina monoliths also cannot withstand contact with water without damage.

Assembling the extra-long 360 Mono-7 meant eschewing chromatographic results at higher flow rates in favor of a higher column volume. Even at flow rates as low as 0.1 mL.min\(^{-1}\), the column worked at a pressure of 150 bar. This proved to be an excellent gamble, as the results obtained from this column were the most interesting and accurate yet. Dynamic conditions experiments were therefore performed. While not as complete a characterization by ISEC as the commercial column, the monolithic column yielded satisfying results.

One peculiarity of the results obtained from 360 Mono-7 is that smaller and larger probes had HETP slopes which were exploitable, unlike in the case of the commercial column, where only the midrange polymers provided adequate results for dynamic conditions. The diffusion values obtained for smaller probes were uncharacteristically small. The fact that positive slopes were obtained for the entire molecule range is probably an effect of the pore size distribution’s complexity.

One of the main drawbacks of ISEC is that it is restricted to the analysis of cylindrical extrudates. Some industrials catalyst supports have a multilobed shape (trilobe, quadrilobe). Making a perfectly sealed column with such complex shapes would be a challenge.
The monoliths show a very high tortuosity which makes it very difficult for large molecules to traverse the porous network. This is of the utmost importance when discussing the behavior of asphaltenes. This is no more evident than on the results of the tortumeter experiments, where it is shown that in the transverse plane, the tortuosity of the monoliths can be as high as 3.

The tortumeter shows great promise and versatility and its power should be further explored into what can, perhaps, become a routine experimental setup within a characterization laboratory. Equation 58 must be solved numerically, which complicates data processing, however, improvements to the geometry of the setup can simplify these formulae.
5.4 Adsorption and transport of asphaltene molecules

With a solid understanding of non-adsorbing transport within different alumina supports, the main goal of studying the complex mechanisms of asphaltene diffusion is finally the focus of study.

5.4.1 Batch asphaltene adsorption tests

The first step in studying the behavior when exposed to alumina surfaces is the measurement of an experimental adsorption isotherm. The C5PeC11 is very similar to the molecules of some organic dyes (its central aromatic island is identical to that of pigment Violet 29). Both dry and in solutions with a concentration above 2 g.L\(^{-1}\), the molecule has a dark red appearance. At lower concentrations the color tends toward progressively lighter shades of orange as can be seen in Figure 5.35.

\[ \text{Figure 5.35} \quad \text{Solutions of C5PeC11 in toluene with concentrations ranging from 0.01 g.L}^{-1} \]

\[ \text{to 2 g.L}^{-1} \]

Experiments were performed on M161 powder and 360 Mono extrudates with and without heat treatment (150 °C under helium). The adsorption isotherm was obtained according to the methods described in section 4.5.

\[ \text{Figure 5.36} \quad \text{Adsorption isotherms of C5PeC11 at 25 °C for alumina powder, monolith and treated monolith (dashed lines are best approximations of the Langmuir adsorption model)} \]
As Figure 5.36 shows, the C5PeC11 asphaltenes have a high affinity for the alumina surface, regardless of morphology or treatment. Equation 60 shows the Langmuir model in its dimensionless form, with the concentration compared to a reference state with concentration, \( C_0 = 1 \text{ mol.L}^{-1} \).

\[
\Gamma_{ads} = \frac{\Gamma_{max}b_0 \frac{C}{C_0}}{1 + b_0 \frac{C}{C_0}}
\]

Adjusting the maximum capacity, \( \Gamma_{max} \), and affinity, \( b_0 \), parameters, the Langmuir model fits all the curves quite adequately and has been used on both the modelling of the adsorption of real asphaltene fractions (Tayakout et al. 2010, Gaulier 2016) as well as the model asphaltenes used in this study (Pradilla et al. 2016/2). Thermodynamically, \( b_0 \) is equivalent to the equilibrium constant of the adsorption mechanism, which means it can be used to calculate the Gibbs free energy, \( \Delta G \), via Equation 61.

\[
\Delta G^0 = -RT \ln b_0
\]

Table 5.6 shows the parameters which best fit the Langmuir model to the experimental results.

**Table 5.6 – Best fit Langmuir model parameters for C5PeC11 adsorption isotherms**

<table>
<thead>
<tr>
<th></th>
<th>( \Gamma_{max} ) (mg.m(^{-2}))</th>
<th>( b_0 )</th>
<th>( \Delta G^0 ) (kJ.mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>M161 Powder</td>
<td>1.16</td>
<td>5.12 \times 10^5</td>
<td>-32.59</td>
</tr>
<tr>
<td>360 Mono (Untreated)</td>
<td>1.12</td>
<td>8.66 \times 10^3</td>
<td>-22.47</td>
</tr>
<tr>
<td>360 Mono (Treated)</td>
<td>1.61</td>
<td>1.01 \times 10^4</td>
<td>-22.86</td>
</tr>
</tbody>
</table>

Untreated monolith and powder supports have a similar capacity, around 1.1 - 1.2 mg.m\(^{-2}\) while heat treated monoliths, unsurprisingly present a much higher capacity, as the water molecules which are typically adsorbed on the hydrophilic alumina surface are released when the sample is treated under the inert atmosphere and at high temperature. This leaves more of the alumina surface exposed as well as creating more energetic adsorption sites (as will be discussed later). For the purposes of these experiments, the treatment is performed at 150 °C, however thermogravimetric analysis (Figure 5.37) shows that water is continuously released even at much higher temperatures, with only a slight inflexion point present close to the treatment temperature of 150 °C.

It is, therefore, difficult to remove all the water adsorbed on alumina surfaces. Temperatures higher than 700 °C border on the phase change temperatures from \( \gamma \)-alumina into other crystalline configurations (Wefers and Misra 1987).
Figure 5.37 – Thermogravimetry performed at two different heating rates

Figure 5.38 shows a comparison between the adsorption behavior observed in alumina and different materials studied by Pradilla et al. (2016/1). Alumina and silica surfaces have similar surface capacities which is to be expected since they have the same functional interaction even if silica is weakly acidic and alumina tends to be neutral or weakly basic. Stainless steel and calcite have different surface chemistry and different interactions with the asphaltene molecules.

Figure 5.38 - Adsorption isotherms of C5PeC11 on different surfaces at 25 °C; results on silica, calcite and stainless steel are taken from Pradilla et al. 2016/1

The kinetics of adsorption were determined using a solution of C5PeC11. Adsorption on the powder sample was predictably quick, as equilibrium was reached after around 60 minutes. In the monolithic supports, however, achieving equilibrium took much longer, at over 24 hours. The surface chemistry of the powder and monoliths is the same, therefore, it is safe to assume
that these results are, in fact, not strictly related to the kinetics of adsorption, but indeed a convolution of the adsorption kinetics and the diffusion of the asphaltene molecules within the monolith support, as they scour the surface for higher energy adsorption sites. Interestingly, the kinetics of adsorption were not affected by heat treatment, which again, supports the hypothesis that mass transfer limitations are the limiting factor, rather than the kinetics of adsorption (Figure 5.39).

Assuming an effective diffusion coefficient of $D_{eff} = 1 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ (a value commonly seen in the literature, as discussed in section 3.5.2) one can calculate the characteristic time for diffusion, $t_d = d^2 / D_{eff}$, with $d$ being the characteristic length of each support. It is possible to verify that given the ratio of the particle to monolith radius, it is expected that the kinetics observed with the monolithic sample should be at least 200 times slower than the powder sample.

Microcalorimetric studies further elucidate the interactions between the asphaltene model molecules and the alumina surface. These experiments were performed on M161 powder as well as small pieces of 360 Mono with the procedure detailed in section 4.5. During the dilution measurement, it is observed that the heat released as the concentration of C5PeC11 increases in the sample cell follows a pattern expected from self-association, more specifically, dimerization. As the molecules in the high concentration stock solution enter the sample cell, they come in contact with the solvent at low concentrations and the molecules that would be dimerized in the stock solution dissociate, which is the source of the endothermal peaks observed.

$$ (C5PeC11)_2 \leftrightarrow 2(C5PeC11) $$

$$ K_d = \frac{[(C5PeC11)]^2}{[(C5PeC11)_2]} $$
Using the van ‘t Hoff equation (Equation 64) it is possible to calculate equilibrium constant of the dissociation reaction, \( K_d \), from its relationship with the molar enthalpy of dissociation, \( \Delta H_d \).

\[
\frac{d}{dT} \ln K_d = \frac{\Delta H_d}{R T^2}
\]

Each step \( n \) of the calorimetric experiment, the total concentration of asphaltene molecules in the cell, \( C_{cell,n} \), either monomers or dimers, is known and can be calculated using Equation 65, where \( C_s \) is the concentration of the stock solution, \( V_{inj} \) is the volume introduced per injection and \( V_i \) is the initial volume of solvent within the cell.

