

Effect of physicochemical heterogeneity on adhesion phenomenon between bitumen and aggregates in asphalt mixtures

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In memory of Dr. Larissa Chiman

To

My parents Israel and Teresa

My sisters Johanna, Katherine and Paola

My husband Luis

I love you all dearly

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RESUMEN

TITULO: EFECTO DE LA HETEROGENEIDAD FISICOQUÍMICA EN EL FENÓMENO DE ADHESION ENTRE MINERALES E HIDROCARBUROS EN MEZCLAS ASFÁLTICAS¹

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PALABRAS CLAVE: mezcla asfáltica, propiedades fisicoquímicas de mezclas asfálticas, isotermas de adsorción, microbalanza de cristal de cuarzo, mojabilidad, adhesión.

DESCRIPCIÓN:

Esta tesis doctoral contribuyó a avanzar en el entendimiento de la influencia de las propiedades fisicoquímicas de los materiales a nanoescala sobre el fenómeno de adhesión entre asfalto y agregados minerales en mezclas asfálticas. Diferentes técnicas a escala macroscópica, y a escala nanométrica se emplearon para el estudio de la mojabilidad, adsorción y adhesión de sistemas asfalto-agregado. Los resultados obtenidos fueron analizados para identificar sus posibles efectos sobre las propiedades de las mezclas asfálticas, y la correlación entre escala macroscópica y nanométrica fue evaluada. Una metodología para monitorear en tiempo real la adsorción de las moléculas de asfalto sobre la superficie de minerales haciendo uso de la QCM fue desarrollada, esto teniendo en cuenta que no se dispone en la literatura de aplicaciones de la QCM para la evaluación de las propiedades del sistema asfalto-agregado. A partir de los datos de obtenidos con la QCM es posible construir isotermas de adsorción para estudiar de una manera más confiable y precisa las propiedades fisicoquímicas del sistema.

Se observó una buena correlación entre los resultados obtenidos a escala macroscópica de energía superficial libre y la medición de adhesión por tracción. Los resultados para el análisis de adhesión con AFM indican una mayor fuerza adhesiva entre los asfaltos con superficies de SiO₂ que con CaCO₃. Los datos de adsorción obtenidos con QCM siguieron la misma tendencia observada a escala macroscópica. Los datos de adsorción obtenidos con QCM mostraron la formación de una película viscoelástica sobre la superficie de los minerales empleados, que corresponde a la naturaleza viscoelástica del asfalto. El fenómeno de adsorción fue satisfactoriamente descrito por la isoterma de Freundlich para sistemas heterogéneos, lo cual confirma la influencia de la heterogeneidad fisicoquímica en el fenómeno de adhesión entre asfalto-agregado.

¹ Tesis Doctoral

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ABSTRACT

TITLE: EFFECT OF PHYSICOCHEMICAL HETEROGENEITY ON ADHESION PHENOMENON BETWEEN BITUMEN AND AGGREGATES IN ASPHALT MIXTURES³

AUTHOR: YULY FERNANDA LOPEZ CONTRERAS⁴

KEYWORDS: asphalt mixture, physicochemical heterogeneity, physicochemical properties of asphalt mix, adsorption isotherms, quartz crystal microbalance, wettability, adhesion.

DESCRIPTION:

This dissertation contributed to the better understanding at nanoscale of the influence of physicochemical properties on adhesion phenomenon between bitumen and aggregates as present in asphalt mixtures. Different macroscopic and nanoscopic techniques were used to study the wettability, adsorption, and adhesion of the bitumen-aggregate system. Results were analyzed to identify the possible effect on asphalt mixture properties, and the correlation between macroscopic and nanometric scale was assessed. A methodology to monitor in real time the adsorption of bitumen molecules on minerals surface using the QCM was developed. This considering that there is no evidence in the literature of its application to study the properties of bitumen-aggregate systems. QCM results were used to obtain adsorption isotherms, which allows the study of the physicochemical properties of the system in a more reliable and accurate way.

Results indicate that there is a good correlation between surface free energy and bitumen bond strength measured at macroscopic scale. Results for adhesion measured with AFM showed a higher adhesive force between bitumens and SiO₂ surfaces than with CaCO₃. From AFM, it was identified that the nitrogen content in bitumens would have a positive effect in adhesion force evaluated at nanoscale. Adsorption data obtained with QCM support the observed trend at macroscopic scale. A higher mass adsorbed at equilibrium was obtained for bitumens with lower surface energy. A viscoelastic film was deposited on minerals surfaces, which is consistent with the viscoelastic nature of bitumen. Adsorption phenomenon was satisfactory described by Freundlich isotherm for heterogeneous systems, a fact that demonstrates the influence of physicochemical heterogeneity on adhesion between bitumen and mineral aggregates.

³ Ph.D. Dissertation

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Introduction

Problem statement

The roads are an important factor for economic growth of any country, but require a substantial investment for construction and maintenance. One of the main and most important constraints to economic growth constitutes infrastructure, which in turn has become one of the major challenges in terms of competitiveness and has proven to be one of the biggest obstacles to mitigate poverty. Despite efforts on developing schemes for maintenance and the improvement of the existing road network, investment in transport infrastructure has been insufficient.

Currently, despite the ongoing development of experimental techniques to study the characteristics and behavior of the components in asphalt mixtures, the relationship between the interfacial properties of its main components and their impact on the damages that occur on pavements it is not yet understood. One cause of this lack of scientific knowledge is the few studies about the chemical interaction and / or affinity between bitumen and mineral aggregates at molecular and microscopic scale. A proof of this situation is the fact that the currently standards used to evaluate the performance of asphalt pavements, only consider mechanical properties but do not measure physical or chemical properties related to the adhesion phenomena and debonding. Also, according to the literature, the ability of these methods to accurately predict the field performance of asphalt concrete is questionable.

Asphalt pavement is an essential part of the Nation's transportation infrastructure. Thus, it is critical to improve the performance of asphalt concrete. The asphalt concrete or asphalt mixture,

is a composite material which consist of asphalt binder or bitumen that bound together mineral aggregates of different sizes and air voids. Mineral aggregates are obtained by quarrying and processing natural rocks. The bitumen is a by-product from distillation process of crude oil. Since materials properties are affected by its source, the final behavior of asphalt concrete varies significantly depending on the mix design and source of the constituent materials.

There are different methods to design asphalt mixtures. Superpave, Marshall, or Hveem methods are currently used worldwide. These methods use the density and void properties of asphalt mixtures to calculate the volumetric proportions of mixture materials to ensure durable asphalt concretes. Although some methods are based in performance to obtain the final mixture design such as Superpave, none of them measures cohesion or adhesion properties for bitumen – aggregate system. The adhesion properties of the system are a key issue to avoid different failures in pavements such as stripping. The accurate estimation of adhesive properties will help researchers to improve the design of asphalt mixtures in order to obtain pavements with higher performance and service lives.

Adhesion has a positive effect on the conservation of bitumen film as opposed to its debonding from the aggregate surface. However, there is still no complete knowledge about the elements that have influence on this factor. In fact, the adhesion covers a wide variety of concepts and ideas depending on whether the study is approached from a molecular, microscopic or macroscopic level, or refers to interface formation or system failure. The term adhesion is, therefore, ambiguous, meaning both the establishment of interfacial bonds and the mechanical load required to break bonds (Nardin & Schultz, 2003).

The work of adhesion in asphalt mixtures is directly influenced by bitumen – aggregate interactions. These interactions are due to long-range forces such as van der Waals, and forces

between the functional groups present on the surfaces of both materials. However, the characteristics of the contact area including roughness and porosity have a significant effect on adhesion (Christine W. Curtis, 1992; Christine W. Curtis, Ensley, & Epps, 1993; Hefer & Little, 2005a; Howson, Masad, Bhasin, Little, & Lytton, 2011). Therefore, it is of interest for understanding the phenomenon of adhesion to measure these forces either directly or indirectly through other macroscopically measurable properties.

The recent development of techniques such as Atomic Force Microscopy (AFM) and Quartz Crystal Microbalance (QCM) have enhanced research related to the study of adhesion phenomena of some materials that at macro scales have failed to find an explanation (Arifuzzaman, 2010; John, 2009). The AFM technique allow us to quantify the adhesion strength measured as the force required to break bonds represented as the sum of all the forces of interaction that take place during contact between two materials. On the other hand, QCM allows the real monitoring of the adsorption process of bitumen molecules over the minerals surface. The application of these techniques in the study of asphalt mixture, enable the opportunity to obtain proper results for measurements of the thermodynamic properties and characterization of the interfacial phenomena in adhesion process.

Motivation and scope of research

Nowadays, although there are different techniques to study adhesion in asphalt mixtures through macroscopic properties of materials, there is no a developed methodology to study and measure directly, in real time, at nanoscale the adsorption process of bitumen over mineral surfaces. Therefore, this research is motivated by the understanding that, development and application of accurate and efficient methods to evaluate material properties related to adhesion in asphalt

mixtures at interface will serve to bridge the gap between the current state of knowledge and current state of practice to measure properly adhesion and identify better bitumen-aggregate combinations. This will in turn improve the efficiency of materials design process in identifying better materials to construct pavements with higher resistance, performance and service life.

Considering the above, the main goal of this dissertation is to study of the relationship between adhesion at macroscopic scale using available techniques and nanoscale techniques such as Atomic Force Microscopy and Quartz Crystal Microbalance (QCM). Adhesion between bitumen and aggregates at macroscopic scale using the contact angles and surface free energy theory were calculated and compare with adhesion at nanoscale measured with Atomic Force Microscopy (AFM). To compliment the study of bitumen-aggregate interaction at nanoscale the adsorption process was monitored and studied with QCM.

Outline of the dissertation

This dissertation is organized into 5 chapters as follows:

Chapter 1 presents a literature review of subjects related to this study. The main part of this task focuses on techniques to properly measure adhesion in asphalt mixtures and the importance of adsorption in the adhesion phenomena between bitumen and aggregates. The state of the art of surface free energy theory applied to bitumen and aggregates and commonly used techniques to measure this property are reviewed. Chapter 2 provides test results for adhesion at macroscopic scale with techniques widely known worldwide. Materials properties effect on the work of adhesion calculated from measured contact is discussed. Chapter 3 introduce adhesion at nanoscale using an Atomic Force Microscopy and present test results for adhesion between modified tips of silicon dioxide and calcium carbonate with bitumen. Finally, chapter 4 presents a methodology to

directly follow and measure of bitumen adsorption on different minerals using a quartz crystal microbalance. Adsorption isotherms are obtained for all systems and thermodynamic parameters related to adhesion and bitumen-aggregate compatibility and its relevance in this research are discussed. General conclusions and recommendations are presented in chapter 5.

1 Literature review and theoretical concepts

Following, a brief literature review of subjects related to this study is presented. Techniques to properly measure adhesion in asphalt mixtures and the importance of adsorption in the adhesion phenomena between bitumen and aggregates are discussed. Moreover, the state of the art of surface free energy theory applied to bitumen and aggregates and commonly used techniques to measure these properties are reviewed. Also the most important issues related to adhesion at nanoscale and materials properties influence in molecular forces are studied.

1.1 Bitumen - aggregate interaction and wetting

Wetting, spreading and contact angle terms have been used to describe adhesion. Wetting of an adhesive liquid onto the substrate is the first step in obtaining adhesion. When a drop of liquid, in this case hot bitumen, is placed onto a solid surface such as an aggregate, it remains stationary when the contact angle is higher than 90° or it spreads for contact angles less than 90° . If bitumen

spreads such in Figure 1 for $\theta \ll 90^\circ$, the surface of the aggregate has to be wetted properly and adhesion between the liquid and the solid is likely to be high. If, on the other hand, the bitumen does not spread, then adhesion is lower (Yuan & Lee, 2013).

During the wetting process, as soon as bitumen molecules get into contact with the surface of a mineral aggregate, they orientate themselves towards the interface, in such a way that a definite mineral aggregate charged molecule is equalized by an opposite charged part of the bitumen molecule. Then charges of mineral aggregate surfaces are neutralized.

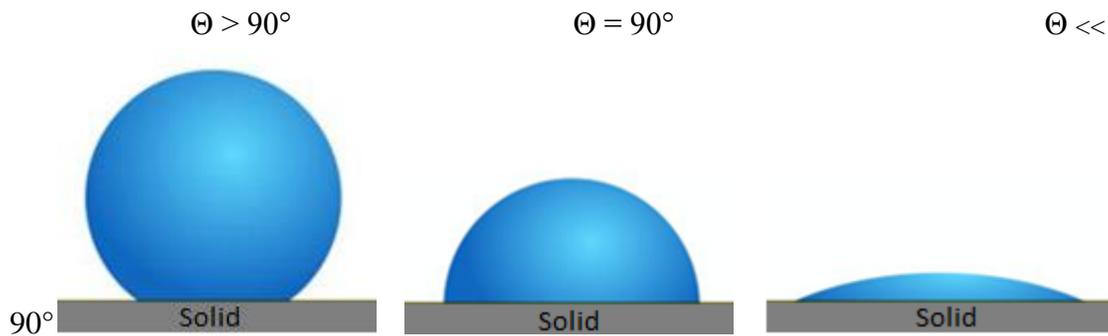


Figure 1. Contact angles at solid – liquid interface. If the contact angle is less than 90° it is said that the liquid wets the surface, zero contact angle representing complete wetting. If contact angle is greater than 90° , the surface is said to be non-wetting with that liquid.

Adsorption at solid-liquids interfaces is considerable a more complex process than at either air-liquid or liquid-liquid interfaces, mainly due to the wider range of molecular interactions that can occur between the solid and liquid molecules. When adsorbed at the mineral surface, bitumen molecules tend to interact with other bitumen molecules. Thus, depending on the conditions of adsorption process and mineral surface, different adsorbed structures are possible, reflecting the balance of interactions between bitumen molecules and between the bitumen and surface, shown schematically in Figure 2.

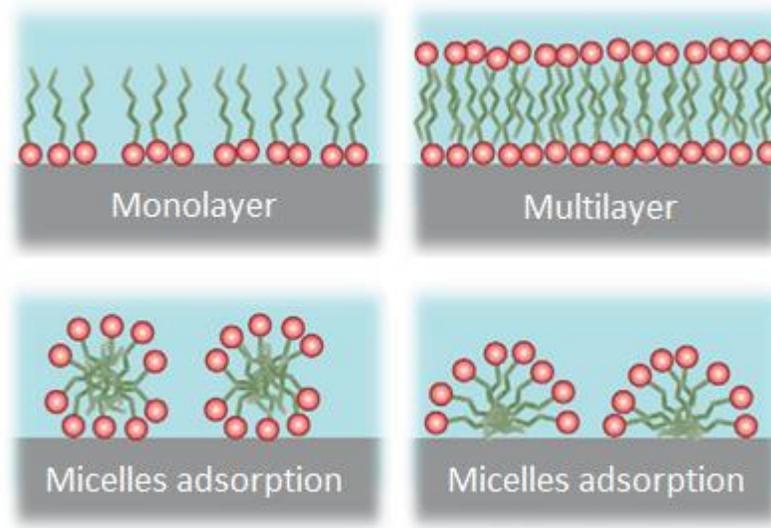


Figure 2. Illustration of the adsorption process of asphaltenes onto minerals indicating the molecular orientation of asphaltene molecules to the surface and possible configurations (adapted from (Eastoe & Tabor, 2014)).

Attraction forces govern wetting between the solid surface and the liquid. The chemical forces developed can be weak (Van der Waals forces) or moderately strong to weak (dipole-dipole interactions) depending on bitumen and aggregate composition, thus both components partly determine the adhesion strength developed for the system (Christine W. Curtis et al., 1993).

Several researches have studied bitumen - aggregate interaction in the past. Curtis in 1992, observed that the adsorption differences of three different bitumens for a given aggregate were much less than that of one bitumen on several aggregates. In other words, they state that the influence of aggregates on the adsorption process between bitumen-aggregate system, is greater than the exerted by the bitumen. Although the influence of bitumen chemistry was smaller than that of the aggregate, it did affect bitumen – aggregate interactions (Christine W. Curtis, 1992). In 1994, Ensley (Ensley, 1994) studied the bitumen structural properties and how they are related to bitumen-aggregate bonding. The thermodynamics related to the system were studied from

macroscopic and microscopic approaches and conclude that for that time, the limited structural information of materials only allow a qualitative relationship with thermodynamic and rheological measurements for interpreting mix characteristics (Ensley, 1994).

Although, interest in adhesion processes for asphalt mixtures has increased immensely during the past 10 years, very little work had been done on the wetting of aggregates by bitumen or on the related techniques to measure directly adhesion of bitumen to different aggregates. A greater understanding of the effect of wetting propensity is required to maximize bitumen-aggregate compatibility. In this regard, the direct study of bitumen adsorption on aggregate surface is of particularly importance.

In addition, adsorption process precedes adhesion and dictates the extensive wetting of aggregates by the bitumen. Therefore, using available techniques to follow the process of bitumen adsorption on different minerals in real time, also allow the study of bitumen molecules assembly over the mineral surface. As mentioned before a proper wetting of the mineral surface means high adhesion, then would be beneficial to assess the effect of materials composition on bitumen – aggregate adhesion including the adsorption process.

In the next section, the available techniques used to assess the above mentioned properties in asphalt mixtures are presented and its advantage and disadvantages discussed.