\[
C_{cell,n} = [(C5PeC11)] + 2[(C5PeC11)_2] = \frac{C_s \cdot n V_{inj}}{V_i + n V_{inj}}
\]

Combining Equations 63, 64 and 65, as well as performing the mass balance described in Hallén et al. (1988) gives us the enthalpy observed in each step, \( \Delta H \), is given by Equation 66:

\[
\Delta H = \frac{\Delta H_d [(C5PeC11)]^2}{K_d C_{cell,n}}
\]

The concentration of monomer in the cell is a function of the total concentration as well as \( K_d \).

\[
[C5PeC11] = \sqrt{\frac{K_d^2 + 8K_d C_{cell,n} - K_d}{4}}
\]

Finally combining Equations 66 and 67 and algebraically simplifying, one finally obtains Equation 68:

\[
\Delta H = \frac{\Delta H_d \left[K_d + 4(C_{cell,n} - C_s) - \sqrt{K_d^2 + 8K_d(C_{cell,n} - C_s)}\right]}{8(C_{cell,n} - C_s)}
\]

This model fits remarkably well with the measurements. Figure 5.40 presents the experimental results as well as the model fit and Table 5.7 shows the parameters obtained, including the free energy of dissociation, \( \Delta G_d \), and the entropy, \( \Delta S_d \), calculated from Equation 69.

\[
\Delta G_d = \Delta H_d - T \Delta S_d
\]

<table>
<thead>
<tr>
<th>( K_d ) (mol.L(^{-1}))</th>
<th>( \Delta H_d ) (kJ.mol(^{-1}))</th>
<th>( \Delta G_d ) (kJ.mol(^{-1}))</th>
<th>( \Delta S_d ) (J.mol(^{-1}).K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.021</td>
<td>22.5</td>
<td>-9.5</td>
<td>107.4</td>
</tr>
</tbody>
</table>

Table 5.7 – Best fit parameters for dissociation model
The dissociation equilibrium constant is quite low, meaning the dimerization reaction is favored. At 2 g.L\(^{-1}\), the initial concentration, around 50% of the asphaltenes molecules are present as dimers. Simon et al. (2016) performed these same dilution experiments with stock solutions of C5PeC11 in xylene at different concentrations. The values were found to be in the same order of magnitude for both \(\Delta H_d\) and \(\Delta S_d\), though, about twice as high as the values obtained in this study. This difference may be due to different solvent used (a xylene mixture).

The structure proposed by Simon et al. is a stacking of two asphaltene molecules with stacked aromatic rings (\(\pi-\pi\) bonds) as well as hydrogen bonds in the acidic functionalization (Figure 5.41). This is confirmed in the paper by comparison with the heats of adsorption obtained for the dimerization of stearic acid (aliphatic compound with 18-carbon chain and one carboxylic acid functionalization).

Following the dilution study, the asphaltene solution was titrated with M161 alumina powder and 360 Mono in the sample cell. Results can be found in Figure 5.42.
Figure 5.42 – Calorimetry results for the adsorption of C5PeC11 in different alumina surfaces

There is a marked difference between the adsorption in untreated and treated powder. The enthalpy of displacement at low concentrations is much higher, meaning a lot more energy is being released by the initial adsorption of asphaltenes. An enthalpy curve with the shape observed in the adsorption in treated powder is characteristic of heterogeneous systems, meaning there are different adsorption sites. The enthalpy measured is, in fact, an enthalpy of displacement encompassing the desorption of the solvent from the surface and the adsorption of the species in question, in this case C5PeC11 (Denoyel et al. 1990).

The alumina’s surface chemistry is identical with and without in both cases, therefore it is the displacement that must be causing this difference. As previously discussed, heat treatment removes some of the water adsorbed in the alumina surface. As before, treatment consists in exposing the sample to a vacuum at 150 °C, which, according to thermogravimetric results, removes about 50% of the water adsorbed in the alumina’s hydrophilic surface. The desorption of water must, therefore account for some of the loss of energy released by the adsorption of asphaltenes in the untreated sample. These higher energy sites are filled by the first molecules arriving in the sample cell and, as concentration increases, newly arriving C5PeC11 must compete with the water still present after heat treatment for the remaining sites.

The trend is precisely the same in the monolith sample, though there is a slight dip in the adsorption enthalpy at the start. The equilibration time used might not have been enough in the experiment with monoliths, especially given the highly diffusion-dependent kinetics of adsorption. However, the monolith used in the calorimetry experiments was much smaller (length-wise and mass-wise) than the monoliths used in the batch adsorption isotherm
experiments. It is more difficult to explain, however, why the enthalpy of adsorption in the monolith seems to be so much higher than the one obtained by with the powder sample.

As a point of comparison to the C5PeC11 model asphaltenes, a mixture of asphaltenes extracted from crude (dubbed RC7) was studied in using the same methods. It terms of color, the dried RC7 is much closer to black and grey than the bright orange C5PeC11. In solution with toluene, this translates to a translucent sandy color at low concentration, evolving into darker and darker shades of caramel as concentration increases. At concentrations above 1 g.L⁻¹, the solution becomes opaque.

![Figure 5.43](image)

**Figure 5.43** – Solutions of RC7 in toluene at concentrations ranging from 0.01 g.L⁻¹ to 3 g.L⁻¹

Experiments were performed with both untreated and heat-treated 360 Mono extrudates as adsorbate with precisely the same setup as the one used for the C5PeC11 experiments. Figure 5.44 displays the results obtained as well as Langmuir model fits (parameters in Table 5.8) for both untreated and treated samples.

![Figure 5.44](image)

**Figure 5.44** – Adsorption isotherms obtained with RC7 on untreated and treated monoliths

<table>
<thead>
<tr>
<th>Table 5.8</th>
<th>Best fit Langmuir model parameters for RC7 adsorption isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Gamma_{\text{max}}$ (mg.m⁻²)</td>
</tr>
<tr>
<td>360 Mono (Untreated)</td>
<td>0.44</td>
</tr>
<tr>
<td>360 Mono (Treated)</td>
<td>0.29</td>
</tr>
</tbody>
</table>
It is immediately evident that adsorption of RC7 in alumina is much weaker than the model molecule both in terms of affinity and capacity. The acidic functionalization in C5PeC11 interact much more strongly with the alumina surface. It would be hasty to assume that none of the asphaltenes in the RC7 fraction have an acidic functionalization but it is evident that most do not, due to their notorious polydispersity. It is strange, however, that treated alumina samples have a lower maximum capacity than the untreated alumina. In both cases, the plateau of adsorption was never experimentally observed. Gaulier (2016) performed similar experiments with asphaltenes extracted from the same source by the same process and required concentrations at equilibrium of well above 4 g.L\(^{-1}\) to achieve the isotherm plateau.

It can be, therefore, assumed that at these low concentrations relative to the concentrations necessary to achieve the plateau of adsorption experimental errors are too great for accurate results. This does not mean that these results are without worth. The capacity and affinity of RC7 can definitively be said to be significantly lower than that observed with the C5PeC11 molecule, meaning that it alone cannot complete model the behavior of real asphaltene systems.

Kinetics of adsorption were also studied (Figure 5.45). Both untreated and treated samples seem too follow the same kinetics, the same behavior observed with C5PeC11. Consistently enough, equilibrium with RC7 is also reached after roughly 24 hours. Since it is known that diffusional phenomena are the limiting factor in the kinetics, this somewhat implies that, on average, the diffusional properties of the molecules in the RC7 mixture are similar to the ones of the C5PeC11 model molecule.

**Figure 5.45** – Kinetics of adsorption of RC7 on untreated and treated monoliths

### 5.4.2 Study of asphaltene adsorption and diffusion chromatographic columns

Combining the knowledge of the chromatographic techniques and results obtained from sections 5.1 and 5.3 with the data on asphaltene adsorption gathered in section 5.4.1, the adsorption and diffusion of C5PeC11 were studied using chromatography and spectrometry.
Prior to any injection in a column, Taylor Dispersion Analysis (TDA) was performed on the C5PeC11 asphaltenes, with the objective of determining the molecule’s bulk diffusion coefficient. Given the asphaltenes’ propensity for adsorption in stainless steel, the tests were performed using PTFE capillaries, as described in section 4.3. Three different flow rates were used, however, only one fulfilled the necessary requirements.