1.2 Surface free energy

The strength of the bonds formed between molecules of the two materials; bitumen and stone aggregates can be related to thermodynamic quantities measured at macroscopic scale allowing

the characterization of solid-liquid interface. These amounts are directly related to the Gibbs free energy involved in the adhesive bond, or the excess free energy of the system associated with the surface or interface, and the work of adhesion as the energy required to detach surfaces. Although equal in magnitude, the work of adhesion (W_a) and the Gibbs free energy of adhesion (ΔG^a) are interpreted as follows,

$$W_a = -\Delta G^a. \quad (1)$$

When two different materials being in intimate contact form an interface, it is necessary to apply a tensile force to split them into dissimilar parts. For a brittle interface of unit cross sectional area, the energy consumed is the sum of the individual surface energies for the materials involved. However, when separated some of the forces developed by molecules of each materials present during the intimate contact are missing. That is, the interfacial energy which have exited before separation that should be subtracted from the energy done to create the two new surfaces (Hefer & Little, 2005a). To explain this phenomenon, Dupré in 1867 postulated the following equation, which plays an important role in adhesion studies for liquid – solid systems (Clint, 2001; Hefer & Little, 2005b)

$$W_a = \gamma_s + \gamma_L - \gamma_{SL} \quad (2)$$

or,
$$\Delta G^a = \gamma_{SL} - \gamma_s - \gamma_L, \quad (3)$$

were γ_s is the surface energy of solid, γ_L is the surface energy of the liquid and γ_{SL} is the interfacial energy between the solid and liquid in contact.

As mentioned earlier, the terms wetting, spreading and contact angles are strongly related to adhesion. In 1805, Young, proposed a relationship between the contact angle formed when a drop

of liquids is placed on a smooth solid surface and the surface tension described as triple junction, or three phase boundary:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta. \quad (4)$$

An interfacial free energy or tension is attributed to each interface forming the triple line. Thus, γ_{SL} is the solid – liquid interfacial energy, γ_{SG} is the surface energy of the solid in equilibrium with the saturated vapour of the liquid, and γ_{LG} is the surface tension of the liquid in equilibrium with the solid. Figure 3 shows a schematic of the contact angle, where θ is the contact angle between the solid – liquid interface and the tangent of the liquid – gas interface.

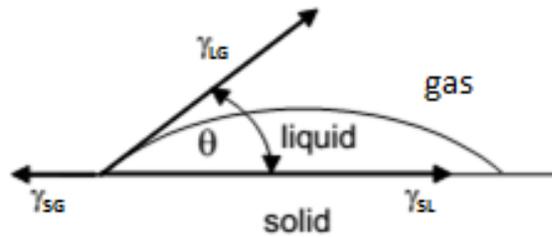


Figure 3. Three phase boundary of a liquid drop on a solid surface in gas.

However, it has been shown that the effect of gas adsorption in the solid – gas interfacial region and liquid – gas interfacial region is negligible for high-energy liquids on low energy solids, which is similar to the contact angles measured on polymeric surfaces, (Good & van Oss, 1992) that is the case of bitumen. Therefore, γ_{SG} and γ_{LG} are taken as the surface energy of the solid (γ_s) and liquid (γ_L) respectively. If equations 2 and 4 are combined in the Young-Dupré equation

$$W_a^{LS} = \gamma_L(1 + \cos \theta). \quad (5)$$

The equation 5 is the way to use contact angles to obtain surface free energies and relate the contact angles to the work of adhesion. On this basis, high energy substrates are more easily wet

than low energy substrates. In addition, more complete wetting will occur if the substrate has a much higher surface energy than the liquid.

This thermodynamic theory is based on the concept that the adhesive adheres to the substrate due to intermolecular forces established at the interface. This theory assumes that the interfacial energy is a function of average surface composition where intimate contact between the materials is achieved (Hefer & Little, 2005b). Therefore, multi-component surface of a mineral has been treated as a uniform surface regardless of their true complexity and structure at nanometer scale. The type of bond formed in the interface by the aggregate with the specific molecules within the bitumen depends on the presence of domains over aggregate surface covered by hydrophobic or hydrophilic molecules. Thus, once again the adhesion depends on the surface composition of both components bitumen and aggregates (Jaroslaw Drelich & Wang, 2011).

Since several model have been proposed for the calculation of the work of adhesion using the surface energy, in 1694, Fowkes proposed a model based on the assumption that surface energy is comprised of a non-polar and a polar component (Fowkes, 1964). But different researchers involved in the study of adhesion science suggest that the best available theory is the one developed by van Oss, Chaudhury and Good (Hefer & Little, 2005a; Carel J. Van Oss, Chaudhury, & Good, 1988).

In the model suggested by Fowkes, the non-polar component of attraction include London, Keesom, and Debye forces also referred to Lifshitz-van der Waals (LW) and the polar component is represented by the acid – base interaction (AB), or specifically interactions mainly due to hydrogen bonding. These components are related by the following equation,

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}. \quad (6)$$

Given that the free energy of adhesion constitutes two components i and j , the Gibbs free energy of adhesion (ΔG_{ij}^a) is,

$$\Delta G_{ij}^a = \gamma_{ij} - \gamma_i - \gamma_j = \Delta G_{ij}^{aLW} + \Delta G_{ij}^{aAB} \quad (7)$$

Using the Berthelot (geometric mean) combining rule, the van der Waals forces representing the interaction of two symmetric molecules is expressed by,

$$\Delta G_{ij}^{aLW} = -2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} \quad (8)$$

However, the acid base interaction cannot be represented by Berthelot rule because they are specific and only possible between molecules with complementary acid-base properties. Thus, the relationship to describe the free energy for this component was obtained empirically by van Oss *et al.* (1988) (Carel J. Van Oss et al., 1988),

$$\Delta G_{ij}^{aAB} = -2\left(\sqrt{\gamma_i^+\gamma_j^-} + \sqrt{\gamma_i^-\gamma_j^+}\right) \quad (9)$$

Based on relationship between the Gibbs free energy of adhesion ($\Delta G_{L,S}^a$), work of adhesion ($W_{L,S}^a$), contact angle (θ) of a probe liquid (L) in contact with a solid (S), and surface energy characteristics of both liquid (γ_L^{LW} ; γ_L^+ ; γ_L^-) and solid (γ_S^{LW} ; γ_S^+ ; γ_S^-), Van Oss, Chaudhury and Good propose the following equation:

$$-\Delta G_{LS}^a = W_a^{LS} = \gamma_L^{Tot}(1 + \cos \theta) = 2(\sqrt{\gamma_L^{LW} + \gamma_S^{LW}} + \sqrt{\gamma_L^+\gamma_S^-} + \sqrt{\gamma_L^-\gamma_S^+}) \quad (10)$$

Where, γ_L^{LW} and γ_S^{LW} are the apolar components of surface energy, γ_L^+ and γ_S^+ are the acid contribution for polar component, and γ_L^- and γ_S^- are base contribution for polar component of surface energy, for liquid and solid respectively.

Based on contact angle technique and the above equation Hefer and Cheng *et al.*, (Cheng, Little, Lytton, & Holste, 2001; Hefer & Little, 2005b) proposed a suitable methodology to measure surface energy of bitumen and aggregates to predict the performances of asphalt mixtures. Although the contact angle technique is theoretically correct in this research, they state that to calculate the surface free energy of bitumen, an improper choice of liquids combined with small experimental errors can significantly affect the accuracy of the calculated surface energy components. Different liquids were proposed to be used as probe liquids for contact angle measurements but some such as formamide dissolve bitumen to some extent and can interact with its surface introducing significant errors to the measurement.

However, it is important to point out that the contact angle, used as a balancing force, only serve as a measure of interaction energies on a macroscopic scale and the used techniques does not allow the study of interactions at molecular level ("Contact Angle and Surface Tension Determination and Preparation of Solid Surfaces," 2006), which makes phenomenological and subjective the bonding assessment between mineral and hydrocarbon materials. The macroscopic scale study of aggregate-bitumen interactions, is based on the acidic or basic aggregate character without deepen into its no homogeneous surface structure and composition at molecular level (Hefer & Little, 2005b). These limitations for experimental macroscopic and indirect analysis of the above mentioned measures have made it difficult or otherwise no satisfactory explanation of unusual behaviours, such as the strong bond developed between some bitumens or its saturated components and acid minerals (A.R & Vinay, 1991). Moreover, there are some issues in the procedure used to calculate surface energy components which negative values of acid or base component arose in some cases. As surface free energy and its components should be positive real numbers, the results must be carefully analyzed. However, because the magnitude of the component is very small,

researchers proposed that can be neglected or considered to be equal to zero for all practical purposes (Hefer, Bhasin, & Little, 2006). This assumption may affect the real significance and values obtained for surface free energy of solids and liquids.

After the identification and improvement of contact angle technique to measure surface free energy of bitumen researchers focused on the application of these techniques to evaluate the stripping potential of asphalt mixture or moisture damage (Aksoy, Şamlioglu, Tayfur, & Özen, 2005; Bagampadde, Isacsson, & Kiggundu, 2006; Bhasin, 2006; Cheng, 2002; D. Little, Bhasin, & Hefer, 2006; Lytton, Masad, Zollinger, Bulut, & Little, 2005). Moisture damage can be defined as the loss of strength and durability in asphalt mixtures due to the effects of moisture and is a primary form of distress in HMA pavements. Lytton *et al.*, (Lytton et al., 2005) evaluated the susceptibility of aggregates and bitumen to moisture damage and the cohesive strength and durability of the bitumen. They proposed a ratio between the adhesive bond energy under wet condition to the adhesive bond energy under dry condition that can be used to identify possible problematic combinations of aggregates and bitumen. The results show some inconsistency with an asphalt mixture that was considered to have poor resistance to moisture damage based on field performance and exhibited good resistance with the ratio proposed. They argued that this difference can be attributed to construction issues that are not related to material properties.

To measure the surface free energy of aggregates were proposed the Universal Sorption Device (USD) (Cheng et al., 2001). Researchers at Texas A&M University used a gravimetric static sorption technique to obtain the surface energies of different aggregates (Hefer & Little, 2005a). With this method, an aggregate sample is placed in a sample chamber, the chamber is vacuumed and a solute is injected to the system. The amount of solute adsorbed on the surface of the sample at determined levels of pressure is measured. The work of the liquid on solid is expressed in terms

of the surface energy of the liquid, γ_L , and the equilibrium spreading pressure of adsorbed vapor on the surface of the solid, π_e , by the following equation:

$$W_a = \pi_e + 2\gamma_L \quad (12)$$

The equation 10 proposed by van Oss et al. (Carel J. Van Oss et al., 1988), therefore becomes :

$$\mu_e + 2\gamma = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^+\gamma_L^-} + 2\sqrt{\gamma_S^-\gamma_L^+} \quad (12)$$

were γ is the surface tension of each liquid probe and μ_e is the spreading pressure of the solute at saturation vapor pressure. The surface energy of the aggregate is calculated after measuring the adsorption of three solutes with known characteristics. The unknown surface energy components of the solid (S) can be solved first with a non-polar solute, such as n-hexane enabling the solving for the Lifshitz van der Waals component, then equilibrium spreading pressures for the polar solutes, such as methyl propyl ketone and distilled water, are subsequently used to determine the remaining acid and base components.

Recently, several methodologies have been proposed to compliment the study of adhesion in asphalt mixtures including macroscopic and microscopic techniques (Grenfell et al., 2013; Guerrero-Barba, Cabrerizo-Vílchez, & Rodríguez-Valverde, 2014; Å. L. Lyne, Krivosheeva, & Birgisson, 2013; Å. L. Lyne, Wallqvist, & Birgisson, 2013; Tan & Guo, 2013). To evaluate the physico-chemical bond between bitumen and aggregates at temperatures closer to the mixing plants, Guerrero *et al.* (Guerrero-Barba et al., 2014), designed a high temperature goniometer to monitor bitumen spreading over limestone substrates. It was found that at high temperatures the configuration of the bitumen drop over the surface was changed by a pancake-drop after spreading, and a near complete and apparently similar wetting was observed regardless of the bitumen origin.

Other researches complement surface energy measurements with mechanical moisture sensitivity assessment techniques for identification of compatible bitumen - aggregate combinations. But the degree of coverage by bitumen over the aggregate particles with these techniques is estimated by visual observation (Grenfell et al., 2013). Results showed that the percentage of bitumen coverage varies depending on the aggregate type and was higher for limestone aggregates than granite.

It has been shown that the presence of nanoscale domains with different composition and charge over the surface of different materials affects the selectivity and dynamics of adhesion and colloidal forces between molecules (Duffadar, Kalasin, Davis, & Santore, 2009; Kozlova & Santore, 2006). Frequently is reported that adhesion forces are dominated by the heterogeneity of surface, which differs from the present thermodynamic theory. As previously exposed the actual theory for adhesion forces uses the average of the surface chemical character, without taking into account that for structures assembled with different fractions or domains, localized interactions cause fluctuations in surface chemistry. This surface heterogeneity results in more attractive local regions or in repulsive surfaces available for adhesion (see Figure 4) (Jaroslaw Drelich & Wang, 2011; Serro, Colaço, & Saramago, 2008). An adequate knowledge of these domains would allow manipulation of nanoscale surfaces to improve adhesion (Clint, 2001; Kozlova & Santore, 2006).

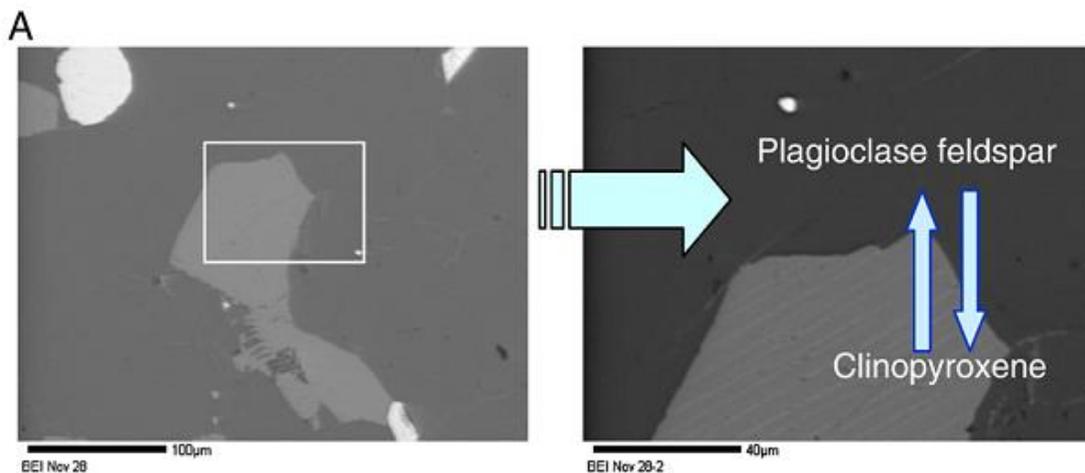


Figure 4. SEM backscattered electron images of Duluth Gabbro sample under the magnification of 300× (left) and 1500× (right) (Jaroslaw Drelich & Wang, 2011).

1.3 Material properties and adhesion at nanoscale

Nowadays, international research has focused on a) to examine the structural surface effects at nano-scale and its relationship to surface energy and b) to study the effects produced by the molecular structure of surfaces on adhesion energy.

Several microscopic techniques have been developed for the study of these interactions, within which interactions established in the bitumen-aggregate interface are included. In the late sixties and early seventies, the growing interest in the relationship between surface topography and adhesion increased the need for the development of microscopy to facilitate the study of this phenomenon. Electron microscopy and electronic spectroscopy allowed to establish in detail the physical structure and chemical composition of surfaces impossible to study previously with other empirical techniques (Henderson, Vrdoljak, Eby, Wicks, & Rachlin, 1994; Hilal, Johnson, Bowen, & Williams, 2009; Sayed Hassan, Villieras, Gaboriaud, & Razafitianamaharavo, 2006; Stipp, Eggleston, & Nielsen, 1994; Xu, 1997).

In recent years, the development of atomic force microscopy, AFM has been indispensable to the study of some findings in the behaviour of macro-scale materials that could not find explanation within the phenomenon of adhesion (Arifuzzaman, 2010). The AFM has become an indispensable device for studying the adhesion between materials at nanoscale and to quantify the adhesion strength measured as the force needed to breaking of links that represents the sum of all forces of interaction developed during the contact (John, 2009). This includes long-range forces

and chemical bonds between groups on surface. Additionally, the AFM can identify individual reactive sites, atoms, and defects in structures.