**Table 5.9 - TDA parameters and results for different flow rates**

<table>
<thead>
<tr>
<th>Q (mL.min⁻¹)</th>
<th>u (mm.s⁻¹)</th>
<th>t'</th>
<th>Pe</th>
<th>Dₘ (m².s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>21.7</td>
<td>0.8</td>
<td>4853</td>
<td>1.56 × 10⁻⁹</td>
</tr>
<tr>
<td>0.1</td>
<td>4.33</td>
<td>1.3</td>
<td>3091</td>
<td>4.90 × 10⁻¹⁰</td>
</tr>
<tr>
<td>0.01</td>
<td>0.43</td>
<td>11.4</td>
<td>363</td>
<td>4.17 × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

The value obtained for Q = 0.01 mL.min⁻¹ is the only one which respects both of the conditions imposed, therefore it is the one used. The molecular diffusion coefficient for C5PeC11 is in the same order of magnitude as the values obtained for real asphaltene fractions, previously discussed in section 3.5.2. The hydrodynamic radius of the asphaltene molecule was calculated using the Stokes-Einstein equation (70) where $k_B$ is the Boltzmann constant, $\eta$ is the viscosity of the mobile phase (toluene) at the temperature, $T$, at which the experiment was performed.

$$r_m = \frac{k_B T}{6\pi \eta D_m}$$  \hspace{1cm} (70)

The hydrodynamic radius of C5PeC11 was calculated to be 0.94 nm, very similar to the size of polystyrene P3 ($r_m = 0.95$ nm). The molecular structure C5PeC11 supports this result. The molecule’s core has a total length of 1.11 nm (calculated using geometrical considerations and with a C-C aromatic bond size of 139 pm) and width of 0.556 nm. With the addition of the alkyl chains on either side, a hydrodynamic radius of around 1 nm is expected.

The initial asphaltene injection test used 10 µL of a solution with 0.08 g.L⁻¹ of C5PeC11 in toluene which were injected into a column filled with M161 alumina powder (column M161-1) with toluene as a solvent and mobile phase. No elution peak was observed after a long period of time. Instead, the pressure inside the column increased until at least 100 bar. This same experiment was performed in the ESI-1 commercial alumina column, this time with THF as a solvent and mobile phase. The exact same behavior was observed: no elution peak, large increase in pressure (this time, the last recorded pressure was of 238 bar).

To reverse this pressure increase, the columns were flushed overnight with toluene at 50 °C, followed by a change back to THF. Chromatograms of toluene in THF before and after this asphaltene injection and the subsequent washing showed identical elution peaks, which points
toward a complete reversibility of this extreme pressure increase. Given that the adsorption behavior of the asphaltenes is quite strong and that such a minuscule quantity of asphaltene molecules was injected, it is likely that those asphaltenes were never released from the alumina surfaces. This became abundantly clear when 11 µL of the same solution were injected into column 360 Mono-4. Initially, the pulse of the C5PeC11 molecule can be clearly seen entering the column (due to the molecule’s orange color), however, it did not leave the first few centimeters of the column after washing at 50 °C for 24 h. Even after 5 h of washing at 100 °C, the region coated with asphaltenes had axially expanded but not beyond the first 10% of the column length (Figure 5.46).

![Column 360 Mono-4 after asphaltene injection](image)

*Figure 5.46* – Column 360 Mono-4 after asphaltene injection a) immediately after injection; b) after washing at 100 °C

This lack of elution peaks, of course, prevents the study of diffusion through ISEC. It was therefore decided that the following tests should be performed at saturation conditions, that is, the monoliths must be preloaded with adsorbed C5PeC11.

The powder columns in which the previous tests were performed contain a relatively large volume and, consequently, a large absolute surface area for the asphaltenes to adsorb to. Work at saturation with such columns would require an excessive amount of C5PeC11 to be adsorbed. Columns M161-1 and ESI-1 have a second drawback as they are lined with stainless steel and require a stainless steel frit on either side to prevent powder from entering the chromatographic setup. As C5PeC11 adsorbs strongly on stainless steel surfaces, this can introduce further uncertainty. Given these conditions, monolithic columns with singular monoliths were chosen as a stationary phase for C5PeC11 chromatographic study. The use of very small columns also removes the possibility of peak parking experiments.

Since the columns must withstand high temperatures so that the PTFE lining shrinks around the monoliths, it is not viable for the monolith to be saturated before column assembly. Thus, the surface of column **360 Mono-8** (L = 1.43 cm; mₐ = 30.3 mg) was progressively covered with C5PeC11 asphaltenes using the HPLC. A solution of 2 g.L⁻¹ was, over several injections, introduced into the column. Throughout the course of these injections, the elution peak was
eventually observed and progressively became larger and larger. It was considered that the column had reached a pseudo-steady state when the height of the elution peaks had stabilized, which would imply that the quantity of asphaltenes being introduced into the column and exiting the column is equal. Figure 5.47 shows the profile of the column after it reached its pseudo-steady state.

**Figure 5.47** – Column 360 Mono-8 in pseudo-steady state

The concentration profile along the column appears to be irregular. The color of the entire column has changed from the monoliths' bright white to a pink hue, however, the first few millimeters of the column are significantly darker than the remainder of the column. This is most likely due to the flow path within the column. The capillary connecting the HPLC apparatus to the monolith has a small internal diameter, 0.17 mm, while the monolith has a diameter of 1.88 mm. This sudden shift in diameter creates very pronounced dead volumes at the beginning and end of the monolith. The purple patch at the beginning of the column is a lot more noticeable, however, near the end the monolith does also become a darker shade of pink.

Dynamic conditions experiments were using the C5PeC11 molecule with flow rates ranging from 0.01 mL.min\(^{-1}\) to 0.2 mL.min\(^{-1}\). Even at these seemingly low flow rates, the residence time within the column is quite low, given the columns small width and short length. At the quickest flow rate, the interstitial velocity of the mobile phase is 0.38 cm.s\(^{-1}\), meaning that, to traverse the entirety of 360 Mono-8 takes less than four seconds.

As a point of comparison, it is expected that a non-adsorbing molecule of a similar size (P3) would have a retention time of about 0.36 min in this single monolith system, which is very close to what is observed with the asphaltene molecule (0.40 min), which seems to indicate that there is indeed a fraction of the asphaltenes which pass through the column with minimal to no interaction with the alumina surface. However, as Figure 5.48 shows, there is heavy tailing in the peak observed when injecting C5PeC11. The molecules which generate the tailing part of the peak are the ones interacting, more or less strongly, with the surface. The peak is, therefore, not gaussian. An exponentially modified gaussian fit was attempted but it was found that the asymmetry is too great even for such a function.
Reactive Transport through Nanoporous Materials

Results and Discussion

Figure 5.48 - Chromatogram obtained from an injection of 5 μL of a 2 g.L⁻¹ solution of C5PeC11 into a saturated 360 Mono-8 at 0.2 mL.min⁻¹ as well as attempts at curve fitting

Both functions failing, the analysis of the peak must be performed by calculating the first and second moments of the peak, \( \mu_1 \) and \( \mu'_2 \), given by Equations 71 and 72 as a function of the absorbance over time, \( A(t) \).

\[
\mu_1 = \frac{\int_{0}^{\infty} tA(t)dt}{\int_{0}^{\infty} A(t)dt} \tag{71}
\]

\[
\mu'_2 = \frac{\int_{0}^{\infty} A(t)(t - \mu_1)dt}{\int_{0}^{\infty} A(t)dt} \tag{72}
\]

This, of course, comes with a complication when it comes to choosing the end point for the integration. Since the tailing is exceedingly large, the baseline does not quite reach zero at the end of each experiment. This also means that there are asphaltenes being released from the column at time-scales theoretically stretching out to infinity. The pseudo-steady state is therefore the only possible condition to work under. One possible idea would be to flush the column until a true zero is achieved, where no asphaltenes are released. This is not possible since the stationary phase is pure toluene and, theoretically, asphaltenes would be continually released until complete or close to complete desorption. In reality, as seen previously with column 360 Mono-4, such would seem to involve absurdly large time-scales to flush the column after each injection. If there is an irreversibly adsorbed portion of C5PeC11, this mean no asphaltenes are released, which could facilitate the arrival at a stable baseline. However, at this point in the adsorption isotherm, an elution peak is not observed, as the amount of C5PeC11 being added to the column at each injection gets immediately and strongly adsorbed, only to
be slowly released over long periods of time as the column gets flushed with pure toluene. The concentration at which these asphaltenes would reach the HPLC detector would be low enough as to be indistinguishable from noise.

This was, in fact, observed experimentally with the dynamic conditions experiments. One injection was performed at each flow rate, starting at the highest flow rate, going down in 0.01 mL.min\(^{-1}\) increments. As the flow rate decreased, the height and area of peak observed decreased to the point where there is barely an observable peak when flow rates become lower than 0.05 mL.min\(^{-1}\). This decrease in peak height is shown in Figure 5.49. This also implies an apparent influence of flow rate on adsorption (which will be discussed further ahead in this section).