Despite the potential of this experimental technique, its use in the study of interfacial phenomena in asphalt mixtures has been limited mainly to understanding of the composition and properties that affect bituminous pavement damage due to the action of water and the study of damage on different minerals surfaces (R Grover Allen, Little, & Bhasin, 2012; H. R. Fischer & Dillingh, 2014; Å. L. Lyne, V. Wallqvist, et al., 2013; Masson, Leblond, & Margeson, 2006; Masson, Leblond, Margeson, & Bundalo-Perc, 2007; Rebelo et al., 2014; Yu, Burnham, Mallick, & Tao, 2013). AFM allow the morphological characterization at nanoscale of bitumens having different chemical composition and mechanical properties such as Young's modulus. The first AFM studies of films made of melted bitumen on thin sheets of glass were aimed to study in depth its bee-like structure, called catana phase, attributed to asphaltenes present in bitumen (Loeber, Sutton, Morel, Valleton, & Muller, 1996; A. T. Pauli, Branthaver, Robertson, Grimes, & Eggleston, 2001). A few years later, Abraham *et al.* (Abraham, Christendat, Karan, Xu, & Masliyah, 2002), directly measured the interaction between asphaltenes and silica surfaces in aqueous solutions using AFM (Abraham et al., 2002). Nano and macro structures of bitumen that show different phases named catana, peri, and para phases presented in Figure 5 were characterized by Masson and his coworkers (Masson et al., 2007). Fischer *et al.*, (Hartmut R. Fischer, Dillingh, & Hermse, 2013) identify the typical bee structure in bitumen and its relationship with adhesive forces measured. It was observed that in the region surrounding the bee structures the adhesion forces are lower than the measured in the smooth matrix. Likewise the Young's modulus for the bees region was higher than of the smooth matrix.

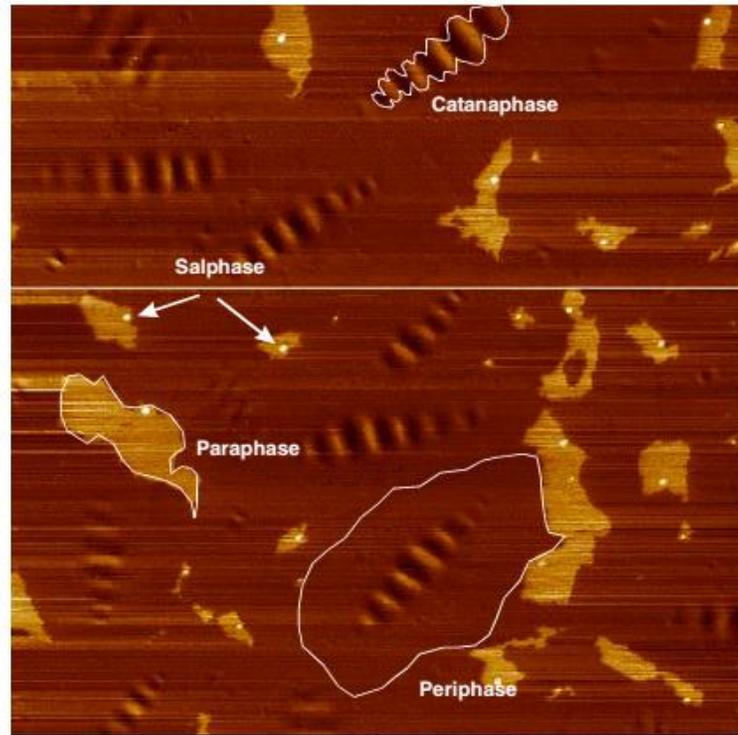


Figure 5. Phase detection image obtained with Atomic for microscopy. Horizontal line result from imperfect image processing (Masson et al., 2006).

Also physical properties such as stiffness could be related to chemical composition of bitumen and pavement performance (R Grover Allen et al., 2012). It was shown that in cases where the saturates fraction of bitumen is maximized, the structuring and chemical polarity of the bitumen microstructure is significantly higher. On the other hand, in bitumens with a low saturates fraction, the structuring and chemical polarity are much lower at the surface. Allen and his co workers (R Grover Allen et al., 2012) also demonstrated that there exists an incompatibility issue which affects the asphalt mixture performance between asphaltenes and saturates. If one of the two fractions is substantially increased a poor asphalt mixture performance was observed. Other researchers have used AFM to study the surface energy and morphology of bitumen, even taking into account the structural changes that occur in real-time with increasing temperature (De Moraes, Pereira, Simão, & Leite, 2010; Liu, Zhang, Xu, & Masliyah, 2006).

Latest research with AFM includes the study of moisture damage produced at nanoscale in bitumen using modified tips. This allows the study of bitumen behavior when get in contact with hydrophilic or hydrophobic surfaces (Al-Rawashdeh & Sargand, 2014; Arifuzzaman, 2010; R. A. Tarefder & Zaman, 2010; R. Tarefder & Zaman, 2011). Other research covers the wetting behavior between bitumen and different mineral surfaces, and adhesion of bitumen different phases such as saturates, aromatics, resins and asphaltenes by AFM force mapping (Arifuzzaman, 2010; Hartmut R. Fischer et al., 2013; Å. L. Lyne, V. Wallqvist, et al., 2013; Rebelo et al., 2014). However, there is not a complete study of bitumen - aggregate adhesion at interface using AFM.

1.4 Conclusions

Theories and associated mechanisms of adhesion were reviewed and presented with specific relationship to bitumen – aggregate systems. Wetting of the aggregate remains an important prerequisite for good adhesion and does not only rely on aggregate properties, but also on bitumen chemical composition. Wetting is required to obtain intimate contact between the materials, and thereby establish fundamental forces ultimately responsible for adhesion.

The fact that thermodynamic theory is the most widely applied in the adhesion science community is not surprising. The energy approach makes it universal, creating the opportunity to incorporate different fundamental chemical processes that drive adhesive bonding. It offers the potential to quantify adhesion through the surface energies of the materials involved. An important and direct application of this approach is to assess the compatibility of various bitumen-aggregate combinations. Although there are some limitations for experimental macroscopic and indirect analysis an assumptions that may affect the real significance and values obtained for surface free

energy of solids and liquids. Further analysis of mathematic methods to calculate the work of adhesion is needed, in order to avoid negative values for the surface free energy components.

Atomic force microscopy was introduced as a technique that can help to analyze the materials properties and they influence on interactions at molecular scale, to explain behavior that at macroscopic scale still have not an explanation. Also bitumen morphology has been study and related to rheological properties ob bitumens.

While the current thermodynamic theory allows the estimation of bitumen-aggregate adhesion due to the van der Waals interactions in these systems, this review indicates that complex interactions at interface can also occur in some bitumen-aggregate combinations. Nanoscale techniques have proved the potential to contribute to the understanding of this complex behavior which constitutes the main objective of this research work.

2 Adhesion at macroscopic scale

2.1 Introduction

The fact that good adhesion between bitumen and aggregate is one of the most important prerequisites in obtaining a good performance in asphalt mixture is as old as pavements constructed in the late 1800s. The main concern that stimulates research into this matter was adhesive failure

induced by water, called moisture damage, or stripping. The most significance outcome of research to these days has been the identification of chemical compounds that could be used as adhesion promoters between bitumen and aggregate (Aksoy et al., 2005; C.W Curtis, 1990; Mogawer, Austerman, & Bahia, 2011).

Although surface tension has long been considered an important parameter to estimate adhesion in asphalt mixtures attempts to place this in a quantitative bases have take long research and time. Nowadays, there are many methods available to measure surface tension of liquids (surface free energy), while methods to evaluate this property in solids are not common. The application of surface energy in adhesion science gained huge interest when Fowkes (1964) (Fowkes, 1964), proposed the division of surface energy into independent components, which are related to different intermolecular forces on the surface, namely polar and dispersive components. Years later, van Oss *et al.*, (1988) (Carel J. Van Oss et al., 1988) proposed a three component theory, based on a modified form of the acid-base theory.

The chemical properties of an aggregate, rock or mineral surface are controlled by surface chemical composition, surface morphology, and surface coatings, which have a direct impact on the magnitudes of the surface energy components. The chemical composition is the responsible for the presence of nonpolar and polar active sites on mineral surface. Adsorbates bond primarily with van der Waals components of nonpolar sites. Because these nonpolar surfaces have no charge and no permanent dipole moment they are termed hydrophobic. On the other hand, polar active sites on surfaces can have permanently charged sites, conditionally charged sites, have exchangeable metal cations, or exposed uncoordinated metal atoms. Surfaces with predominantly polar sites are termed hydrophilic due to their charge and dipole moments (Deng & Dixon, 2002; Johnston & Tombacz, 2002). Consequently, if the chemical composition of the surface of the

aggregates differs much; bitumen may be compatible with aggregates at one site and incompatible with that at another. Therefore, to know the surface properties of common minerals can serve as a useful resource to understand and explain the interaction between aggregates and other materials such as water, bitumen, and other chemical additives used in pavement construction (C. Miller, Little, Bhasin, Gardner, & Herbert, 2012).

The thermodynamic theory of Gibbs free energy has been used in several researches to study the surface energy characteristics of bitumens and aggregates and to predict the performance of hot mix asphalt (Bhasin, Dallas, & Little, 2007; Cheng et al., 2001; Hefer & Little, 2005b; Howson et al., 2011). Although the surface free energy of a number of bitumens has been characterized, there has not been a comprehensive study of the surface energies of mineral aggregates and much less of a variety of the most common minerals that compose aggregates with consistent methodology. Undoubtedly, the prediction of the magnitude of these components as a function of material properties is valuable in determining the dominant interfacial interactions between different chemical species and rock or mineral surfaces that control adhesion. The work of adhesion in the presence of a third medium, such as water, can also be predicted (Cheng, Little, Lytton, & Holste, 2002; Elphinstone, 1997). In addition, surface energy and its components are fundamentally related to the fracture damage and healing phenomena induced by repeated wheel loads in bituminous paving mixtures (D. N. Little, Lytton, & Williams, 1997).

At the same time, pull-off tests initially developed for non-viscous paint to evaluate pull-off strength of coatings on rigid substrates such as metal, concrete and wood was adapted and used to study bitumen – aggregate interaction and to predict the adhesion and moisture susceptibility of the system at macroscopic scale. The bitumen industry first utilized the Pneumatic Adhesive Tensile Testing Instrument, or PATTI, in the late 1990s to evaluate adhesive loss of bitumen-

aggregate systems exposed to moisture conditioning. Improvements to the pull-out stub design, loading rate control and substrate preparation procedures represented significant advancements from the original PATTI test to its current form as the Bitumen Bond Strength (BBS) test method. While the original test procedure did yield quantitative information related to bond strength characteristics and failure behavior, research at University of Wisconsin-Madison in partnership with the University of Ancona – Italy (UAI) and the University of Stellenbosch-South Africa (USSA) identified several factors influencing the effectiveness of the test method (Canestrari, Cardone, Graziani, Santagata, & Bahia, 2010; Kanitpong & Bahia, 2003; T. Miller, Arega, & Bahia, 2010). Further modifications and the development of a new BBS Testing procedure (AASHTO TP-91, 2011) made the testing of the bitumen – aggregate bond a reality.

In this chapter, the surface free energy of three bitumens are obtained using the contact angles measured with different liquid probes. Work of adhesion using the surface free energy of bitumens and aggregates were calculated in order to evaluate the adhesion strength for different materials combinations. Additionally, aggregates commonly used in the fabrication of asphalt mixtures in Colombia and the same three bitumens were employed to evaluate the adhesion and cohesion by the Pneumatic Adhesion Tensile Tester Instrument.

2.2 Materials and methods

2.2.1 Materials properties. Four different aggregates used in road construction in Colombia named AGC, AGE, AGI, AGM, were used for testing adhesion at macroscopic scale with Pneumatic Adhesion Tensile Tester Instrument (PATTI). These aggregates were

characterized by Corasfaltos as a part of a research project developed to study the characteristics of the main aggregates used for asphalt mixtures in Colombia and its influence in mixtures performance. The main components for all aggregates samples obtained by petrographic analysis are presented in Table 1. Tables 2 and 3 present results for mineralogical composition analysis using X-ray Diffraction (XRD) and chemical composition by means of X-ray Fluorescence (XRF) respectively.

From the petrographic analysis results, aggregates can be classified into two groups based on their formation process. AGC and AGM aggregates are composed mainly by igneous rocks while AGE and AGI come from rocks of metamorphic origin. In general, all aggregates samples show an intermediate character with acidity level close to 50%. This contribute to the bitumen - aggregate adhesion according to the historical acidic behavior of Colombian bitumen. This suggests that aggregates should not have serious problems regarding adhesion to conventional bitumen.

Table 1. Aggregate samples composition

Constituent	Particle percentage (%)											
	Coarsed aggregate				Coarse sand				Fine sand			
	AGC	AGE	AGI	AGM	AGC	AGE	AGI	AGM	AGC	AGE	AGI	AGM
Igneous	100.0	27.8	1.1	77.5	90.2	19.0	7.5	75.2	17.3	48.2	0.7	28.4
Sedimentary	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.7	0.3
Metamorphic	0.0	72.2	98.6	22.5	0.0	81.0	64.2	23.6	0.0	16.1	16.7	8.1
Monomineralic	0.0	0.0	0.0	0.0	9.8	0.0	20.1	0.4	82.7	35.8	79.3	61.5
Others	0.0	0.0	0.0	0.0	0.0	0.0	8.2	0.3	0.0	0.0	2.7	1.8

The DRX and FRX results for AGC and AGE aggregates show a higher content of minerals such as feldspar, amphibole, and kaolinite. The presence of motmorrillonite in AGC (10,3%) and

AGE (8,8%), being considered an expansive clay could generate adhesion problems when used in asphalt mixtures, although the percentages in these samples do not represent a significant problem.

Table 2. *Aggregates mineralogical composition with XRD*

Constituent	AGC Percentage (wt/wt %)	AGE Percentage (wt/wt %)	AGI Percentage (wt/wt %)	AGM Percentage (wt/wt %)
Montmorillonite	10.3	8.8	0.0	0.0
Chlorite	6.9	6.6	7.0	11.4
Mica	6.9	5.1	9.1	6.0
Kaolinite	14.70	11.8	24.2	20.8
Quartz	4.3	3.7	37.6	26.8
Feldspars	34.5	30.1	5.4	16.8
Amphibole	21.6	33.8	5.9	18.1
Calcite	0.9	0.0	0.0	0.0
Interbedded	0.0	0.0	2.7	0.0
Metahalloysite	0.0	0.0	2.7	0.0
Cristobalite	0.0	0.0	2.7	0.0
Unidentified	0.0	0.0	2.7	0.0

The mineralogical composition of AGI and AGM identified by XRD, guarantee the absence of plasticity because as shown in Table 2 this materials do not contain motmorrillonita. The only identified clay is kaolinite, which does not present volumetric changes in the presence of water, and promotes the binder-aggregate adhesion. The main minerals identified in these aggregates are kaolinite and quartzite.

From XRF analyzes can be conclude that the main chemical constituents for all samples are silica, alumina and iron, all in the form of oxide compounds.

Table 3. *Aggregates chemical composition with XRF*

Constituent	AGC wt/wt %	AGE wt/wt %	AGI wt/wt %	AGM wt/wt %
SiO ₂	54.37	50.82	54.70	51.68
Al ₂ O ₃	15.76	16.91	18.90	15.95
Fe ₂ O ₃	9.93	11.06	10.40	11.95

Constituent	AGC wt/wt %	AGE wt/wt %	AGI wt/wt %	AGM wt/wt %
CaO	8.34	10.58	5.80	8.01
MgO	4.58	5.70	3.50	4.75
Na ₂ O	3.92	3.59	1.40	2.54
K ₂ O	0.80	0.25	1.60	1.07
TiO ₂	1.35	1.34	1.81	1.80
P ₂ O ₅	0.49	0.35	0.12	0.26
MnO	0.19	0.21	0.16	0.20
Cl	0.04	0.00	0.03	0.03
Cr	0.02	0.02	0.03	0.05
V	0.03	0.03	0.03	0.04
Ba	0.04	0.03	0.06	0.04
Sr	0.03	0.02	0.01	0.03
Zr	0.05	0.02	0.02	0.06
Zn	0.01	0.01	0.01	0.01
S	0.03	0.12	1.46	1.53
Y	0.01	0.00	0.00	0.01
Rb	0.00	0.00	0.01	0.00
As	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.01
Ce	0.00	0.00	0.00	0.00

Three different bitumen samples named A, B and C, were provided by the Colombian Institute of Petroleum, ICP, ECOPETROL S.A. (Colombia) and used as received, properties are shown in Table 4.

Table 4. Properties and Compositions of Bitumen Samples

Property	A	B	C
Penetration@25°C mm/10)	71.2	5.2	34.0
Viscosity @ 80 °C (cP)	21687	2960610	35514
Saturates (%)	16.06	10.62	12.22
Aromatics (%)	50.87	46.62	51.6
Resins (%)	25.83	22.11	25.88
Asphaltenes (%)	7.24	20.65	10.3
Nitrogen (wt%)	0.17	0.201	0.214
Sulfur (wt%)	1.63	1.92	1.93
Acid number (TAN)	0.93	0.362	1.299
Resins/asphaltenes ratio	3.57	1.07	2.51
Colloidal Index	3.29	2.20	3.44

From Table 4 it can be seen that bitumen A has penetration similar to bitumen used in conventional asphalt mixtures of 60-70. Bitumen B and C with different properties were selected to study the influence of bitumen properties in adhesion and adsorption. It was previously suggested by other researchers that the chemical composition of bitumen is related with its surface free energy and therefore with adhesion with mineral aggregates. Asphaltenes plays an important role, lowering the value of the surface free energy. On the contrary, the resins, ratio of resins/asphaltenes, and the colloid index have a significant effect increasing the value of the surface free energy (Wei, Dong, Li, & Zhang, 2014).