![Figure 5.49 - Deterioration of the pseudo-steady state over the course of the tests](image)

The experiment was repeated at 5 injections per flow rate. If the last three to four injections had a peak height within 5% of each other, the system was considered to be in a pseudo-steady state. This caused peaks at lower flow rates to become a lot more defined and distinct from the noise as a higher percentage of the asphaltenes that were injected made their way out of the column. Figure 5.50 illustrates the difference between the peaks obtained with the two methods. It is of note that the tailing is nevertheless extremely wide.

One critical point to consider, then, is that these results and the conclusion taken denote that the order in which the injections are performed matters. Experiments are performed from the highest to the lowest flow rate, a protocol which was followed in subsequent experiments. The HETP is calculated in the same way as in non-adsorbing conditions (Equation 11), this time with the first and second moments substituting the mean and variance of the peaks (Figure 5.51).
Results and Discussion

Figure 5.50 – Differing C5PeC11 elution peaks at a flow rate of 0.4 mL.min\(^{-1}\) by different experimental methods

Figure 5.51 – Uncorrected HETP values for dynamic conditions experiments with C5PeC11

Calculated HETP values are extremely high, ranging from 5 to nearly 15 mm, bigger than the column itself, indicating extremely low efficiency, which is expected given the width of the tailing observed. The HETP curve does not follow the characteristic shape of the van Deemter equation. A quick analysis of the area under the peaks shows that, even at the pseudo-steady state, the amount of C5PeC11 recovered after the peak elutes completely (when the absorbance measured reaches zero after the long tailing) varies with the flow rate used.

Quantitatively, the amount of substance recovered at the end of an experiment is given by the area under the elution peak. Peak areas are proportional to the flow rate used, so to compare areas obtained in different flow rates, the area must be multiplied by the flow rate (or interstitial velocity) used. The quantity presented on the y-axis of Figure 5.52 is the ratio between this recovered quantity at each flow rate (the average of the injections after stabilization) and what is recovered when an injection is performed without column. The
concentrations used in the experiments with column saturates the detector when injected on a system without column, therefore, a calibration curve of absorbance vs concentration is created from which the would-be recovered quantity at 2 g.L\(^{-1}\) can be extrapolated.

![Graph showing normalized recovered quantity vs flow rate.]

**Figure 5.52** – Average percentage of C5PeC11 recovered at each flow rate in 360 Mono-8

Stunningly, the quantity recovered on the experiments with column is less than 3% of what is injected. Furthermore, this value decreases at lower flow rates. Two distinct possibilities arise as explanations for this decrease in amount detected. Either the time chosen to stop the experiment is not enough to elute the entire peak, in which case, some of the area under the peak is lost - even if its intensity is so low as to be indistinguishable from the baseline - or there is some mechanism shifting the adsorption equilibrium at lower flow rates which increases the amount adsorbed and lowers the amount recovered.

Experimentally, the time at which the experiment is stopped is determined by the return to zero of the peak eluting at the highest flow rate, with some added tolerance. This means that the amount of elution time at 0.1 mL.min\(^{-1}\) is a little over twice experiment time at 0.2 mL.min\(^{-1}\). This means that the volume of mobile phase eluted in both cases is similar, with some small portion extra. The extra time/volume eluted should not matter, as the peak is supposed to be fully eluted, thus, not impacting calculations. It is observed, however, that peak tailing is proportionally more prominent at low interstitial velocities, again, evidence of an extra delay effect.

It is unclear whether the peaks can or should be exploited given these possible sources of inaccuracies but an HETP correction was attempted nevertheless. The HETP was corrected using Equation 12, where the retention times and variances used were taken from the experiments performed with P3 without column.
Several salient aspects spring from this HETP correction, shown in Figure 5.53. Firstly, the HETP values increase after correction. As calculated by Equation 12, the HETP in non-adsorbing conditions decreases when corrected for extra-column volumes, as seen in Figure 5.7. This means that the column itself is more efficient than the system as a totality. The use of a chromatographic column is precisely that, the efficient separation of elution peaks of different substances (in the case of SEC, by molecular weight).

A low volume capillary system is not very efficient at all at separating compounds, as such, when the HETP is corrected and these extra-column volumes are accounted for and removed, the HETP becomes lower - the amount of plates in the column is higher than what is measured experimentally where both the column and the capillaries are inevitably part of the experiment. In this highly adsorbing system, the peaks are so large compared to an unretained compound that an increase in HETP is instead observed. The column causes an amount of tailing such that it is extremely inefficient at separating compounds; less efficient, evidently, than the system without column. Both the extra-column and column increase the variance of the peak, to be sure, however, the mean retention time (as calculated by the method of the moments) of the system is vastly greater with column than without.

Other than that, the dashed lines at low and high flow rates depict a transition between regimes. In adsorbing conditions, a low flow rates, the slope is quite high, indicating very slow diffusion. This can be calculated using a combination of Equations 20 and 57.

\[ C = \frac{2}{1 - \varepsilon_e} \left( \frac{k_1}{1 - k_1} \right)^2 \left[ \frac{d'_s^2}{4k_m} + \frac{d'_s^2}{32D_a^{eff} \left[ r_m \right]} + \frac{k_2}{k_a} \right] \]

Since it was observed that the kinetics of adsorption were mostly limited by diffusion, the adsorption term \( k_2/k_a \) was assumed to be negligible. The \( D_a^{eff} \) term is a combination of the pure
mesoporous diffusion coefficient and the surface diffusion (Equation 23). $D_a^{\text{eff}} / D_m$ varies from 0.0084 at low flow rates to 0.687 at the highest flow rates used. This means that diffusion is greatly hindered at low flow rates. This could be due to constrictions, affecting the liquid phase diffusion in the mesopores as well by the already implied shift in adsorption equilibrium, which likely affects the surface diffusion parameter.

Even after the dynamic conditions experiments, the column was not uniformly covered with asphaltenes (maintaining the appearance shown in Figure 5.47). Attempting to mitigate some of the uncertainties observed using 360 Mono-8, a different column filling method was used to saturate a new column. An HPLC piston pump was used to drive a solution of 3 g.L$^{-1}$ of C5PeC11 in toluene through column 360 Mono-9 ($L = 1.69$ cm, $m_b = 3.66$ mg). At the start, the concentration profile in the column was identical to the one observed in the column filled by repeated injection. Though a fair bit more concentrated, it is clear to see in Figure 5.54 how the area around both the inlet and outlet of the column are darker than the middle, which is the same behavior observed in column 360 Mono-8.

![Figure 5.54](image)

*Figure 5.54 – Top: pump-through filling setup; bottom: after some time 360 Mono-9 attains the same concentration profile along the monolith as 360 Mono-8*

Eventually, the pressure caused an internal leak in this column, most likely caused by a mistake in the epoxy preparation which made it more malleable than what is ideal. Due to this structural
failure, a new column, 360 Mono-11 (L = 1.52 cm; m₀ = 31.9 mg) was built and filled in the same way. The transitory concentration profile along the column was again observed. After enough time, however, the coloration along the column became fully homogeneous as can be seen in Figure 5.55.

**Figure 5.55** – Close-up of the 360 Mono-11 column after complete saturation

Once the monolith was saturated, dynamic conditions tests were performed two times, in identical fashion as was described in the case of 360 Mono-8 (five injections method). Likewise, the extra-column correction was performed in the exact same manner. It’s worth looking at the recovered quantity results first, this time (Figure 5.56).

**Figure 5.56** - Average percentage of C5PeC11 recovered after at each flow rate

360 Mono-11 (dotted lines as visual aid)

Not only is the relative amount of C5PeC11 detected after an experiment about 3 to 6 times lower using 360 Mono-11, it also follows a different trend across flow rates. Interestingly, in 360 Mono-11, the pattern is repeatable, exhibiting an increase of asphaltenes recovered at pseudo-equilibrium as the flow rate decreases, with a sharp decrease at very low flow rates. This is a different behavior as the one observed in column 360 Mono-8 and could be a result of the different filling procedures.

The only difference in execution between experiment 1 and experiment 2 is the number of flow rates studied, which was cut in half to save time. The same pattern should be and was observed though the maximum of curve with 10 flow rates was not as high as the experiment with 20
flow rates, which can be explained by the fact that throughout course the experiment, only half as many asphaltenes were made to pass through the column, thus, pseudo-equilibria were achieved with a different quantity of asphaltenes retained. Interestingly, these different pseudo-equilibria affect the HETP results but not in a catastrophic way.

Figure 5.57 – HETP obtained with column 360 Mono-11

Figure 5.57 shows an unexpected yet cogent relationship between experiments 1 and 2. Two regimes appear to be present, with a drastic shift at around 2.7 - 2.8 mm.s⁻¹. This shift is rather more noticeably when more flow rates are tested, as the number of asphaltenes introduced is, again, double that of experiment 2. The slope is, then, more tilted. The transition is a fair bit smoother when less flow rates are tested. Experiment 1 exhibits a value of $D_a^{eff}/D_m$ varying from 0.122 (at lower flow rates) to 0.0062, while experiment 2’s values are somewhere in between these extremes, ranging from 0.056 to 0.020. With that said, it is also clear that Figure 5.57 completely contradicts the results shown in Figure 5.53.

An extension of experiment 2 was carried out at higher flow rates. In the interest of caution, injections were performed from lowest to highest, in case the column might not be able to handle the elevated working pressures (upwards of 130 bar) which is why they are not presented along with the previous tests. HETP results for this extension are presented in Figure 5.58.

Apart from the last point at 0.3 ml.min⁻¹, the slope of the corrected HETP curve has a similar magnitude as the one measured in experiment 2 overall, corresponding to a value of $D_a^{eff}/D_m$ of 0.050, much closer to the value obtained at lower flow rates.
Due to the extreme nature of the tailing in the peaks, experiments with long elution times were attempted. In the injections described above, elution was stopped when peaks reached a slope indistinguishable from the desorption of asphaltenes on long time scales. An example of an elution peak under these conditions is shown in Figure 5.59.

**Figure 5.58** – *HETP at high flow rate on 360 Mono-11*

**Figure 5.59** – *C5PeC11 elution peak for experiments at long time scales @ 0.3 ml.min⁻¹; top – complete chromatogram; bottom left – first minute (peak); bottom right – return to descending baseline beyond A = 0 mAu*
Since asphaltene desorption is an extremely slow process, the baseline never attained a perfectly flat profile, instead retaining an ever so slight, yet undoubtedly noticeable, constant descending slope. Experiments reaching a flat baseline would require an extremely large span of time, not only in preparation after column saturation, but after each injection. Even then, there is no guarantee that an elution peak would be observed.

**Figure 5.60 – HETP results for long time scale experiments**

The corrected HETP curve in Figure 5.60 looks a lot more familiar than any of the curves shown so far, with a much stronger similarity to the typical van Deemter curve. As before, the recovered quantity is around 1%. The slope of the last few points (the highest flow rates; where the relationship tends toward linearity) is taken to calculate $D_{a \text{ eff}}/D_m$ giving us a value of 0.041. It is not clear whether the slope is completely stable at the velocities used, however, to prevent a catastrophic failure of the column due to pressure increases, experiments were concluded safely at 0.3 ml.min$^{-1}$ (at a total working pressure of 160 bar). Table 5.10 contains a summary of the results obtained for the different parameters.

**Table 5.10 – Compilation of results obtained in the asphaltene chromatography tests**

<table>
<thead>
<tr>
<th>Column</th>
<th>Exp.</th>
<th>Lowest flow rates</th>
<th>Moderate flow rates</th>
<th>Highest flow rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C, s$^{-1}$</td>
<td>$D_{a \text{ eff}}/D_m$</td>
<td>C, s$^{-1}$</td>
</tr>
<tr>
<td>360 Mono-8</td>
<td>1</td>
<td>6.5</td>
<td>0.0092</td>
<td>2.6</td>
</tr>
<tr>
<td>360 Mono-11</td>
<td>1</td>
<td>0.53</td>
<td>0.119</td>
<td>0.53</td>
</tr>
<tr>
<td>360 Mono-11</td>
<td>2</td>
<td>1.2</td>
<td>0.051</td>
<td>3.3</td>
</tr>
<tr>
<td>360 Mono-11</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The apparent influence of the flow rate on adsorption was studied using the setup described in section 4.6. As with the HPLC measurements, concentrations at the plateau of the isotherm of adsorption were shown to saturate the UV-Vis detector. As such, the recirculating concentration was progressively lowered until the detector was no longer at risk of saturation. A blank was performed by connecting the pump directly to the cell. The initial flow rate was 0.2 mL.min⁻¹, the same flow rate to be used with the monolithic columns. Due to the volume of the UV flow-through cell (0.113 mL), it is expected that the equilibrium time should be around 30 s. The blank experiment (without column) revealed that there is no influence of the flow rate on the measurement. A slight increase of absorbance is observed over time, caused by the slow evaporation of the toluene in the C5PeC11 solution which was corrected for in the experiments with column. Otherwise, the system is highly stable, as is shown in Figure 5.61, where $A/A_0$ is the absorbance, relative to the initial absorbance at $t = 0$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure561.png}
\caption{Absorbance over time without column: green - flow rate change @ 5 min from 0.1 mL.min⁻¹ to 0.2 mL.min⁻¹; yellow - flow rate change @ 76 min from 0.2 mL.min⁻¹ back to 0.1 mL.min⁻¹;}
\end{figure}

With columns in the system, equilibrium time becomes even longer, as it must now account for the kinetics of adsorption. Two of the previously saturated one-monolith columns were used in these experiments, 360 Mono-8 and 360 Mono-11.

Figure 5.62 shows the evolution of the absorbance over time in one of the experiments performed. Prior to the experiment, the absorbance is stable. When the flow rate is changed from 0.2 to 0.1 mL.min⁻¹, the absorbance begins to slowly decrease. This implies a decrease in the concentration at the outlet of the column, thus, an increase in the amount of C5PeC11 adsorbed in the column. It’s likely that the kinetics of adsorption in continuous flow conditions are different than what is observed in batch conditions. For the monoliths in batch conditions, diffusion is the limiting step when it comes to kinetics of adsorption. By comparison to the powder samples, the kinetics of adsorption on monolith is several orders of magnitude slower,
as described in section 5.4.1. With the addition of flow, advective processes accelerate the dispersion of the solute through the monolith. Even with this added mobility, kinetics are not as quick as the powder sample due to the high tortuosity of the monolithic porous network ($\tau_{LONG} = 2.39; \tau_{NMR} = 2.54; \tau_{TRANS} = 3.00$; more details in section 5.3). This means that even after 150 minutes, the new equilibrium state might not have been achieved. As the flow rate is set back to its original value, concentration increases, dramatically at first, suggesting a quick release of weakly adsorbed molecules. Molecules continue being desorbed over time until the concentration measured eventually returns to its initial value after 500 min.

**Figure 5.62** – Absorbance over time in 360 Mono-8: yellow – flow rate change @ 13 min from 0.2 mL.min$^{-1}$ to 0.1 mL.min$^{-1}$; green – flow rate change @ 160 min from 0.1 mL.min$^{-1}$ back to 0.2 mL.min$^{-1}$

Descriptions of adsorption behavior outside the time domain (i.e. adsorption kinetics) in the literature sit squarely and overwhelmingly within the domain of thermodynamics (Rouquerol et al. 2012). As such, flow rate would, theoretically, have no influence on adsorption behavior whatsoever. Using front chromatography methods, (Gritti and Guiochon 2005) observed a very small increase of amount adsorbed with higher flow rates. This effect was attributed to the increase in pressure within the column causing the equilibrium to become more favorable toward adsorption. The behavior observed by Gritti and Guiochon is, in fact, the reverse of what is observed by the experiments above described.

The literature remains regrettably scarce on this subject. Studies by Ghorai and Pant (2005), Malkoc et al. (2006) and Mohammed et al. (2016) have noted increases in amount adsorbed at equilibrium with lower flow rates but since these are breakthrough experiments, it is not certain that the final uptakes calculated for each flow rate are at equilibrium. Residence time is, therefore, the primary culprit for less adsorption at high flow rates. Aside from residence times, causes for adsorption fluctuations with flow rate are seldom discussed.
When it comes to the asphaltene situation, two related and possibly concurrent hypotheses are proposed. Higher flow rates increase friction on the surface of asphaltenes adsorbed in the macropores (where advection is the main form of mass transfer) which releases some of the weakly adsorbed asphaltenes. These molecules may be only adsorbed on top of other asphaltenes through relatively weak $\pi-\pi$ interactions, forming the stacked microaggregates discussed in section 2.2. The first hypothesis posits that the shear force at higher flow rates is somehow enough to disaggregate and displace some of these asphaltenes which are weakly retained at lower flow rates.

Simultaneously, low flow rates may allow for deposition of asphaltenes in such a way as to block intermediate sized pores. The second hypothesis suggests that a sudden increase in the flow rate may apply enough pressure to break through these blockages, releasing the asphaltenes causing them. This would explain the sudden sharp increase in concentration observed at the outlet after the flow rate increase shown in Figure 5.62.

The drops in concentration after the experiments performed in columns 360 Mono-8 and 360 Mono-11 are low enough that such hypotheses may be at least part of the cause of the observed phenomena. Figure 5.63 shows the concentrations obtained at the end of each experiment with the two flow rates used. An average decrease of 4% in the final concentration is observed.