In the following sections, bitumen samples were used for surface free energy characterization by contact angle measurement and bitumen bond strength with aggregates assessment. Then, the influence of bitumen properties on the measured properties was assessed.

2.2.2 Sessile Drop Method. By definition the surface free energy (SFE), of a material is defined as the energy needed to the disruption of intermolecular bonds to create a new element surface area (Tan & Guo, 2013). Asphalt pavement performance properties are related to adhesive and cohesive strength of the bitumen-aggregate, and can be related to the surface free energy characteristics of the system. SFE theory has been widely used in colloid, lubrication, adhesive coating, and painting industry for many years, and is presented in many textbooks of surface physical chemistry ("Contact Angle Measurements and Solid Surface Free Energy," 2008; John, 2009; "Surface Free Energy and Relevance of Wettability in Adhesion," 2009). However, the SFE

of solids cannot be measured directly, indirect methods are used, and is inferred from the known surface free energy values of several solvents.

The measurement of contact angles are commonly used to calculate surface free energy of bitumen (Cheng et al., 2002; Hartmut R. Fischer et al., 2013; Hefer et al., 2006). The sessile drop method is an optical measurement method based on contact angle, which evaluate the solid surface energy characteristics of bitumen defined in Chapter 1 by equation (10). The schematic diagram of contact angle test is shown in Figure 6. The device includes a microliter syringe that allows the user to comfortably form drops of various liquids on a smooth solid surface positioned on a small table. Drops are backlit by LEDs through groundglass and its shape is instantly photographed by a camera. Contact angle of the liquid with the solid surface from images is calculated either manually or through drop shape analysis performed on a software. More refined techniques such as axisymmetric drop shape analysis (ASDA) can also be used to compute precisely the shape and contact angles of the drop by using computer analysis to fit the observed shape to the drop using theoretical models (Kwok et al., 1998).

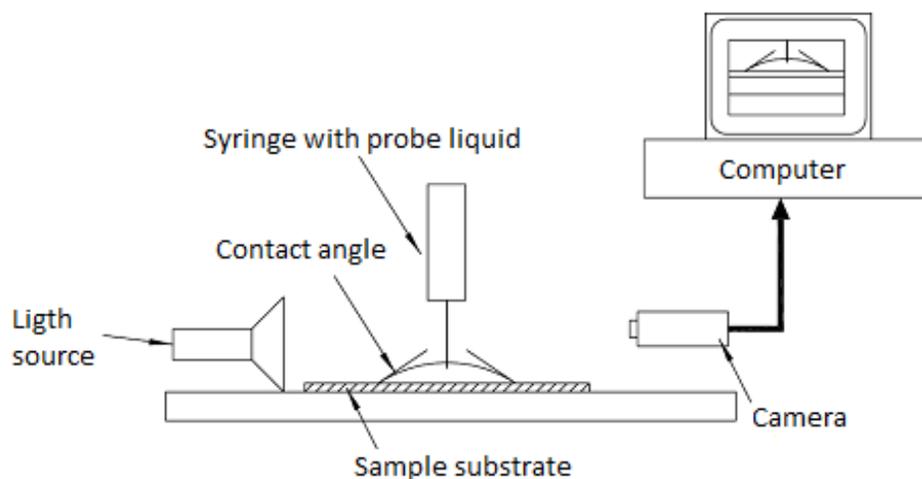


Figure 6. The schematic diagram for contact angle test (Bose, 2006; D. Little et al., 2006)

Although there are several approaches to calculate the surface free energy from contact angle measurements (Ardebrant & Pugh, 1991; Carel J. Van Oss et al., 1988), the theoretical basis of this approach is the Young - Dupre relation exposed in equation (1) in the previous chapter.

For the calculation of the surface free energy of solids, using the results of contact angle measurements Fowkes and van Oss models are employed. Fowkes model (Fowkes, 1964) suggested that surface energy is comprised of a polar and non-polar or dispersion components, where the work of adhesion W_a is expressed in terms of the polar and non-polar components of the surface energy as following (Ahadian, Mohseni, & Moradian, 2009):

$$W_a^{LS} = 2\sqrt{(\gamma_l^{LW})(\gamma_s^{LW})} + 2\sqrt{(\gamma_l^{AB})(\gamma_s^{AB})} \quad (13)$$

where l is for liquid, and s is for solid component in this case replaces by bitumen. Because there are two unknown quantities $(\gamma_s^{LW}, \gamma_s^{AB})$, with this method it is necessary to measure the contact angle with at least two probe liquids which one is polar and the other is non-polar. Diiodomethane is the only non-polar liquid with known surface energy components that could be used without dissolving the bitumen. Combining Young-Dupré equation and equation (13), the components of solid surface energy, in this case replaced by bitumen, can be determined.

For the theory of van Oss *et al.*, or three liquid method, the polar part is divided to Lewis acid and Lewis base as in Equation (14) (Carel J. Van Oss et al., 1988). This polar part includes ionic bonding and hydrogen bonding.

$$W_a^{LS} = 2\sqrt{(\gamma_l^{LW})(\gamma_s^{LW})} + 2\sqrt{(\gamma_l^-)(\gamma_s^+)} + 2\sqrt{(\gamma_l^+)(\gamma_s^-)} \quad (14)$$

In this method, the contact angles have to be measured at least with three different liquid probes.

Using any given liquid l_i the equation 14 can be written as

$$\sqrt{\gamma_{l_i}^{LW}} x_1 + \sqrt{\gamma_{l_i}^-} x_2 + \sqrt{\gamma_{l_i}^+} x_3 = \frac{1}{2} \gamma_{l_i}^{Tot} (1 + \cos \theta_i) \quad (15)$$

where x_1 , x_2 , and x_3 are the square roots of the unknown bitumen surface energy components and other terms are as describe earlier. In practice, the equation 15 for n liquids can be expressed as a matrix of the following form:

$$\begin{bmatrix} \sqrt{\gamma_{l_1}^{LW}} & \sqrt{\gamma_{l_1}^-} & \sqrt{\gamma_{l_1}^+} \\ \sqrt{\gamma_{l_2}^{LW}} & \sqrt{\gamma_{l_2}^-} & \sqrt{\gamma_{l_2}^+} \\ \vdots & \vdots & \vdots \\ \sqrt{\gamma_{l_n}^{LW}} & \sqrt{\gamma_{l_n}^-} & \sqrt{\gamma_{l_n}^+} \end{bmatrix}_{n \times 3} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}_{3 \times 1} = \frac{1}{2} \begin{bmatrix} \gamma_{l_1}^{Tot} (1 + \cos \theta_1) \\ \gamma_{l_2}^{Tot} (1 + \cos \theta_2) \\ \vdots \\ \gamma_{l_n}^{Tot} (1 + \cos \theta_n) \end{bmatrix}_{n \times 1} + \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix}$$

or

$$Ax - B = E \quad (16)$$

were E corresponds to the column error matrix. Although theoretically E is a null matrix, it can have real values due to experimental errors and over determinacy of the A matrix. The probe liquid surface energy components constitutes the A matrix and the measured contact angles matrix B . With an iterative method to minimize the sum or squares of errors (elements of E matrix) the unknown matrix x is determined. The elements of x matrix are then squared to obtain the surface energy components of bitumen. Researchers found that in some cases the square root of a bitumen surface energy component, usually the acid or base component, is negative. However, they state

that in such cases the magnitude of the component is very small and can be neglected or considered to be equal to zero for all practical purposes (D. Little et al., 2006).

Surface free energy of three bitumens A, B, C in the range of representative chemical composition and from various crude sources was obtained using the measured contact angles at Akbulut research group laboratory in Texas A&M University. A micro syringe to put drops of various liquids on bitumen surface was used. Drops were backlit by LEDs through groundglass and its shape was instantly photographed by a high resolution camera. Table 5 presents the surface free energy components from four liquids using as probes in measuring contact angles. Contact angles from images were obtained through ASDA performed on a software.

Table 5. *Surface Energy Characteristics of Probe Liquids at 20 °C (mJ/m²)(C.J. van Oss, 1994)*

Liquid	γ_L (mJ/m ²)	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)
Water	72.8	21.8	25.5	25.5
Glycerol	64.0	34.0	3.9	57.4
Ethylene glycol	48.0	29.0	1.9	47.0
Diodomethane	50.8	50.8	0.0	0.0

Note: γ_L : Surface free energy of the liquid, SFE; LW: Lifshitz van der Walls; +: acid (electron acceptor); and -: base (electron donor).

2.2.3 Pneumatic Adhesion Tensile Tester Instrument, PATTI. Due to the simplicity of Pneumatic Adhesion Tensile Tester Instrument (PATTI) device and its ability to isolate failure near the interfacial region between adhesive and substrate, the pull-off test has the potential for routine use to measure mechanical bond strength of bitumen applied to an aggregate surface. In this test method, the pull-off strength is determined by measuring the maximum tensile force needed to remove a pullout stub adhered to a solid substrate with bitumen. The pull off tension at failure is used to describe the adhesive properties of the bitumen and compatibility between

aggregates and bitumen. This test method provides a value for the maximum strength the bitumen-aggregate bond can tolerate.

A pneumatic load is applied to a pullout stub until failure using an ASTM D 4145 Type IV adhesion tester (see Figure 7) and following the procedure described in the AASHTO TP-91-11 standard for bitumen bond strength test. The adhesion tester applies a pneumatic load via pressure ring to a pullout stub fixed to a rigid substrate with bitumen, as shown in Figure 8. Recording the applied stress on the binder sample allows for calculation of load to failure. The surface of the substrate is visually examined to determine the type of failure mode. Evaluation of pullout tensile strength on different aggregate substrates allows for assessment of bitumen-aggregate compatibility.

Using the PATTI device, the burst pressure (BP) under constant load rate (at least 2 psi/s but not to exceed 6 psi/s) necessary to debond bitumens A, B and C from the aggregate surfaces AGC, AGE, AGI, AGM at room temperature were measured.

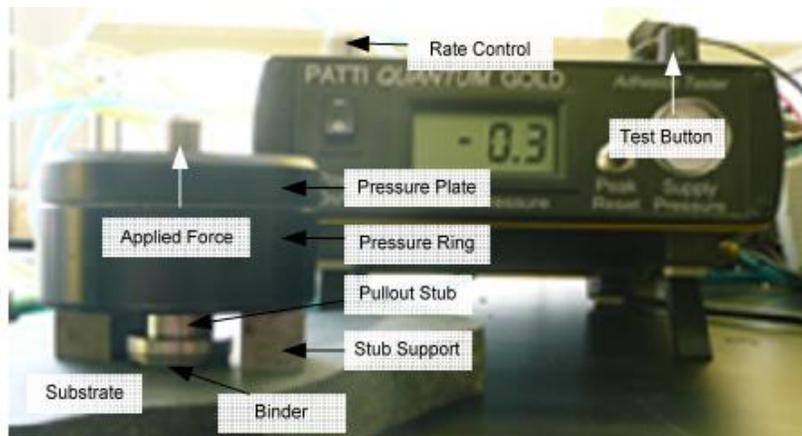


Figure 7. General representation of adhesion tester apparatus

The Pull-Off Tensile Stress (POTS) at failure in psi for each system is determined as follows:

$$POTS = \frac{(BP \cdot A_g) - C}{A_{ps}} \quad (17)$$

where A_g is the contact area of the gasket with the reaction plate (sq in), C is the piston constant (lbs), A_{ps} is the area of the pull-stub (sq in), and BP is the burst pressure (psig).

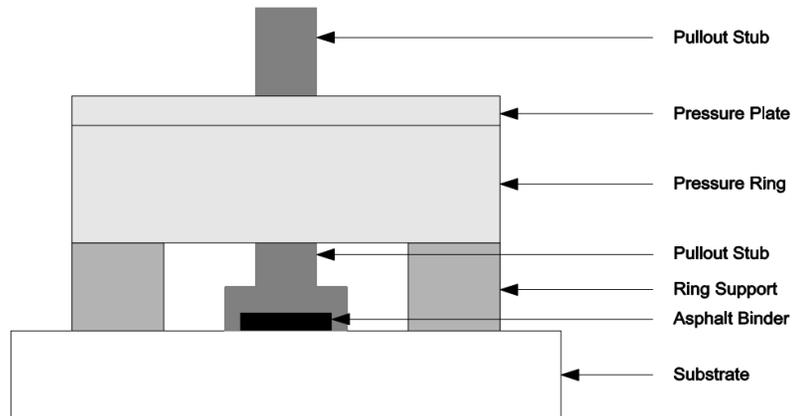


Figure 8. Schematic representation of testing assembly for the bitumen bond strength test, AASHTO TP 91-11

2.3 Results and discussion

2.3.1 Surface Free Energy. In order to study the cohesion and adhesion at macroscopic scale, the surface free energy of bitumen was tested. Table 6 presents the contact angles between different bitumens and test liquids obtained using the sessile drop method. Hot molten bitumen sample was coated on a thin glass slide before dropping liquids over the surface with a micro syringe. In Figure 9 it is shown a picture of a drop of water on bitumen B surface taken to measure

of contact angle. The surface free energy parameters calculated using Equations (13) and (14) are shown in Tables 7 and 8, respectively.

Table 6. Contact Angle (θ) Data from Sessile Drop Method

Bitumen	Water		Glycerol		Ethylene glycol		Diiodomethane	
	$\theta(^{\circ})$	SD	$\theta(^{\circ})$	SD	$\theta(^{\circ})$	SD	$\theta(^{\circ})$	SD
A	93.96	0.40	84.15	0.63	77.17	1.26	52.82	1.11
B	104.79	0.88	93.45	1.22	81.09	0.74	61.83	1.77
C	102.25	0.86	88.65	1.73	76.24	3.38	54.83	3.91

Note: SD is standard deviation.

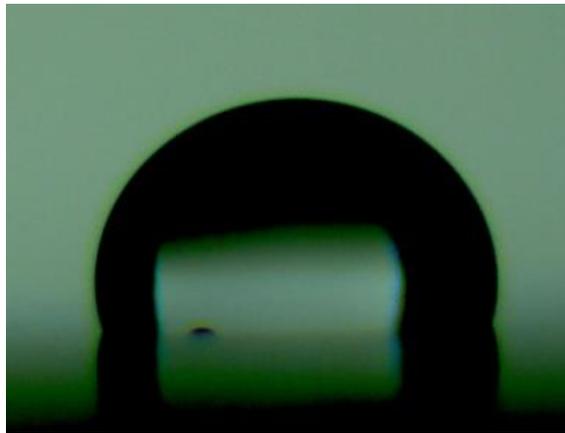


Figure 9. Contact angle from sessile drop of water on bitumen B

It can be seen from Tables 7 and 8 that the surface free energy of bitumen A is higher than bitumen B and C. The most significant contributor to the total surface energy is the Lifshitz-van der Waals (LW) or dispersion component, which suggest that the intermolecular force within bitumen is very strong. This is in accordance with the fact that bitumen is primarily a nonpolar material. The polarity force contributor of bitumen A is stronger than bitumens B and C. However, from one model to another the LW component differs for bitumens B and C.

Total surface energy of bitumen calculated using the contact angles varies from 33.4 to 26.5 mJ/m². These values are in agreement with the typical range reported in previous researches from 13 to 45 mJ/m² (Cheng et al., 2002; Hefer et al., 2006; Howson et al., 2011).

Table 7. Surface Energy of Bitumen Calculated from Contact Angle Data with Fowkes model (mJ/m^2)

	Υ_s		Υ^{LW}		Υ^{AB}	
	Avg	SD	Avg	SD	Avg	SD
Bitumen
A	33.4	0.5	32.9	0.5	1.2	0.05
B	27.5	1.7	27.3	1.7	0.2	0.04
C	32.2	2.6	32.1	2.6	0.1	0.04

Table 8. Surface Energy of Bitumen Calculated from Contact Angle Data with three van Oss et al. model (mJ/m^2)

	Υ_s		Υ^{LW}		Υ^+		Υ^-	
	Avg	SD	Avg	SD	Avg	SD	Avg	SD
Bitumen
A	32.3	0.7	32.3	0.7	0.0	0.0	2.0	0.4
B	29.0	1.1	29.0	1.1	0.0	0.0	0.2	0.2
C	26.5	1.2	26.5	1.2	0.0	0.0	0.8	0.3

Sessile drop method has been used for decades to calculate the surface free energy of solids for different applications (Jouyban & Fathi-Azarbayjan, 2012), although some researchers suggest that improvements are still required to enhance its sensitivity in detecting acid and base components (D. Little et al., 2006). From Table 7 it is observed that *AB* component of surface free energy could be obtained from Fowkes model, although from Table 8 this same component is zero. The zero value was set to solve the matrix according to the suggestions made by other researchers in previous studies (Hefer et al., 2006). These differences in values obtained, and given that for two liquid model it was obtained an adequate value for polar component of surface free energy, suggest that sessile drop method and Fowkes model has adequate sensitivity to the *LW* component and for acid-base (*AB*) component.