![Figure 5.63](image)

**Figure 5.63** – Relative concentrations observed at equilibrium for the different flow rates through different experiments (blue) and average with error bars equal to the standard deviation (orange)

5.4.3 Asphaltene tests overview and assessment:

As expected, asphaltenes are remarkably challenging molecules to study. Working with the model molecule presents several advantages, such as a comparatively simple aggregation process and straightforward adsorption mechanism as well as a strikingly vivid color. The strong,
partially irreversible adsorption with the alumina surface, while representative of real asphaltene fractions, complicates many of the measurements, particularly the chromatographic measurements. In adsorbing conditions, dynamic method chromatography measurements are usually performed with weakly adsorbing molecules, showing clear gaussian (Wernert et al. 2011) or exponentially modified gaussian peaks (Gritti and Guiochon 2012 and Lambert et al. 2014).

It is known that dimerization of the C5PeC11 occurs even at low concentrations, however two peaks are not clearly observed in the ISEC measurements. It is also known that the strongest adsorption occurs as hydrogen bonding of the acidic functionalization onto the alumina surface. This means that at the moment of adsorption, the dimerization equilibrium is shifted toward dissociation as single asphaltene molecules strongly adsorb. Certain conditions provide elution profiles in which two peaks are more easily observed, however, their deconvolution is extremely difficult, given the tailing observed. Interpretation with the method of the moments is a rather elusive endeavor, since, adding to the possibility of hidden, co-eluting peaks, this method is highly influenced by the cut-off points of the peaks.

With that said, most of the vital information about their adsorption behavior, such as isotherms, kinetics, and thermodynamic information, was obtained without any major problems. The model asphaltenes behave differently from the real fraction when it comes to surface interactions, or rather, they model only one type of molecule which is possibly present within an extracted asphaltene fraction, rather than the entire mixture. However, when it comes to diffusion, the molecule is highly representative of typical extracted asphaltenes, as can be seen with the bulk diffusion coefficient obtained by TDA. The value of $D_m$ obtained for C5PeC11 is on the same order of magnitude as the values presented in Table 3.2. The values for effective diffusion, however, are not consistent, but see the diffusion being decreased by somewhere between one to two orders of magnitude.

Finally, the flow rate measurements really elucidate the complexity of the behavior of asphaltenes within the alumina porous network. Even a system as simple as the one studied shows some variance in the results. While, interpretation of the results is not immediately evident, it is clear that the flow rate does have an observable influence on the concentration of asphaltenes in the mobile phase and, thus, on the amount adsorbed within the column. This spectrophotometry setup can and should be used with longer columns so as to increase the amount by which the concentration changes as well as be performed with real asphaltene fractions.
6 CONCLUSIONS AND PERSPECTIVES

The objective of this project is to understand the diffusion properties of asphaltenes in alumina, in order to ultimately improve hydrocracking and conversion processes in refineries. Much of the work on asphaltenes described in the literature was done using diffusion cells, with several different samples of crude from different geological origin and, consequently, without much consensus. This study intended to use model molecules to circumvent this issue and thoroughly describe their behavior using chromatographic methods due to their straightforward analytical approach and versatility.

To begin with, a commercially available spherical alumina powder column was thoroughly characterized in non-adsorbing conditions using the dynamic and peak parking methods. These values were verified and corroborated by complementary standard techniques such as gas adsorption, mercury porosimetry and impedance spectroscopy.

Different assembly techniques were attempted in order to study alumina porous solids with different internal topologies. Eventually, the most consistent assembly method proved to be the construction of monolithic columns with heat-shrink PTFE and epoxy liner. Various columns of different sizes were built to once again fully reveal the intricacies of the porous network of these monoliths.

Many differences could be observed between the monolithic and powder columns. Most notably the macroporosity was much lower in the monolithic samples, which, along with a smaller column diameter, increased the working pressure at which the experiments were performed. Combined with extremely high tortuosity it is clear that diffusion is much more difficult inside the monolithic supports. It is also clear, however, that the chromatographic method is useful in the utmost as it allows for an all-encompassing characterization. Chromatography allows for the determination of porous volume and pore size distribution as well as tortuosity and effective diffusion in the various porous domains with a single technique.

Among the other techniques used, the tortuometer in particular showed very promising results when it comes to observing the tortuosity of monoliths in the transverse direction. With a few tweaks to the setup, even longitudinal tortuosity may be assessed. Deriving mathematical expressions and designing ways to hold a sample without obstructing the measurement are the only challenges. The first obstacle can be tough to solve, particularly for complex geometries. Holder design might also be more involved, however, additive manufacturing techniques greatly ease the construction of complex pieces.

The extraordinary flexibility of the monolithic columns as well as their status as the industry standard within conventional hydrotreatment reactors (though as multilobed rather than
cylindrical extrudates) made them the ideal support to study asphaltene adsorption via liquid chromatography. The adsorbing thermodynamics (adsorption isotherm, kinetics and enthalpy) of this asphaltene model molecules was studied, revealing a strong affinity for alumina and relatively quick adsorption kinetics, greatly delayed by diffusional resistances. Particularly in the chromatographic measures, it is clear that the C5PeC11 asphaltene adsorbs at rates much higher than asphaltene mixtures extracted from vacuum residue. Liquid chromatograph studies on extracted asphaltenes risk separating strongly adsorbing from weakly interacting molecules, providing only part of the picture, but an interesting part nonetheless. This also comes at the risk of the equipment as well, which, after exposure, might become irreversibly polluted. Another interesting avenue includes the development of the chromatographic models that better fit the behavior of strongly adsorbing molecules at saturation as well as deeper dives into the true mechanisms behind the apparent influence of flow rate on adsorbed quantities. Studies with simpler molecules might reveal whether this influence is inherent to the specific adsorption mechanism of the model asphaltene molecule or to a yet unexplored phenomenon.

Ultimately, this document describes yet another step toward a richer understanding of the - literally as well as conceptually - labyrinthine processes typical of the nanoscale. A drop in an ocean of hopefully ever-expanding knowledge.
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References


References


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112 References
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Yang, X., and J. A. Guin. 1998. “Diffusion-Controlled Adsorptive Uptake of Coal and
Petroleum Asphaltenes in a NiMo/Al2O3 Hydrotreating Catalyst.” *Chemical Engineering Communications* 166 (1): 57-79.

APPENDIX I - N\textsubscript{2} ADSORPTION ISOTHERMS AND Hg POROSIMETRY RESULTS

Figure I.1 – N\textsubscript{2} adsorption isotherm for commercial column powder

Figure I.2 – Hg porosimetry results for the M161 powder
Figure I.3 – $N_2$ adsorption isotherms for the IFPEN gel powder samples (540B – red; 700B – green)

Figure I.4 – $N_2$ adsorption isotherms for the IFPEN “MEF” powder samples (540G – orange; 700G – purple)
Figure I.5 – $N_2$ adsorption isotherms for the FG Mono sample

Figure I.6 – $N_2$ adsorption isotherms for 360 Mono
**Figure I.7** – Hg porosimetry results for ESI-1

**Figure I.8** – Hg porosimetry results for the M161 powder
**Figure I.9** – Hg porosimetry results for the IFPEN gel powder samples (540B – red; 700B – green)

**Figure I.10** – Hg porosimetry results for the IFPEN "MEF" powder samples (540G – orange; 700G – purple)
Figure I.11 – Hg porosimetry results for FG Mono

Figure I.12 – Hg porosimetry results for 360 Mono
Appendix II - List of Columns Used

What follows is a table containing the entire gamut of chromatographic columns used throughout the course of this work. The columns are listed in chronological order, along with the different tests in which they were used as well as their performance and end-result.

Table II.1 – Complete list of columns

<table>
<thead>
<tr>
<th>Name</th>
<th>Support</th>
<th>Used in</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>700G-0</td>
<td>Powder</td>
<td>Powder column assembly</td>
<td>Plugged</td>
</tr>
<tr>
<td>700G-1</td>
<td>Powder</td>
<td>Powder column assembly</td>
<td>Double peaks</td>
</tr>
<tr>
<td>FG Mono-1</td>
<td>Monolith (6)</td>
<td>Monolith column assembly; peak parking</td>
<td>Peak tailing</td>
</tr>
<tr>
<td>700G-2</td>
<td>Powder</td>
<td>ISEC</td>
<td>Double peaks</td>
</tr>
<tr>
<td>FIT-1</td>
<td>-</td>
<td>FG Mono-1 troubleshooting</td>
<td>-</td>
</tr>
<tr>
<td>ESI-1</td>
<td>Powder</td>
<td>ISEC; dynamic; peak parking; asphaltene injection</td>
<td>Dismantled for further tests</td>
</tr>
<tr>
<td>700B-1</td>
<td>Powder</td>
<td>Powder column assembly; peak parking</td>
<td>Negative variance</td>
</tr>
<tr>
<td>995 Mono-1</td>
<td>Monolith (5)</td>
<td>Monolith column assembly</td>
<td>Overheated</td>
</tr>
<tr>
<td>995 Mono-2</td>
<td>Monolith (6)</td>
<td>Monolith column assembly</td>
<td>Capillary detached</td>
</tr>
<tr>
<td>540B-1</td>
<td>Powder</td>
<td>Powder column assembly</td>
<td>Double peaks</td>
</tr>
<tr>
<td>700B-2</td>
<td>Powder</td>
<td>Powder column assembly; toluene flush</td>
<td>Plugged</td>
</tr>
<tr>
<td>M161-1</td>
<td>Powder</td>
<td>Asphaltene injection</td>
<td>Pressure increase</td>
</tr>
<tr>
<td>360 Mono-1</td>
<td>Monolith (6)</td>
<td>Monolith column assembly</td>
<td>Capillary failure</td>
</tr>
<tr>
<td>360 Mono-2</td>
<td>Monolith (6)</td>
<td>Monolith column assembly</td>
<td>Outer tube dissolved</td>
</tr>
<tr>
<td>360 Mono-3</td>
<td>Monolith (6)</td>
<td>Monolith column assembly</td>
<td>Lining burst</td>
</tr>
<tr>
<td>360 Mono-4</td>
<td>Monolith (6)</td>
<td>Monolith column assembly; ISEC</td>
<td>Capillary leak</td>
</tr>
<tr>
<td>360 Mono-5</td>
<td>Monolith (3)</td>
<td>Monolith column assembly</td>
<td>Plugged by epoxy</td>
</tr>
<tr>
<td>360 Mono-6</td>
<td>Monolith (4)</td>
<td>ISEC; longitudinal tortuosity</td>
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</tr>
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<td>360 Mono-7</td>
<td>Monolith (12)</td>
<td>ISEC</td>
<td>-</td>
</tr>
<tr>
<td>360 Mono-8</td>
<td>Monolith (1)</td>
<td>Asphaltene saturation (ISEC; flow rate tests)</td>
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</tr>
<tr>
<td>SES-1</td>
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<td>Powder column troubleshooting</td>
<td>-</td>
</tr>
<tr>
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<td>Powder</td>
<td>ISEC; peak parking</td>
<td>-</td>
</tr>
<tr>
<td>360 Mono-9</td>
<td>Monolith (1)</td>
<td>Asphaltene saturation</td>
<td>Inner tube leak</td>
</tr>
<tr>
<td>360 Mono-10</td>
<td>Monolith (1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>360 Mono-11</td>
<td>Monolith (1)</td>
<td>Asphaltene saturation (ISEC; flow rate tests)</td>
<td>-</td>
</tr>
</tbody>
</table>
APPENDIX III - DETERMINATION OF THE SIZE OF THE MONOLITHIC SKELETON FROM SEM IMAGES

Original Image

Crop

Denoising

Segmentation

Cleaning

Granulometry by opening
The process of granulometry by opening uses a binarized image to calculate grain size. In this case it is used to compute the size of the monolith skeleton:

- Denoising: Bilateral filter (Tomasi and Manduchi 1998), spatial parameter 3 pixels, intensity parameter 0.01.
- Segmentation: From grey level histogram of image by maximization of inter-class variance (Otsu 1979) for 3 classes and union of two brightest classes.
- Cleaning: Morphological closing by a disk of radius 2 pixels (Matheron 1967) and removal of white and black objects whose surface is smaller than 16 pixels.

In the segmented and cleaned images, the white pixels correspond to the solid mesoporous phase. The white surface covered by circles of a given radius is calculated on images with 250x magnification. The average of the frequency distribution of radii is then calculated.

\[
\sigma_s = \sqrt{\frac{\langle r^3 \rangle}{\langle r \rangle}}
\]

Table III.1 presents the results obtained using both transverse and longitudinal monolith slices. The porosity obtained only accounts for macropores and, due to the image treatment, greatly underestimates the true values.

**Table III.1 – Results obtained from granulometry**

<table>
<thead>
<tr>
<th>Slice direction</th>
<th>Number of slices</th>
<th>(r_s ) / (\mu m)</th>
<th>(\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transverse</td>
<td>17</td>
<td>17.7</td>
<td>0.117 ± 0.009</td>
</tr>
<tr>
<td>Longitudinal</td>
<td>50</td>
<td>18.2</td>
<td>0.122 ± 0.052</td>
</tr>
</tbody>
</table>
APPENDIX IV – TORTUMETER DETAILED CALCULATIONS

The system can be thought of as a series of 3 resistances:

\[ R_t = R_1 + R_2 + R_3 \]

Resistance is a function of \( L \), the distance between the two electrodes, the resistivity of the material, \( \rho \), and the area of the cross-section of the material, \( A \).

\[ R = \frac{L \cdot \rho}{A} \]

\( R_1 \) and \( R_3 \) have the same cross-section, \( A_a \) (the shape of the aperture of the monolith holder) and the same resistivity (the resistivity of the electrolyte, \( \rho_l \)). The length of these two slices is equal to the distance between the electrodes minus the size of the monolith (with radius \( r_c \)), therefore:

\[ R_1 + R_3 = \frac{(L - 2r_c) \cdot \rho_l}{A_a} \]

\( R_2 \) is the resistance of the slice containing the monolith. Using a method similar to the one used in the Coulter counter, one can assume the resistance in this section is a series of infinitesimally thin slabs with a resistance equal to the equivalent resistance of a system in parallel.

\[ \frac{1}{R_2} = \frac{1}{R_l} + \frac{1}{R_c} + \frac{1}{R_l} = \frac{2}{R_l} + \frac{1}{R_c} \]

\( R_l \) is the resistance in the liquid volume (equal above and below the monolith) and \( R_c \) is the resistance of the monolith. Substituting the resistances by their proper equations one obtains:

\[ dR_c = \frac{\rho_c \cdot dx}{A_c}; \quad dR_l = \frac{\rho_l \cdot dx}{A_a - A_c} = \frac{2 \rho_l \cdot dx}{A_a - A_c} \]

With \( \rho_c \) as the apparent resistivity of the monolith. Since the monolith is a cylinder, the area of the cross-section of the monolith, \( A_c \) varies. As such, it is necessary to calculate \( R_2 \) as the sum of slices of size \( dx \), where \( dx \) is an infinitesimal length. It is, however, easier to substitute \( dx \) with a radial coordinate.
system based on the angle θ (angle from the radial centerpoint of the monolith until its edge).

\[ dx = -d(r_c \cos \theta) = r_c \sin \theta \, d\theta \]

The equation for \( R_2 \) can, thus, be expanded with this approach.

\[
\frac{1}{dR_2} = \frac{1}{dR_c} + \frac{2}{dR_t} = \frac{A_c}{\rho_c \cdot r_c \sin \theta \, d\theta} + 2 \frac{A_a - A_c}{2 \rho_t \cdot r_c \sin \theta \, d\theta} = \frac{A_c \rho_t + \rho_c A_a - \rho_c A_c}{\rho_c \cdot \rho_t \cdot r_c \sin \theta \, d\theta}
\]

\[ dR_2 = \frac{\rho_c \cdot \rho_t \cdot r_c \sin \theta \, d\theta}{A_c \rho_t + \rho_c A_a - \rho_c A_c} \]

Following this, both the areas of the monolith and of the aperture must be determined. The section of area of the monoliths is a rectangle with circular edges on either side. It’s possible to calculate the area of this shape by introducing another angle, \( \gamma \), in the longitudinal direction of the monolith. The area of the sector of the circle within the angle \( \gamma \) is the area of the whole circle times the ratio of the angle over 2\( \pi \). Adding to this, the area of the triangle above this sector and multiplying it by four (all four quadrants), one can calculate the total cross-sectional area of the monolith.

\[ A_c = 4 \left[ \pi r_e^2 \left( \frac{\gamma}{2\pi} \right) + \frac{r_c \cos \gamma \cdot r_e \sin \gamma}{2} \right] = 4r_e^2 \left( \frac{\gamma}{2} \right) + \frac{\cos \gamma \cdot \sin \gamma}{2} = 2r_e^2 (\gamma + \cos \gamma \cdot \sin \gamma) \]

If \( \theta = 0 \) then \( \gamma = 0 \) as the area of monolith at the very edge approaches 0. If \( \theta = \pi/2 \) then \( \gamma \) is at its maximum, as is the area of the cross-section of monolith.

\[ \gamma = \sin^{-1} \left( \frac{r_c}{r_e} \sin \theta \right) \]

\[ A_c = 2r_e^2 \left[ \sin^{-1} \left( \frac{r_c}{r_e} \sin \theta \right) + \cos \left( \sin^{-1} \left( \frac{r_c}{r_e} \sin \theta \right) \right) \cdot \sin \left( \sin^{-1} \left( \frac{r_c}{r_e} \sin \theta \right) \right) \right] \]

\[ = 2r_e^2 \left[ \sin^{-1} \left( \frac{r_c}{r_e} \sin \theta \right) + \sqrt{1 - \left( \frac{r_c}{r_e} \sin \theta \right)^2} \cdot \left( \frac{r_c}{r_e} \sin \theta \right) \right] \]

\[ = 2r_e^2 \left[ \sin^{-1} \left( \frac{r_c}{r_e} \sin \theta \right) + \sqrt{\left( \frac{r_c}{r_e} \sin \theta \right)^2 - \left( \frac{r_c}{r_e} \sin \theta \right)^4} \right] = 2r_e^2 [X] \]