The relation of surface free energy of bitumen and its composition has been studied by some researchers (Jada & Salou, 2002; Wei et al., 2014). A further analysis between the experimental data obtained and chemical composition of bitumen samples were done. As seen in Table 4, samples A and C have higher resins content than sample B. Wei *et al.* (Wei et al., 2014) reported that high surface energy was due to the high polarity of resins containing heterocyclic and fused ring compounds. Therefore, higher content of resins in bitumen A and C caused higher polarity and thus higher surface free energy than bitumen B as observed in Table 7 with Fowkes model but opposite behavior was observed in Table 8 for bitumens B and C using the van Oss model. Due to the aggregation tendency of asphaltene in order to reduce the energy of the colloid system, surface free energy dropped with increasing asphaltene content (Jada & Salou, 2002). With high content of asphaltene, it will also cause a low polarity on bitumen surface. At similar resin amount, higher surface energy in bitumen A is expected because bitumen C contains more asphaltene, which one more time is congruent with results obtained using two components method but not for the three component method.

Furthermore, relationship between two important ratios of bitumen samples such as resins/asphaltene ratio and the colloidal index were also analyzed. It is expected that the ratio of resins/asphaltenes is positive correlated with the surface free energy of bitumen in Table 7. If the asphaltene content is high and the resins content is low in bitumen, asphaltenes will form aggregations, which results in a decreased surface free energy of bitumen due to the reduced polarity caused by asphaltene aggregation. The resins play an important role in stability of asphaltenes, a higher resins content with respect to asphaltene will prevent its aggregation and this will be reflected in a high surface free energy. This is reflected in a high surface free energy in

bitumen A. From Tables 4 and 7, bitumen samples with high resins/asphaltene ratio resulted in higher surface free energy.

The components in the bitumen follow a colloidal law expressed by the following relationship:

$$CI = (resins + aromatics)/(saturates + asphaltenes)$$

A higher colloidal index is proper of a more stable colloid structure where asphaltenes are more peptized by resins in the oil-based medium (Loeber, Muller, Morel, & Sutton, 1998). From surface free energy results can be observed that there is positive relationship with colloid index. Even if saturates and aromatics are considered to do not have a significant correlation with surface free energy, they are immersed in the colloid system characterized by *CI*, and play an important role as the dispersion phase. The highest surface free energy values were obtained for bitumens with high colloidal index. This index also probes that there exists a relationship between the chemical composition of bitumen and the surface free energy, and suggest a proper calculation of surface free energy using the two components, Fowkes method.

In order to evaluate the work of adhesion of combinations of materials, the surface free energy of the aforementioned bitumens and surface free energy of different minerals present on aggregates commonly used in asphalt mixtures were used to quantify and analyze differences in the work of adhesion of combinations of these materials. Table 9 shows the surface free energy components of different minerals measured with the universal sorption device (Bhasin et al., 2007) which are part of a previous research to assess the impact of natural minerals on aggregate - bitumen bond strengths and asphalt mixture durability (C. Miller et al., 2012).

Figure 10 presents the work of adhesion in dry condition obtained when combining the surface free energy components of bitumen included in Table 7 with surface free energy components of aggregates reported in Table 9 using Equation 13.

Table 9. Surface Energy of Selected Minerals (mJ/m^2)(C. Miller et al., 2012)

Mineral	Acid	Base	Total Polar Component	van der Waals	Total Surface Energy
Calcite	0.40	85.16	11.60	34.94	46.54
Muscovite	0.55	544.68	34.52	47.55	82.07
Kaolinite	5.01	80.00	40.02	30.48	70.51
Montmorillonite	1.57	80.43	22.45	42.85	65.29
Andesine	0.40	3755.04	77.70	40.64	118.34
Quartz	0.02	365.00	5.04	50.33	55.37
Hornblende	0.91	1338.86	69.70	51.92	121.63
Hematite	2.85	558.07	79.82	48.99	128.81

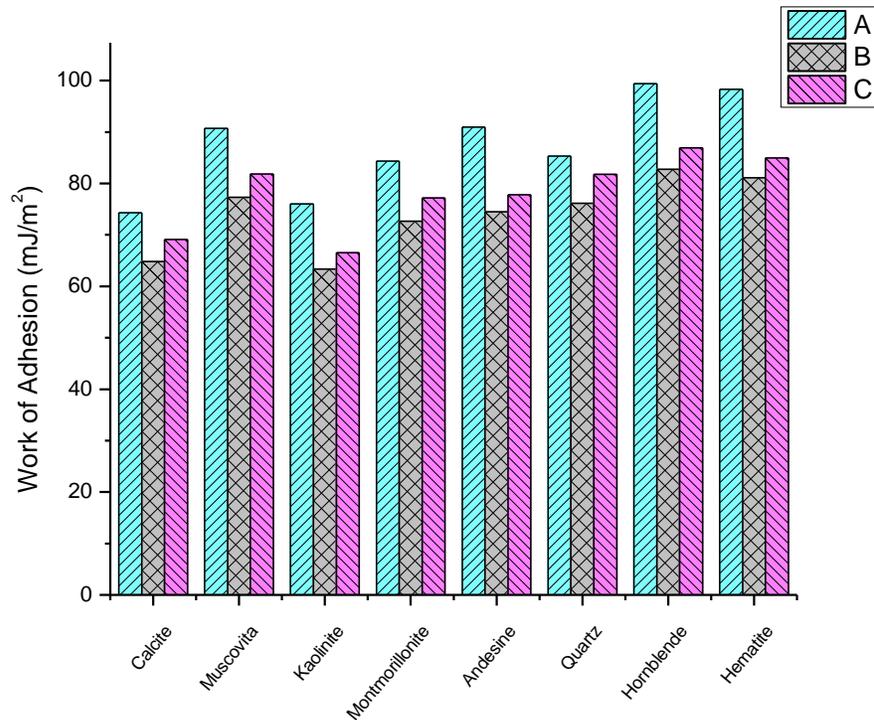


Figure 10. Work of adhesion for different minerals and bitumen systems

For an asphalt mixture to be durable and have a relatively low sensitivity to moisture, it is desirable that the work of adhesion, $W_{L,S}^a$, between the bitumen and the aggregate be as high as possible. From Figure 10 it can be seen that the system with the highest adhesion is composed of bitumen A and hornblende, while the weak work of adhesion was obtained for bitumen B and kaolinite. Although there are differences between the values obtained for work of adhesion for all bitumen–aggregate systems, in general, the results shown higher work of adhesion for bitumen A with all minerals considered.

Based on the results for work of adhesion calculated for bitumens with pure minerals presented in Figure 10, there is a possibility that localized regions on aggregate surfaces containing some minerals may form more stable and strength bonds. This, considering that aggregates used to produce asphalt mixtures consist of more than one mineral it is also possible that the sum effect of all the minerals on the aggregate surface will usually result in aggregate – bitumen bond that is thermodynamically prone to stripping. However, the stability depends on the mineral as well as surface chemistry of the binder.

2.3.2 Bitumen -aggregate bond strength. Each of the samples were tested after allow to dry and acclimate to laboratory conditions for approximately 24 h and the test temperature was controlled. Upon failure the burst pressure was recorded and the location of failure was noted. The average pull-off strength was calculated with Equation 17 from four replicates. The character of the failure was determined by observation. Failure occurs along the weakest plane within the system. If failure occurred anywhere except cohesively within the bitumen or adhesively between the bitumen and aggregate interface, the specimen have to be discarded from calculations to determine pull off tensile strength (POTS) described by Equation 17. In other words, if failure is observed to occur by one edge of the system or other location and not homogeneously in the

bitumen-aggregate interface or within the bitumen, the measurement cannot be used to calculate the POTS. Failure in dry condition typically occurs within the bitumen specimen and is hypothesized to occur at the interface of bitumen specimen and the substrate after soaking in water for certain periods of time.

The mean POTS and standard deviation for each bitumen with AGC, AGE, AGI, AGM substrate in dry condition are shown in Figure 11. The error bars represent the standard deviation from the mean value. The failure type for all samples was cohesive, which indicates that the adhesive bond in the bitumen - aggregate interface is larger than the cohesive strength of bitumens. Also, Figure 11 indicates that AGI aggregates have higher adhesive bond to bitumens than AGC aggregates, and thus more resistance to adhesive failure. Bitumen B showed the highest POTS with all aggregates.

Figure 11 shows selected examples for the failed samples after testing in bitumen bond strength. From these types of figures, the failure is define depending of the percentage of area of aggregate that is exposed, if more than 50% of the aggregate area is exposed, the failure is defined as adhesive; otherwise, the most likely failure mode is due to cohesion within the bitumen.

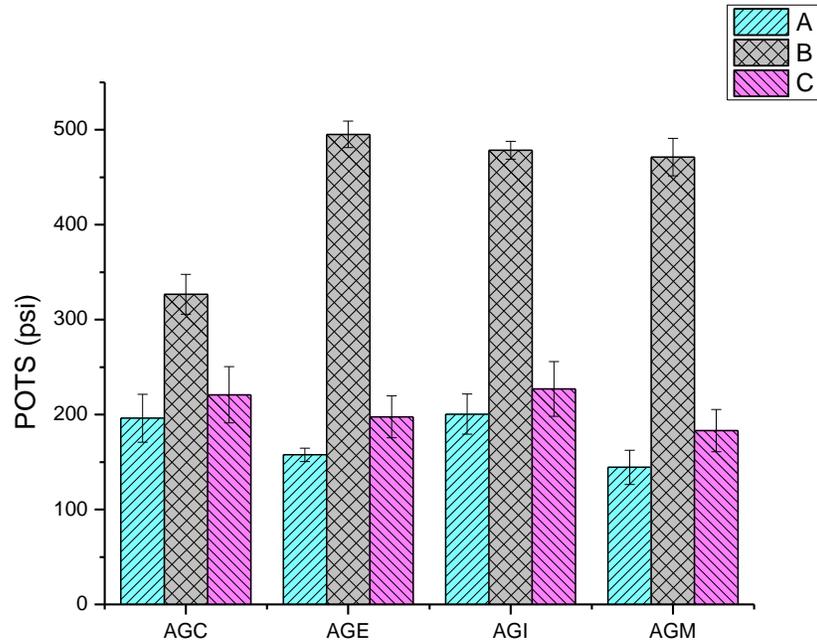


Figure 11. Pull-off Tensile Strength of Bitumens on Different Substrates



Figure 12. Bitumen bond strength specimens after testing under dry conditions for bitumen with aggregate a) AGC and b) AGE.

Due to the cohesive nature of the failure, it can be concluded from Figure 11 that bitumen B has the highest cohesive strength, followed by C and A, respectively. Cohesion may be defined as the internal strength of an adhesive due to various interactions within that adhesive that binds the mass together. Whereas adhesion is the bonding of one material to another, namely, an adhesive to a substrate, due to a number of different possible interactions at the adhesive-substrate interface.

Therefore, in relation to adhesive properties of bitumen-aggregate systems it can be expected that the adhesion of bitumen B with all aggregate samples to be higher than the adhesion between bitumens C and A with the same surfaces.

2.4 Conclusions

Contact angles for bitumen samples using sessile drop with different liquids probes were obtained and used to calculate the surface free energy of bitumen. A relationship between the surface free energy and chemical composition of bitumen was observed. Higher resins content in bitumen caused higher polarity and thus higher surface free energy, contrary to the asphaltene content, a high content of asphaltene will cause a low polarity and therefore lower surface free energy. Also, work of adhesion for different bitumen–aggregate systems was evaluated using surface free energy information for aggregates available in literature. Results suggest that bitumens analyzed develop a strength bond with hornblende and therefore a high work of adhesion.

With regard to the bitumen bond strength assessment with PATTI it was observed that the failure type for all bitumen – aggregate samples were cohesive, hence adhesive bond was not measured but it can be stated that the adhesive force at the interface is larger than of cohesive strength of bitumens. From the results, pull off tensile strength for bitumen B with all aggregate samples was higher than for bitumens A and C.

3 Adhesion at nanoscale with atomic force microscopy

3.1 Introduction

As far as minerals were concerned, the large number of applications that takes place inside the atomic force microscopy (AFM) analysis and systems in which they are present show its importance (Chau, 2009; Das, Becker, & Nair, 2010; J. Drelich et al., 2006). The most relevant studies are concerned with the characterization of mineral surfaces (Bennewitz et al., 1994; Buzio et al., 2007), established forces and the effect of microtopography and chemical heterogeneity in several systems such as oil sands, cements and coatings to name a few (Yurtsever, Gigler, & Stark, 2009). The Western Research Institute (WRI) reported the use of AFM to obtain images that provide data on some material properties and adhesive properties of bitumen with aggregates in the interfacial region (Huang et al., 2005). However, correlations to predict the interfacial behaviour taking into account the chemical composition of contact surfaces at the molecular level have not yet been established.

In the last decades, diverse modern technologies have been used to study surface topography and phase composition of bitumen including atomic force microscopy (AFM), scanning electron microscopy (SEM), and X-ray diffraction (XRD). A majority of publications report the use of AFM to acquire images for the morphological characterization and phase structuring of bitumen (De Moraes et al., 2010; Å. Lyne, Wallqvist, Rutland, Claesson, & Birgisson, 2013; Masson et al., 2006; Masson et al., 2007; Yu, Burnham, & Tao, 2015). More recent researchers are focused on

provide insight into the mechanical and adhesion properties of bitumen and aggregates, to study the adhesion between these materials, bitumen cohesion, and to assess the moisture susceptibility on asphalt mixtures (Al-Rawashdeh & Sargand, 2014; R Grover Allen et al., 2012; T. Pauli, Grimes, Cookman, & Huang, 2014; R. A. Tarefder & Zaman, 2010; R. Tarefder & Zaman, 2011). This is possible through force-distance measurements, the use of colloidal probes and nanoindentation AFM.

This chapter aims the determination of adhesion forces between bitumen samples and minerals of different chemical nature as present in aggregates used in asphalt mixtures. For this study, an Atomic Force Microscope (AFM) was employed enabling not only the force measurement between bitumen and mineral, but also to analyze the morphology of the bitumen samples. The adhesion forces were used to calculate the work of adhesion between materials. Also, a correlation between chemical composition of the bitumen and adhesive behavior was evaluated.

3.2 Materials and methods

3.2.1 Materials. Stock solutions of 200.0 g/L of bitumens A, B, and C were prepared by dissolving bitumen in pure toluene and left overnight to form a homogeneous solution. Then, bitumen films were prepared with spin coating of each stock solution diluted to 100 g/L over a microscope glass slide. This, in order to obtain a thin and smooth bitumen film for an investigation via AFM.

The samples were left in a desiccator previously purge with nitrogen to prevent contamination by dust and humidity for at least 24 hours before imaging and force measurements. This also

assures the evaporation of the solvent from the bitumen samples and the formation of a smooth and homogeneous bitumen film.

Triangular silicon nitride cantilevers with silicon nitride tips (Digital Instruments, NJ) were used to obtain topographic images from sample surfaces. In tapping mode, the cantilevers selected had a spring constant of 0.12 nN/m and the tip was 10 nm in diameter. Silicon cantilevers modified with silicon dioxide (SiO_2) and calcium carbonate (CaCO_3) particles (Novascan Technologies, Ames, IA USA) were used to obtain force curves between SiO_2 , CaCO_3 and bitumen sample surfaces. The particles were 5 μm in diameter and the cantilevers had a spring constant of 5.4 N/m (see Figure 13).

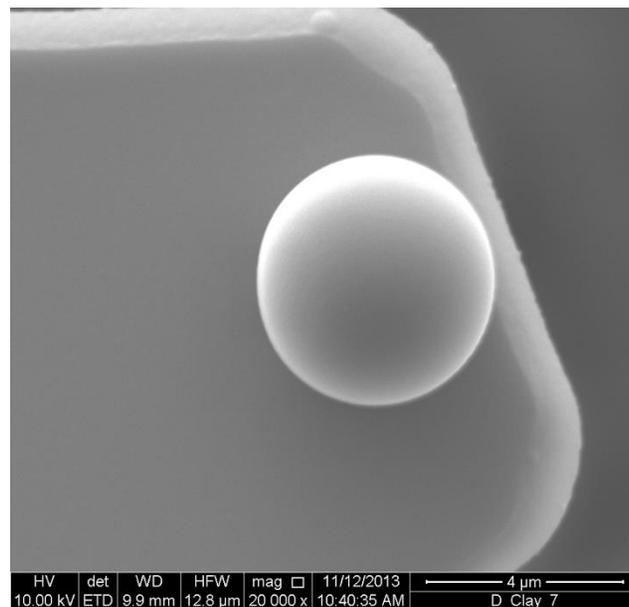


Figure 13. SEM image of SiO_2 particle modified tip obtained at Microscopy and Imaging Center at Texas A&M University.

3.2.2 Atomic Force Microscopy. The atomic force microscope (AFM) is part of a family of instruments referred to as scanning probe microscopes (SPMs). The operation of all SPM

techniques is based in the use of a very sharp probe, which scanned the surface of interest, using the interactions between the probe and the surface being used to produce a very high resolution image of the sample. Depending upon the technique and sharpness of the probe tip, images at sub-nanometre scale can be obtained. In the case of the AFM, the interaction of the probe with the sample surface through repulsive and attractive forces produce high resolution topographic images of the surface.

Figure 14 show the basic set-up of an AFM. Cantilevers are commonly rectangular such as in Figure 13 or V-shaped, as shown in Figure 14. The cantilever has at one end a sharp tip, which is the probe of interactions. Probes and cantilevers are predominantly manufactured of silicon nitride (Si_3N_4) or silicon (Si). Usually the upper surface of the cantilever is coated with a thin surface, typically of either gold (Au) or aluminium (Al). With a piezocrystal the probe is brought into and out of contact with the sample surface. A beam of laser light is reflected from the reverse side of the cantilever onto a position-sensitive photodetector. The changes on deflection of the cantilever due to the topography of the sample will produce a change in the position of the laser on the photodetector. Once the probe is in contact with the surface under analysis, it can be raster-scanned across the surface to build up relative height information to topographic features of the sample.