It is necessary now to choose an aperture shape. The circular aperture presents with it the easier calculations. The circular aperture has a radius equal to that of the electrodes.

\[ A_{a,circle} = \pi r_e^2 \]
The slit aperture will require some extra math, though it is very similar to the equations used to calculate the area of the monolith slices as seen above. All it requires is the introduction of a new parameter, \( w_s \), which is the width of the slit.

\[
A_{a,\text{slit}} = 2r_e^2 \left[ \sin^{-1} \left( \frac{w_s/2}{r_e} \right) + \sqrt{\left( \frac{w_s/2}{r_e} \right)^2 - \left( \frac{w_s/2}{r_e} \right)^4} \right] = 2r_e^2 [Y]
\]

These parameters can now be introduced into the equation for \( dR^2 \):

**Circular aperture**

\[
dR^2 = \frac{\rho_c \rho_l \rho_c' \sin \theta \, d\theta}{A_c \rho_l + \rho_c A_a - \rho_c A_c}
\]

Integration (considering symmetry):

\[
R_c^2 = \frac{\int_0^\pi \rho_l \rho_c' \sin \theta \, d\theta}{2r_e^2 \left( \frac{\rho_l}{\rho_c} - 1 \right)} \left[ X \right] + \pi
\]

**Slit aperture**

\[
dR^2 = \frac{\rho_c \rho_l \rho_c' \sin \theta \, d\theta}{A_c \rho_l + \rho_c A_a - \rho_c A_c}
\]

Integration (considering symmetry):

\[
R_c^2 = \frac{\int_0^\pi \rho_l \rho_c' \sin \theta \, d\theta}{2r_e^2 \left( \frac{\rho_l}{\rho_c} - 1 \right)} \left[ X \right] + \left[ Y \right]
\]

The equations are very similar on either side, differing only in one term, which is due to the aperture shape. The final equation can, thus, be summarized as such:

\[
R_c^2 = \frac{\int_0^\pi \rho_l \rho_c' \sin \theta \, d\theta}{2r_e^2 \left( \frac{\rho_l}{\rho_c} - 1 \right)} \left[ X \right] + \left[ Y \right]
\]
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\[ a = \frac{r_c \rho_l}{r_e^2} \; ; \; b = \frac{r_c}{r_e} \sin \theta \; ; \; c = \left( \frac{\rho_l}{\rho_c} - 1 \right) \]

\[ d_{c\text{ircular}} = \frac{\pi}{2} \; ; \; d_{s\text{litr}} = \sin^{-1} \left( \frac{(w_s/2)}{r_e} \right) + \sqrt{\left( \frac{(w_s/2)}{r_e} \right)^2 - \left( \frac{(w_s/2)}{r_e} \right)^4} \]

**Limit case 1: No monolith (equal resistivities)**

In a case where no monolith is inserted the resistance would be equal to the resistance of a cylinder with only liquid. This is equivalent to saying that the resistivity of the monolith is equal to the resistivity of the liquid, in which case, the parameter \( c \) is equal to 0.

\[
R_2 = \int_{0}^{\pi} a \ast \sin \theta \; \text{d} \theta \div 0 \ast \left[ \sin^{-1} b + \sqrt{b^2 - b^4} \right] + d = \int_{0}^{\pi} \frac{a \ast \sin \theta}{d} \; \text{d} \theta = \frac{a}{d} \int_{0}^{\pi} \sin \theta \; \text{d} \theta = \frac{a}{d} \left[ \cos \frac{\pi}{2} - (-\cos 0) \right] = \frac{a}{d} (-0 + 1) = \frac{a}{d}
\]

Circular aperture

\[ R_2 = \frac{2r_c \rho_l}{\pi r_e^2} \]

Slit aperture

\[ R_2 = \frac{r_c \rho_l}{r_e^2} \left( \sin^{-1} \left( \frac{(w_s/2)}{r_e} \right) + \sqrt{\left( \frac{(w_s/2)}{r_e} \right)^2 - \left( \frac{(w_s/2)}{r_e} \right)^4} \right) \]

This, in the end, brings the equations back to their initial form, as if there is only an aperture with electrolyte

\[ R_2 = \frac{L \ast \rho_l}{A_a} \]

**Limit case 2: Monolith is very conductive**

In a case in which a monolith conducts electricity extremely well, one can perform the same calculation with a resistivity of monolith approaches 0, in which case, \( c \) will approach infinity.

\[
\lim_{c \to \infty} R_2 = \int_{0}^{\pi} \frac{a \ast \sin \theta}{c} \; \text{d} \theta = \int_{0}^{\pi} \frac{a \ast \sin \theta}{\infty} \; \text{d} \theta = 0
\]
Limit case 3: Monolith is not conductive

In a case in which a monolith does not conduct electricity, one can perform the same calculation with a resistivity of monolith approaches infinity, in which case, \( c \) will approach -1.

\[
\lim_{c \to -1} R_2 = \int_0^{\pi} \frac{a * \sin \theta \ d\theta}{c[\sin^{-1} b + \sqrt{b^2 - b^4}]} + d = \int_0^{\pi} \frac{a * \sin \theta \ d\theta}{d - [\sin^{-1} b + \sqrt{b^2 - b^4}]}
\]

Experimental approach:

What is measured experimentally is the total resistance, \( R_t \), between the electrodes. As such, a blank experiment is necessary to calculate the resistivity of the electrolyte:

\[
R = \frac{L * \rho}{A} \rightarrow \rho_l = \frac{R_t * A_a}{L}
\]

The resistances \( R_1 \) and \( R_3 \) are then easy to calculate and \( R_2 \), the resistance in which the monolith resides is the difference:

\[
R_{2, \text{measured}} = R_t - R_1 - R_3 = R_t - \frac{(L - 2r_c) * \rho_l}{A_a}
\]

Rather than going through the arduous integration process, it is easier to assume a value for \( \rho_c \) and solve the equation for \( R_2 \) numerically using the trapezoidal rule with small increments of \( \theta \).

\[
R - \frac{(L - 2r_c) * \rho_l}{A_a} = R_2 = \int_0^{\pi} \frac{a * \sin \theta \ d\theta}{c[\sin^{-1} b + \sqrt{b^2 - b^4}]} + d
\]
APPENDIX V - 215 nm PEAK IDENTIFICATION

As mentioned in the main text, a highly intense peak appears in some of the experiments performed in the less stable columns between 210 and 220 nm. The appearance of this absorbance peak in the spectrum is shown in Figure V.1 and compared to the typical spectrum of toluene in THF.

![Figure V.1 - Spectrum taken at the maximum of the peak after injections of toluene in THF through different columns; y-axis shows absorbance relative to the value at 262 nm](image)

A significant amount of time and effort were spent attempting to identify this mystery compound. Hypotheses such as a reaction between the toluene or THF with PTFE and the accumulation of THF stabilizer - butylated hydroxytoluene (BHT) - were ruled out. The first was tested by putting this solution in contact with a piece of PTFE tubing in a batch setting and injecting the solution bypassing the column. No extra peaks were observed. The second was ruled out by spectral analysis and GC-MS.

![Figure V.2 - UV absorption spectrum of BHT (adapted from Özugüir et al. 2017)](image)
BHT has its maximum absorbance at 278 nm as can be seen in Figure V.2, therefore it is ruled out as a possible culprit. GC-MS results failed to reveal any extra compound besides BHT and toluene.
APPENDIX VI - SEM IMAGES OF 360 MONO EXTRUDATES

Figure VI.1 - Top section view of 360 Mono (45x magnification)
Figure VI.2 - Zoom into top section view of 360 Mono-section I (250x magnification)
Figure VI.3 – Zoom into top section view of 360 Mono – section 2 (250x magnification)
Figure VI.4 - Zoom into top section view of 360 Mono - section 3 (1000x magnification)
Figure VI.5 - Zoom into top section view of 360 Mono - section 4 (100x magnification)
Figure VI.6 – Side section view of 360 Mono (45x magnification)
Figure VI.7 - Side section view of 360 Mono - section 1 (250x magnification)
Figure VI.8 - Side section view of 360 Mono - section 2 (250x magnification)
Figure VI.9 – Side section view of 360 Mono - section 3 (1000x magnification)
Figure VI.10 - Side section view of 360 Mono - section 4 (1000x magnification)