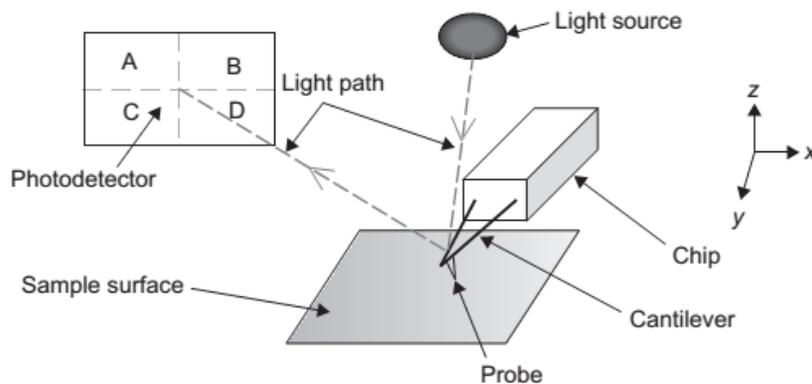


Figure 14. Basic AFM configuration (Johnson, Hilal, & Bowen, 2009).

Base on the information needed about the sample surface being examined, there are many different imaging modes available for the AFM. Figure 15 shows the interaction forces as the probe approaches to the surface. At large distances there are no net forces acting between the probe and the sample surface and as probe is approaching to the sample surface, attractive van der Waals interactions pull the probe towards the sample surface. Once the contact is made, the interaction becomes repulsive and the surfaces repel each other. In Figure 15 repulsive forces are shown as being positive and attractive forces negative.

For operation modes showed in Figure 15, contact mode operation is in the repulsive force regime, where the probe is pressed against the sample surface, causing an upwards deflection of the cantilever. Non-contact mode interrogates the long-range forces experienced prior to actual contact with the surface. With intermittent contact, or tapping mode, the probe is oscillated close to the surface where it repeatedly comes into and out of contact with the surface.

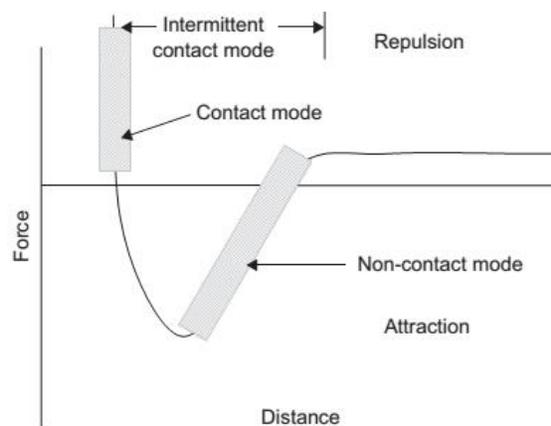


Figure 15. Forces regimes under which each of the three common AFM imaging modes operate (Johnson et al., 2009).

The AFM measurements were performed on a Bruker Dimension Icon AFM (Materials Characterization Facility (MCF) at Texas A&M University, TX) in tapping mode for images recording and contact mode for force measurements. Tapping mode was used for the morphological analysis of the bitumen films throughout this study because contact mode could not generate consistent topographic images of viscoelastic samples. Based on the surface analysis, force curves were acquired in contact mode. The testing procedure for adhesion force studies is the following. First, the cantilever was calibrated with a standard surface for its spring constant and resonant frequency. Then, several force curves were acquired at different locations over the sample surface with a set of appropriate operational parameters. Average values and standard deviation of adhesion force were reported for comparison. After each force measurements, the cantilever was calibrated again with the standard surface and non significant changes of values measured for spring constant and resonant frequency were observed. Additionally, after each test, tip images with SEM were acquired in order to make sure that the tip has no defects and was not contaminated by the bitumen sample. However, a new tip was used for testing each bitumen sample with minerals. The resulting images and force curves were evaluated using Nanoscope Analysis 1.40 software. All experiments were conducted in air at room temperature.

3.3 Results and discussion

3.3.1 AFM Surface Characterization of bitumens. The topographic images of bitumen surfaces were obtained in tapping mode at room temperature with the respective phase image and can be seen in Figure 4.4. Initial settings of AFM were as follows: scan size = 500 nm; scan rate = 1.0 Hz; samples/lines = 512; integral gain = 0.5; proportional gain = 5.0; amplitude set point =

371.2 mV, Z Limit = 9.557 μm . Parameters were then adjusted during imaging to obtain better quality images. Figures 16 a), c) and e) correspond to topographic images while Figures 16 b), d), f) are phase images of the same samples. The imaged area is 15 x 15 μm and the z-scale is around 11 nm for bitumen samples A and C, and 42 nm for bitumen B.

Bitumen can present three different phases: a disperse phase also called catanaphase, a periphase that is peripheral to the catanaphase, and the paraphase that is adjacent to the periphase as shown in Figure 16 d). The catanaphase was identified for one out of three bitumens as observed in Figure 16 c) and d) for bitumen sample B. This phase is represented by a succession of a pale and dark lines often was referred to as bees or bee structure (Masson et al., 2006).

Bitumen samples A and C did not show the catana phase in its morphology. Instead, in Figures 16 b) and f) for bitumen A and C respectively, their phase images showed a flake-like domains of different sizes. The topographic images, Figures 16 a) for bitumen A and e) for C, indicate that these disperse domains were slightly protruding from the surface.

From bitumen characterization, bitumens samples A and C show a close chemical composition. In sample B, the resins content is lower than samples A and C and asphaltene content is the highest within the 3 samples, which may be related to the presence of catana phase. In early work done with AFM by some researchers (Loeber et al., 1996; A. T. Pauli et al., 2001), a direct relationship between the catana phase (bee structure) and asphaltenes was proposed, asphaltens are compounds with high molecular weight and most aromatics molecules. It was found that bitumens with a multi-phase structure contained around 13-20 w/w % of asphaltenes. However, some bitumen with the same asphaltene content did not show bee structure. Also, fairly good correlation was found by researchers who studied the relationship between catana phase and metal content. Metals like vanadium and nickel are concentrated in the asphaltenes. Therefore, this result suggests that

chemical composition affect the final morphology and structure, directly in the case of vanadium and nickel content, and with high asphaltene content that may result in a high metal content. For the results of this research, the bitumen sample B has an asphaltene content of 20.65 w/w% which could validate the observations, in relation to bee structures formation in samples with high content of this fraction.

Moreover, according to the colloidal structural model, asphaltenes are stabilized by resins in a sea of aromatics and saturated hydrocarbons. As mentioned before, a higher colloidal index (*CI*) is proper of a more stable colloid structure where asphaltenes are more peptized by resins in the oil base medium (Loeber et al., 1998). For bitumens A, B, and C the colloidal index are 3.29, 2.19, 3.30, respectively. Therefore, bitumens A and C with almost the same *CI* present similar structure while sample B with a lower *CI* show a multi phase structure with the presence of catana phase. This also suggests that bitumen A and C structures are more stable than that of bitumen B.

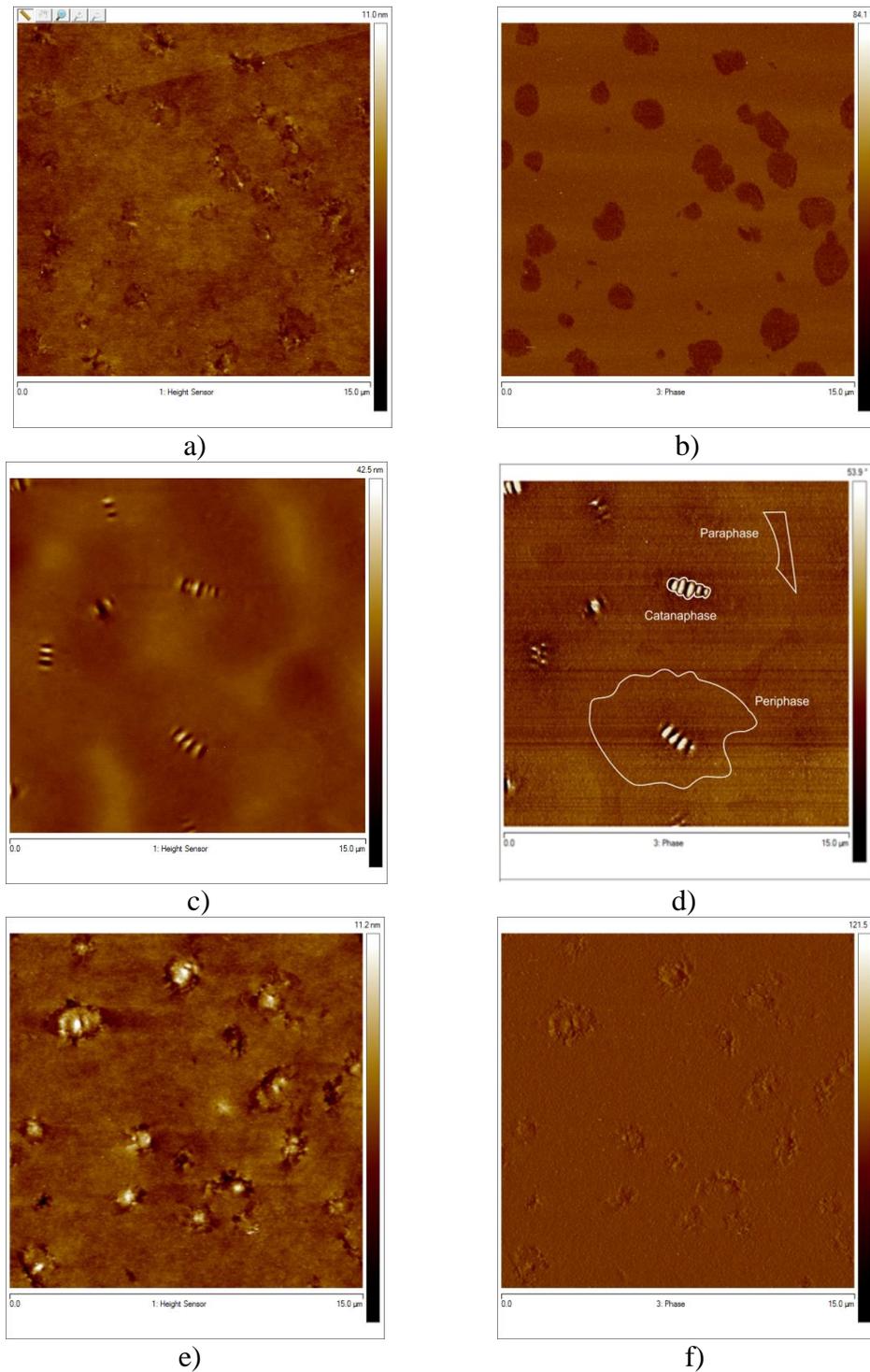


Figure 16. Topography and phase images of bitumen samples. a) and b) are topographic and phase images for bitumen A, respectively. c) and d) are topographic and phase images for bitumen B, respectively showing the multiple phases for this sample. e) and f) are topographic and phase images for bitumen C, respectively.

3.3.2 Adhesion measurements with AFM. A force-distance curve for bitumen A with SiO₂ tip is shown in Figure 17. Initial settings of AFM in contact mode were the following: Z-scan size = 0 μm ; scan rate = 1.0 Hz; samples/line: 256, deflection set point = 3.5 V, integral gain = 2.0, proportional gain = 5.0, Z limit = 9.557 μm . The initial settings were varied appropriately to first obtain a calibration force curve with the standard surface. Several curves were then obtained for calibration and each bitumen surface, using a new cantilever for measurement on each sample.

The x -axis in Figure 17 represents the vertical motion of the cantilever tip and y -axis represents the forces (repulsive and attractive forces) between the bitumen and the tip molecule. When tip is away from bitumen surface there is no interaction between its molecule and the bitumen molecule, therefore, the force is zero. As the tip approach to the surface and the distance between them decreases, the attractive force (negative) between the tip and the sample surface become larger allowing the contact with the bitumen surface. Once the cantilever reaches a target value between 60 and 100 nN, the tip is retracted by the actuator but still in contact with bitumen surface. Finally, the cantilever with tip is pulled off the bitumen sample and the force curves back to zero value (Al-Rawashdeh & Sargand, 2014).

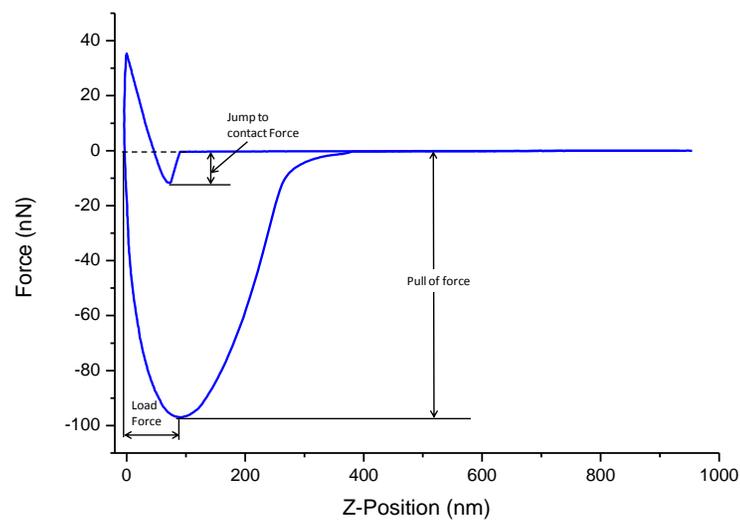


Figure 17. AFM Force curve for bitumen A and SiO₂

AFM can be used to measure only the dispersive component (LW) of the adhesive force, or non polar intermolecular interaction. To measure the polar component, the tip of the cantilever can be functionalized with polar materials (R. Grover Allen, Little, Bhasin, & Glover, 2014; R. A. Tarefder & Zaman, 2010). However, the measurement of adhesive force or so called pull-off force is a frequently used method to calculate the work of adhesion of the system using AFM. Beach *et al.* (Beach, Tormoen, & Drelich, 2002) described the most commonly used Derjagun-Muller-Toporov (DMT) model and Johnson-Kendal-Roberts(JKR) model to compute the work of adhesion. DMT model is applicable to smaller particles that are rigid and with low surface energy, while JKR model is for larger particle, and with higher surface energy. JKR model considers only short-range surface forces related to adhesive bonding. DMT model includes long range interactions that involve not just adhesion effects (Thomas, Houston, Crooks, Kim, & Michalske, 1995). These models to obtain the work of adhesion from adhesion force values are described by de following Equations.

$$\text{DMT model:} \quad F_a = 2\pi RW^a \quad (18)$$

$$\text{JKR model:} \quad F_a = \frac{2}{3}\pi RW^a \quad (19)$$

where F_a is the adhesion force, W^a is the work of adhesion, and R is the particle radius. JKR model was reported underestimated the work of adhesion but reasonably predicts the contact area at pull off. DMT model, in contrast, was reported with accurate work of adhesion at zero contact area (Thomas et al., 1995).

The work of adhesion between the cantilever and bitumen (W_{bc}^a) on substrate is defined as:

$$W_{bc}^a = 2\sqrt{\gamma_c\gamma_b} \quad (20)$$

were γ_c is the surface energy of cantilever tip, and γ_b is the surface energy of bitumen. For pure adhesive interaction, the surface energy will be:

$$\gamma_b = \frac{1}{\gamma_c} \left(\frac{F_a}{4\pi R} \right)^2 \quad (21)$$

Since the adhesion force was measured by detaching the cantilever from bitumen surface, there will be a thin film of bitumen on the probe surface. Therefore, the adhesion force can be seen as cohesive force were:

$$\gamma_b = \frac{F_a}{4\pi R} \quad (22)$$

For polymer-like material such as bitumen, practical work of adhesion is larger than the fundamental work of adhesion because the contribution from dissipation energy which can result from molecular chain entanglement and stretching under applied loads. Experiments done by some researchers showed the practical work of adhesion is a multiplication of some dissipation factor with fundamental work of adhesion (Merrill, Pocius, Thakker, & Tirrell, 1991).

At least three force curves were obtained for each bitumen sample using the same tip. After each measurement realized to build a force curve, a contact mode force curve on a clean, hard standard surface was conducted to evaluate the usefulness of the tip for another measurement with the same bitumen. Then, a thermal tuning was conducted to determine the resonant frequency of the cantilever. As mentioned before, a non significant change of values measured for spring constant and resonant frequency was observed. However, a new tip was used in force measurement

for each type of bitumen. Figure 18 presents an average of force - distance curves for each bitumen with SiO₂ modified tip.

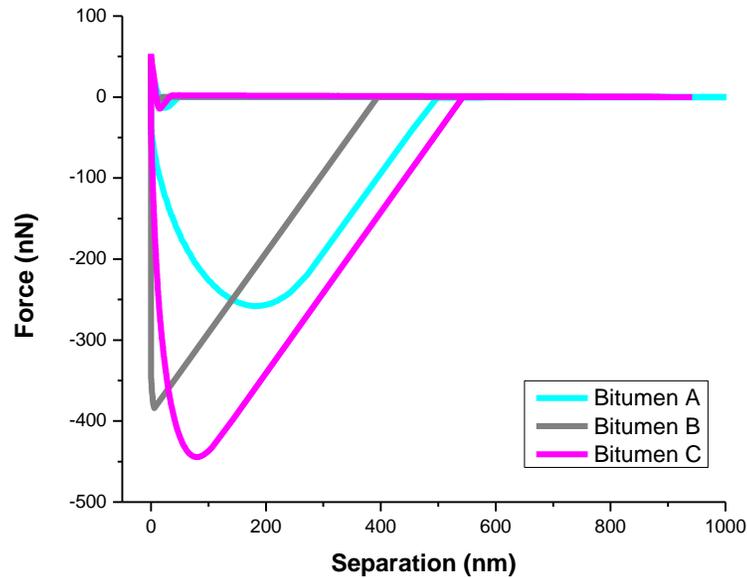


Figure 18. Force curve images for SiO₂ modified tip in contact with bitumen samples

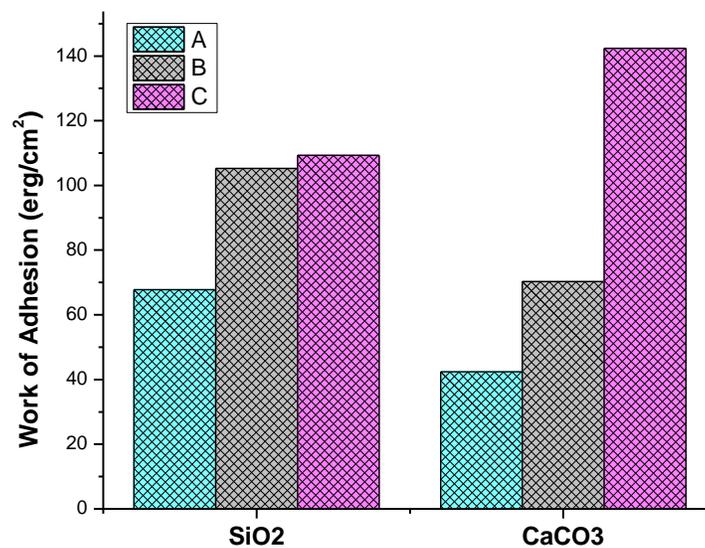
From Figure 18, material properties can also be analyzed. As the tip is retracted from the surface after the max loading, stiffness of the surface is obtained from the slope and deformation distance could also be obtained. Bitumen B showed the highest stiffness and lowest deformation distance which means it is the most brittle of them. Bitumen A, in contrast, is the softest one which is consistent with the penetration of bitumens which are 71.2, 5.2, and 34.0 (mm/10) for A, B, and C, respectively.

Based on contact mechanics theory, the work of adhesion was calculated from pull of force (D. Little et al., 2006). Table 10 and Figure 19 show the average work of adhesion calculated for bitumen samples with both SiO₂ and CaCO₃ modified tips using Equation 22, and the standard deviation (SD) for each set of measurements.

Table 10. Work of Adhesion between bitumen and mineral modified tips

Bitumen	Work of Adhesion (erg/cm ²)			
	SiO ₂		CaCO ₃	
	Avg.	SD	Avg.	SD
A	67.78	8.20	42.43	4.36
B	105.26	3.02	70.30	7.24
C	109.34	10.41	142.39	8.53

The values obtained for work of adhesion calculated from force-distance curves varies from 42.43 to 142.39 erg/cm². As shown in Figure 19 there is a significant difference between the work of adhesion measured for samples A and B with the two tips. It can be seen that the work of adhesion between samples A, B, and SiO₂ tip is higher than the work of adhesion for the same bitumen samples with CaCO₃ tip. A different behavior was found for sample C. Contrary to the trend observed for other samples, the work of adhesion obtained for bitumen C – CaCO₃ tip was higher than with SiO₂. However, the higher values for work of adhesion within the tests conducted were obtained for sample C with both SiO₂ and CaCO₃ tips. This indicates that bitumen C molecules develop a strength bond with both SiO₂ and CaCO₃ molecules.

**Figure 19.** Adhesion force using SiO₂ and CaCO₃ tips.

It is important to mention that the typical bitumen used in hot asphalt mixtures correspond to a bitumen with similar properties that of sample A. From results it can be observed that this sample shows the lower work of adhesion with both SiO_2 and CaCO_3 tips, which suggest that weak bonds are developed between bitumen with both minerals. These weak bonds can be easily broken under the effect of water or the traffic load. Stripping caused by moisture damage is one of the major distresses present in asphalt pavements. The use of additives such as lime, amino-acid, and polymers is a typical practice to control the stripping occurrence. In the last decades, the implementation of different test to effectively assess the performance of antistripping additives have gain significant importance (Mehrara & Khodaii, 2013). But the studies are focused on identifying the best additive to improve the mix performance under the effect of water or the study of bitumen under different moisture conditioning using macroscopic techniques (Aksoy et al., 2005; Iskender & Aksoy, 2012; Vasconcelos, Bhasin, Little, & Lytton, 2011). This suggests that the adhesion phenomena between bitumen and aggregate molecules at nanoscale may have been not well assessed. Not because of the employed techniques but some results evidence the lack of knowledge about the adhesion phenomena for samples which even after the use of different additives, the susceptibility to moisture damage for the system increased (Al-Rawashdeh & Sargand, 2014; R. A. Tarefder & Zaman, 2010; R. Tarefder & Zaman, 2011). That is why the adhesion phenomena and kinetics and thermodynamics properties of the system at nanoscale have not been well understood.

A further investigation based on the adhesion experimental data of this study was conducted. The relationship between work of adhesion obtained and saturates, aromatics, resins, asphaltenes content, including some important ratios such as resins/asphaltenes and colloidal index were investigated using single regression analysis, respectively. The correlation suggests that the

nitrogen content has fairly good linear relationship with the work of adhesion obtained for bitumen and both mineral modified tips used to measure pull off force. The correlation coefficients for SiO₂ and CaCO₃ are 0.967 and 0.767 respectively, as shown in Figure 20. However, other parameters evaluated did not show a significant correlation with work of adhesion and figures are not shown.

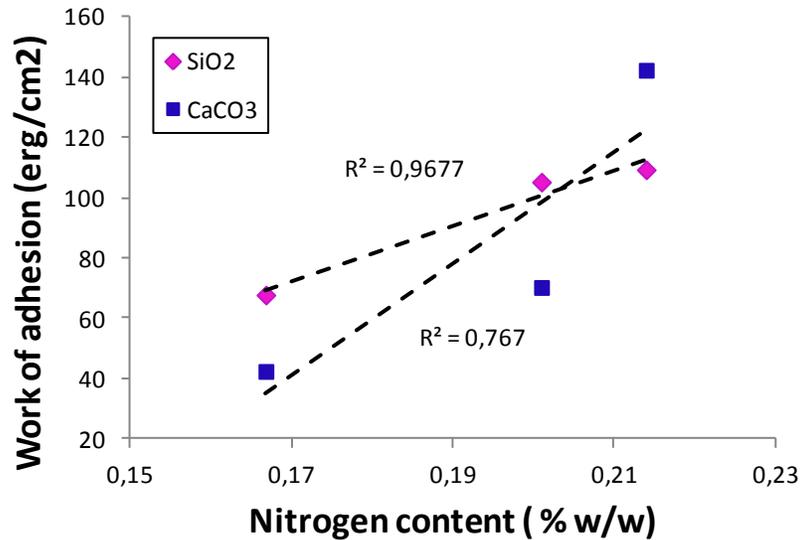


Figure 20. Relationship between nitrogen content and Work of adhesion

Although bitumen is composed by non-polar hydrocarbons, may also contain heteroatoms as part of these molecules such as nitrogen (N). These heteroatoms are present in small amounts, but it was found that give certain polarity to bitumen and introduces a significant effect on properties of bitumen and its interaction with aggregate surfaces. Certain functional groups in bitumen which includes nitrogen such as pyridine and pyrrolic types were reported that are strongly adsorbed and resistant to water displacement (Christine W. Curtis et al., 1993; Hefer & Little, 2005a). This explains, the high work of adhesion developed between bitumen C with the highest nitrogen content (0.214 w/w %) and minerals, followed by bitumens B (0.201 w/w %) and A (0.17 w/w %), and the high correlation coefficients.

3.4 Conclusions

The AFM was used to characterize the morphologies of three bitumen samples with different chemical composition obtained from different crude oil sources. The typical bee structure was observed for one out of three bitumens studied. The peri phase surrounding the catana phase could be identified for sample B. Samples A and C showed flake-like domains of different sizes. The asphaltene content seems to be related with the morphological structure of bitumens as mentioned by other researchers. However, more bitumen samples need to be analyzed to validate this finding.

The work of adhesion using the AFM between bitumen and particles of SiO_2 and CaCO_3 attached to the AFM cantilever was also studied. Bitumen samples A and B showed a higher work of adhesion with SiO_2 than with CaCO_3 while an opposite behavior was observed for bitumen C, which developed a higher work of adhesion with CaCO_3 than with SiO_2 . Future work with more minerals and real aggregates samples are strongly suggested to improve the selection of materials for asphalt mixtures. This will help to reduce the main distresses presents in pavements.

The correlation between the experimental data obtained for work of adhesion and chemical composition of bitumen samples were further investigated. Results suggest that there is a good correlation between the nitrogen content in bitumen and the strength of the bonds formed with minerals. This findings help to better understand the adhesion phenomena between bitumen and different minerals present in asphalt mixtures. Although the data points are the limitation of current research, previous studies done by researchers using different techniques validate results but more bitumen samples should be analyzed using AFM to compliment the findings presented in this study.

4 Asphalt-aggregate adsorption using a quartz crystal microbalance

4.1 Introduction

The adhesion in asphalt mixtures has been evaluated by different techniques, however the main factors that affect the adhesion developed between the main components have not been well understood. The way in the adsorption process is developed significantly affect the resulting adhesion of the system, i.e.: if bitumen does not properly wet and consequently adsorbs on the solid surface a weak adhesion is generated in the system.

Adsorption from liquid solutions is influenced by factors such as solubility of adsorbate in the solvent, temperature, pH, type of adsorbent, and adsorptive concentration ("Index for Volume 5," 2001; Nevskaja, Castillejos-Lopez, Muñoz, & Guerrero-Ruiz, 2004). This is why adsorption of the liquid phase is less studied than adsorption from the gas phase, despite its industrial importance. However, the evaluation of liquid-phase adsorptive processes requires adsorption equilibrium data; these data have to be experimentally measured or calculated using various predictive multicomponent adsorption models or empirical correlations. Multiple isotherm equations for gas-phase adsorption can in principle be applied to liquid-phase adsorption by the replacement of adsorbate pressure by concentration (Rolando, 2007). These models are defined by the Langmuir, Freundlich, Sips, Toth and Dubinin-Radushkevich equations. However, the Langmuir and Freundlich equations are the most widely used to correlate liquid-phase adsorption data (Andrieux

et al., 2004; Balabin & Syunyaev, 2008; Nassar, Hassan, & Pereira-Almao, 2011b; "Sorption Isotherms," 2014).

During the asphalt mixtures production process, materials have to be heated to decrease the bitumen viscosity obtaining a viscous liquid that can be mix it with aggregates. Then, the process can be studied such as adsorption at solid/liquid interface.

In the past decade, quartz crystal microbalance (QCM) has been widely used to study direct monitoring of asphaltene adsorption/deposition on different solid surfaces (Abudu & Goual, 2008; Dudášová, Silset, & Sjöblom, 2008; Nassar et al., 2011b; Zahabi, Gray, & Dabros, 2011); stability and heavy oil recovery using surfactants (Chen & Akbulut, 2012). The asphaltene fraction is the major contributor to several issues in the petroleum industry. Complications related to asphaltene stability and damages caused within the production well, reservoirs, fouling of pipelines, transportation equipment, and through the entire production chain are the principal issues studied by researchers (Adams, 2014; Nassar, Hassan, & Pereira-Almao, 2011a; Rudrake, Karan, & Horton, 2009). However, to the best of our knowledge, applications of QCM to study the adsorption and thermodynamics of asphalt mixtures have not been realized. *In this Chapter is proposed a methodology to study adsorption kinetics and thermodynamics of the main components of asphalt mixtures such as bitumen and different mineral surfaces as present in asphalt mixtures through direct monitoring and measured in real time with QCM-D .*

4.2 Materials and methods

4.2.1 Materials. Three different bitumen samples named A, B and C, were provided by the Colombian Institute of Petroleum, ICP, ECOPETROL S.A. (Colombia) and used as received

(see Chapter 2, Table 4 for bitumen properties). Toluene (anhydrous, 99.8%) and tetrahydrofuran (THF, >99.9%) were obtained from Sigma Aldrich and Sodium dodecyl sulfate (SDS, >85%) from TCI America.

Three stock solutions of 200.0 g/L for each bitumen sample A, B, and C were prepared by dissolving bitumen in pure toluene and left overnight to form a homogeneous solution. These samples were used for the entire series of experiments. Stock solutions were then diluted to 0.05, 0.1, 0.5, 1.0, 3.0 and 5.0 g/L for QCM experiments.

Quartz sensors covered with SiO_2 and Fe_2O_3 were purchased from Q-sense. A sample of aggregate AGC was sent to the sensor manufacturer to make a third sensor covered with a real material used in the fabrication of asphalt mixtures. The properties for AGC aggregate sample can be seen in Chapter 2, Tables 1, 2 and 3.



Figure 21. Q-sense sensors for QCM

4.2.2 Quartz crystal microbalance with dissipation (QCM-D). Adsorption of bitumen on mineral surfaces was studied using a QCM with dissipation (QCM-D E1, Q-sense) and a quartz sensor covered with a layer of 50 nm of each mineral (SiO_2 , Fe_2O_3 , and AGC aggregate) at Akbulut

Research Group, in Chemical Engineering Department, Texas A&M University. The QCM-D principle is based on a thin quartz crystal ($\sim 300 \mu\text{m}$) between two electrodes and the piezoelectric effect discovered by Curies (Marx, 2003; Reviakine, Johannsmann, & Richter, 2011). With an applied AC voltage across its electrodes, the quartz crystal will oscillate at a certain frequency. The frequency (f) change of a quartz resonator can be used to measure the mass deposited on the quartz resonator surface. Additionally, depending on the elastic property of the adsorbed material, dissipation value will change accordingly (see Figure 22). The dissipation (D) of crystal oscillation is a measure of the softness of the film (viscoelasticity). For a rigid adsorbed layer with no significant changes in D , where f to D ratio is larger than 10, the adsorption mass is proportional to the decreasing of the resonant frequency and Sauerbrey equation (Reviakine et al., 2011) can be used to calculate the adsorbed mass:

$$\Delta f_n = -\frac{n}{C} m_f = -\frac{n}{C} \rho_f h_f. \quad (23)$$

In before equation, m_f is the mass per unit area of the adsorbed film, and ρ_f and h_f are the density and the thickness of the adsorbed film, respectively, and $n = 1, 3, 5, 7, 9, 11, 13$ is the overtone number. The constant C for mass sensitivity depends only on the material properties of the quartz crystal and its fundamental resonance frequency f_F . The mass sensitivity of the QCM-D (E1, Q-sense) is $1.8 \text{ ng/cm}^2 \text{ Hz}$ in liquids (hydrocarbons) and the crystal resonance frequency $f_F = 5 \text{ MHz}$. For rigid layer, third overtone of fundamental resonance frequency was used to calculate the adsorbed mass. This overtone is used because the fundamental mode is very sensitive to environmental fluctuation and a higher overtone number is related to a lower penetration or detection depth.

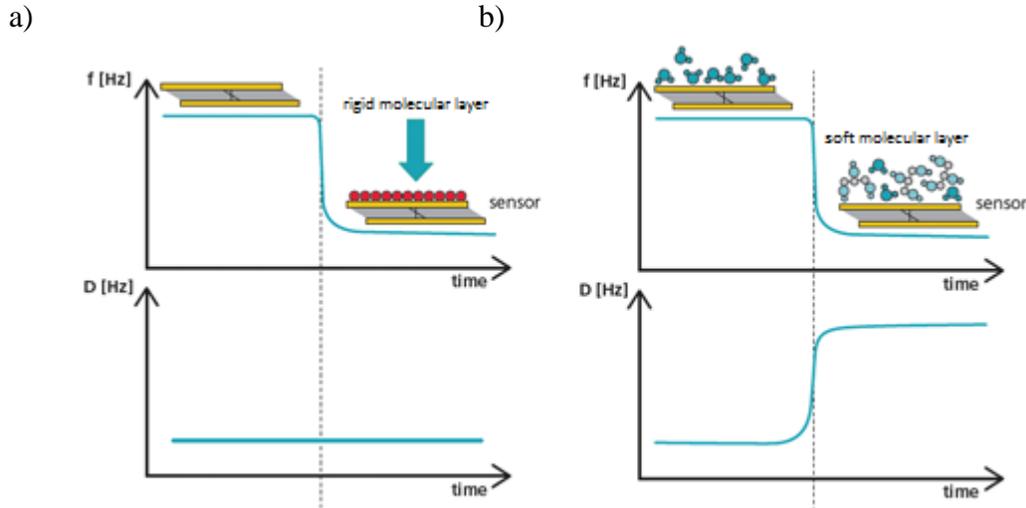


Figure 22. Illustration of frequency and dissipation changes for different materials adsorbed. Frequency changes with mass deposition and dissipation which occurs inside the film that is related to the viscoelastic properties of the material. a) Thin and homogeneous rigid films. b) Films that do dissipate energy such as viscoelastic films.

For high D changes during adsorption and $f/D < 10$, the adsorbed film is soft (viscoelastic) and the Sauerbrey equation becomes invalid. Then viscoelastic modeling is used to describe the mass adsorption by fitting multiple frequency and dissipation harmonics at the same time. A film that is soft (viscoelastic) present a response out phase respect to the oscillation of the crystal because a soft film dampens the sensor's oscillation, doing that Sauerbrey relation will underestimate the mass at the surface. By other side, dissipation factor (D) is described as the energy loss of an oscillatory system by Equation 24 and reveals the film softness (viscoelasticity):

$$D = \frac{E_{dissipated}}{2\pi E_{stored}} \quad (24)$$

were $E_{dissipated}$ is the energy dissipated during one oscillation and E_{stored} is the energy stored in the oscillating system. For an adsorbed viscoelastic layer, the energy dissipated increase through of the thickness. Therefore, the mass of the adsorbed film were obtained with Q-Tools software from Q-Sense, by fitting the theoretical representation based on the Kevin - Voigt model shown in Figure 23, assuming that thinly coated mineral aggregate with crystal forms a rigid body and the adsorbed layer covers the entire active area; it is homogeneous and with uniform thickness.

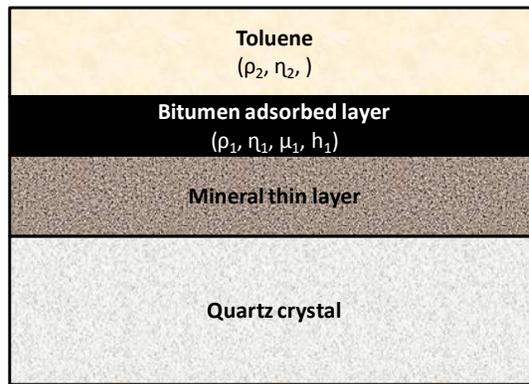


Figure 23. A schematic diagram of Kevin – Voigt viscoelastic model related to bitumen – mineral aggregate adsorption on a quartz crystal surface.

The properties such as density, viscosity, elasticity, and thickness of the adsorbed bitumen layer can be correlated to Δf and D from the QCM-D responses, based on Kevin-Voigt model. According to Voinova *et al.* (Voinova, Rodahl, Jonson, & Kasemo, 1999), the relationship between QCM-D response and viscoelastic properties of the adsorbed soft film layer can be explained with the following equations:

$$\Delta f \approx -\frac{1}{2\pi\rho_0 h_0} \left\{ \frac{\eta_3}{\delta_3} + h_1 \rho_1 \omega - 2h_1 \left(\frac{\eta_3}{\delta_3} \right)^2 \frac{\eta_1 \omega^2}{\mu_1^2 + \omega^2 \eta_1^2} \right\} \quad (25)$$

$$\Delta D \approx \frac{1}{\pi f \rho_0 h_0} \left\{ \frac{\eta_3}{\delta_3} + 2h_1 \left(\frac{\eta_3}{\delta_3} \right)^2 \frac{\eta_1 \omega}{\mu_1^2 + \omega^2 \eta_1^2} \right\} \quad (26)$$

were ρ_0 and h_0 are the density and thickness of the crystal, η_3 is the viscosity of the bulk liquid and δ_3 is the viscous penetration depth of the shear wave in the bulk liquid, ρ_3 is the density of the liquid and ω is the angular frequency of the oscillation. In this model, the adsorbed bitumen layer is represented by four parameters: density (ρ_1), viscosity (η_1), shear elasticity (μ_1), and thickness (h_1). A depth explanation for this model can be found in the literature (Reviakine et al., 2011; Voinova et al., 1999).

The measurement started with the acquisition of a baseline for the clean sensor. Pure toluene was injected for about an hour to establish a stable baseline. Next, the solvent was replaced by bitumen in toluene solution to initiate the adsorption process of bitumen film on each mineral surface. Flow rate was maintained at 150 $\mu\text{L}/\text{min}$ and the temperature in flow chamber was of 23 ± 0.1 °C. Frequency and dissipation values at several harmonics were simultaneously recorded. Each bitumen concentration was repeated at least three times. The equipment and configuration for test execution is shown in Figure 24.

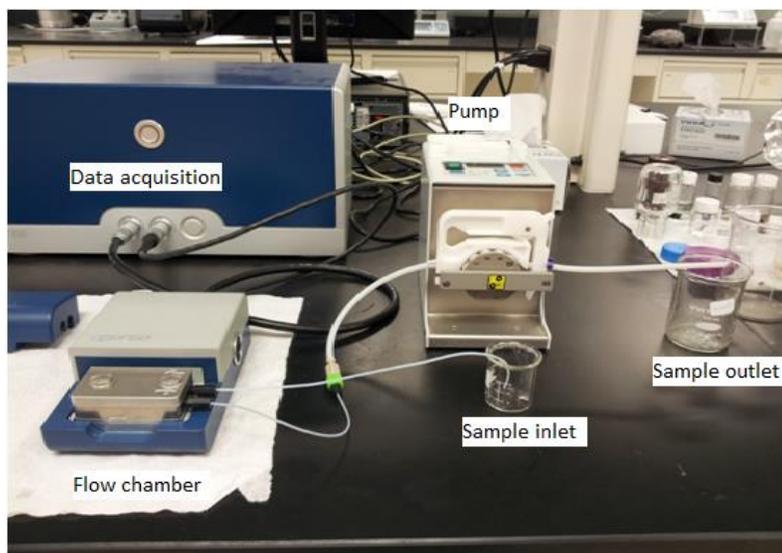


Figure 24. QCM-D test configuration for experimental adsorption of bitumen on minerals tested.

4.2.3 Cleaning Procedure of QCM-D Crystals and Flow Modules. Sensor cleaning is of paramount importance to its reutilization as a surface for the adsorption process. Considering that removal of bitumen is a complex process because of its nature, different solvents and cleaning process were tried and a complete removal of bitumen was achieved with the following procedure. A chemical treatment procedure was used to remove organic contamination from the sensors surface. The dry sensors were first introduced in plasma cleaner for about 10 - 15 min, and then placed in a sensor holder and immersed in tetrahydrofuran for 15 minutes three times and then rinsed with milliQ water. Sensors were then immersed in a 3% sodium dodecil sulfete solution for 30 min and rinsed with milliQ water and dried with nitrogen. Dried sensors were cleaned with plasma for another 10-15 min. The QCM-D flow modules were also cleaned after each run. The modules were flushed with toluene and dried with nitrogen. The efficiency of the cleaning process was studied obtaining AFM images of new sensors, used sensors and cleaned sensors after the

cleaning process. It was observed that cleaned sensor exposes a cleaned surface similar to a new sensor.

4.3 Results and discussion

4.3.1 Adsorption kinetics of Bitumen on Mineral Surfaces with QCM-D. The adsorption process of three different bitumens on SiO_2 , Fe_2O_3 and a real aggregate surface, AGC, was monitored using the QCM-D. Once the bitumen adsorbs on the surface, the system was left to reach the equilibrium. Figures 25 and 26 shows frequency and dissipation for different concentrations of bitumen A, B, and C, over SiO_2 respectively. It can be seen that frequency decrease and dissipation increase with an increase in bitumen concentration. From Figure 27, f/D values for concentrations until 1 g/L in bitumen A and 0.5 g/L in bitumen B and C, the adsorbed film was rigid and it was observed that subsequent rinsing with toluene did not induce significant frequency or dissipation changes suggesting that bitumen was firmly bound to the surface. At higher concentration, ratio of frequency to dissipation became lower suggesting the formation of a much softer adsorbed layer. A slight change in frequency and dissipation observed after rinsing of soft layers with pure toluene could be attributed to the detachment of the particles in the outer layer of the adsorbed mass. The same behavior was observed for all bitumen samples over Fe_2O_3 and AGC aggregate sensors surface.

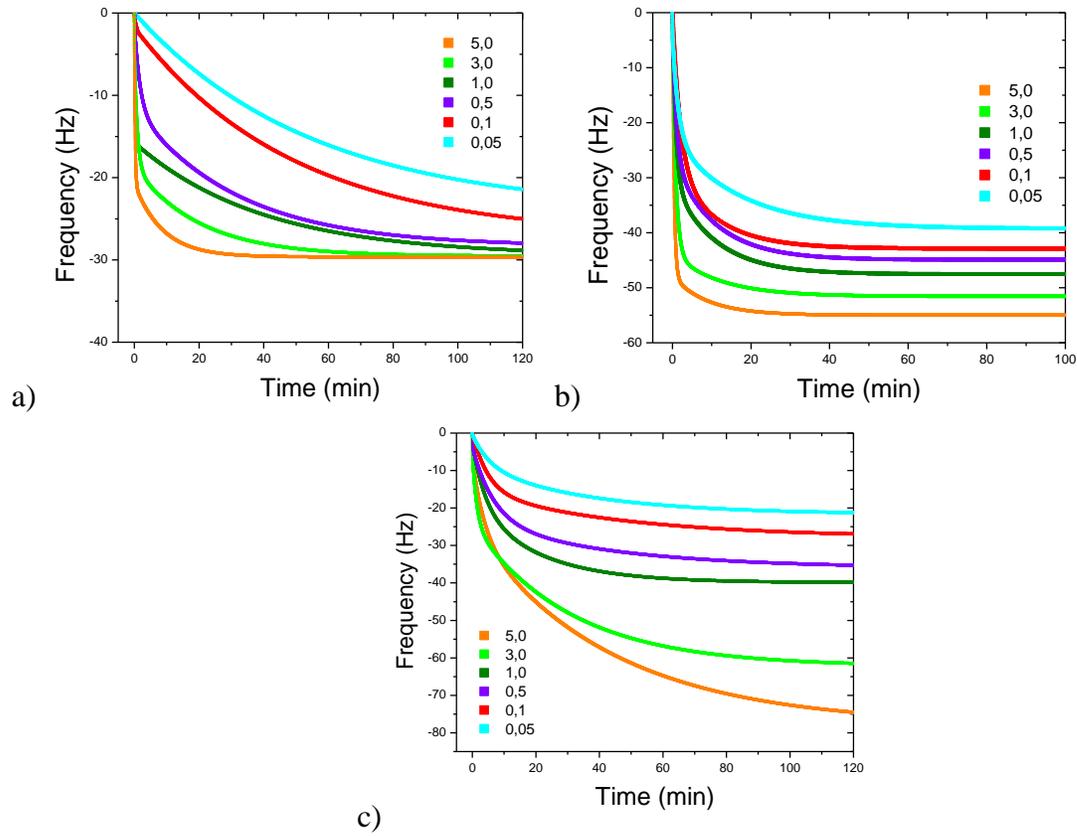


Figure 25. Real time frequency of Bitumen A, B, C adsorption on SiO₂ surface at 25 °C. a), b), c) shows the frequency responses for each bitumen at 3rd overtone.

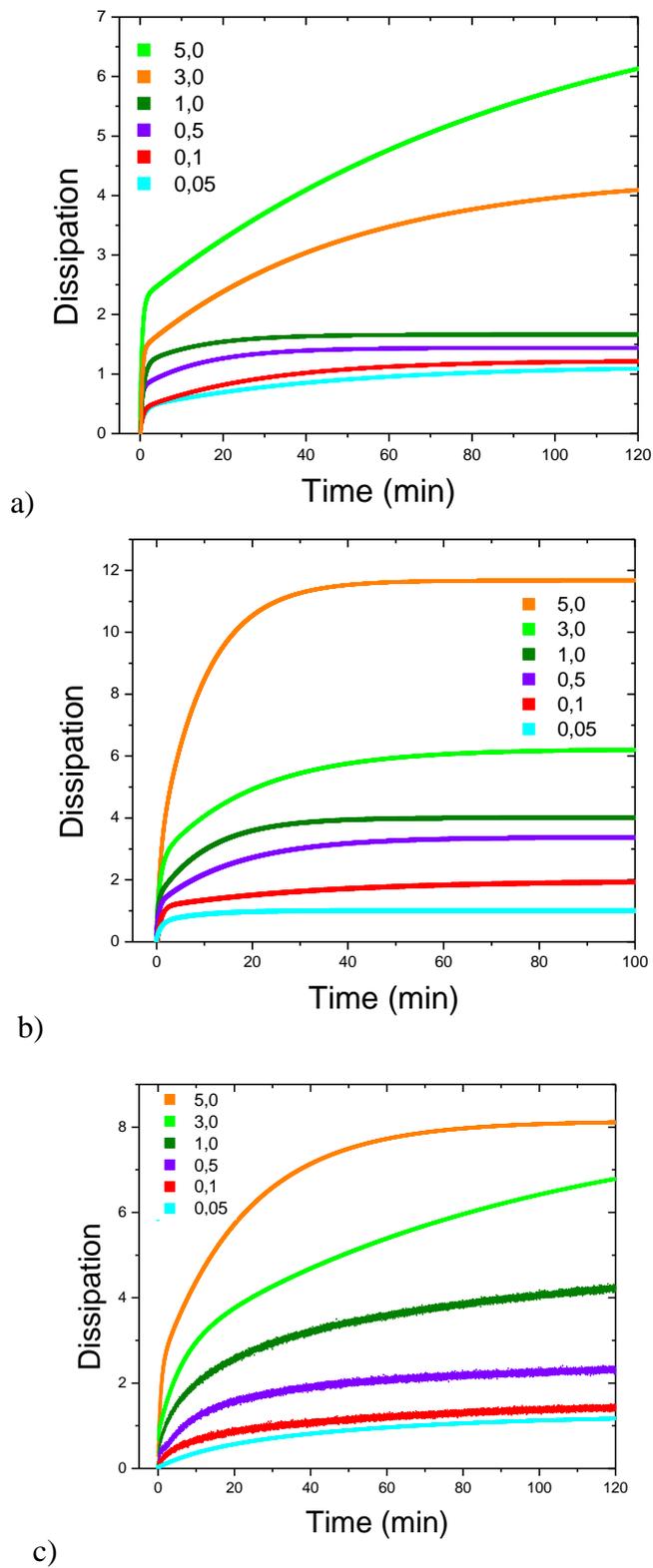


Figure 26. Real time dissipation of Bitumen A, B, C adsorption on SiO₂ surface at 25 °C, a), b), c) shows the dissipation responses for each bitumen at 3rd overtone.

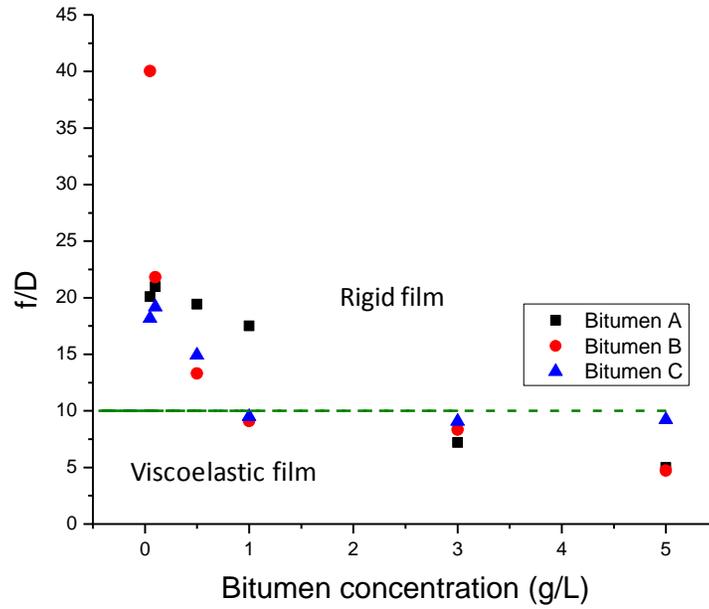


Figure 27. Relationship between f/D and viscoelasticity of the layer adsorbed on mineral surfaces.

Figure 28 show the mass adsorbed on SiO_2 surface sample as a function of time at different bitumen A, B and C concentrations. In general, for all surface-bitumen systems it was found that the adsorption kinetics exhibit a rapid initial response followed by a slower approach to equilibrium. This behavior can be represented by an exponential kinetic model given by Equation 27 which was have into account kinetics with fast and slow rate of adsorptions (Chen & Akbulut, 2012). Parameters of m_1 , m_2 , k_1 and k_2 were obtained by fitting experimental values of mass adsorbed versus time for each one of the systems studied and are listed in Table 11.

$$m = m_1(1 - e^{-k_1 t}) + m_2(1 - e^{-k_2 t}) \quad (27)$$

Of Figure 28, note that the equilibrium mass of bitumen increased with increasing bitumen concentration. In addition, dissipation shifts presented in Figure 27 indicated that the adsorbed bitumen film structure varied from rigid to more elastic. Therefore, Sauerbrey equation was appropriate for calculating the adsorbed masses on the sensor at concentration

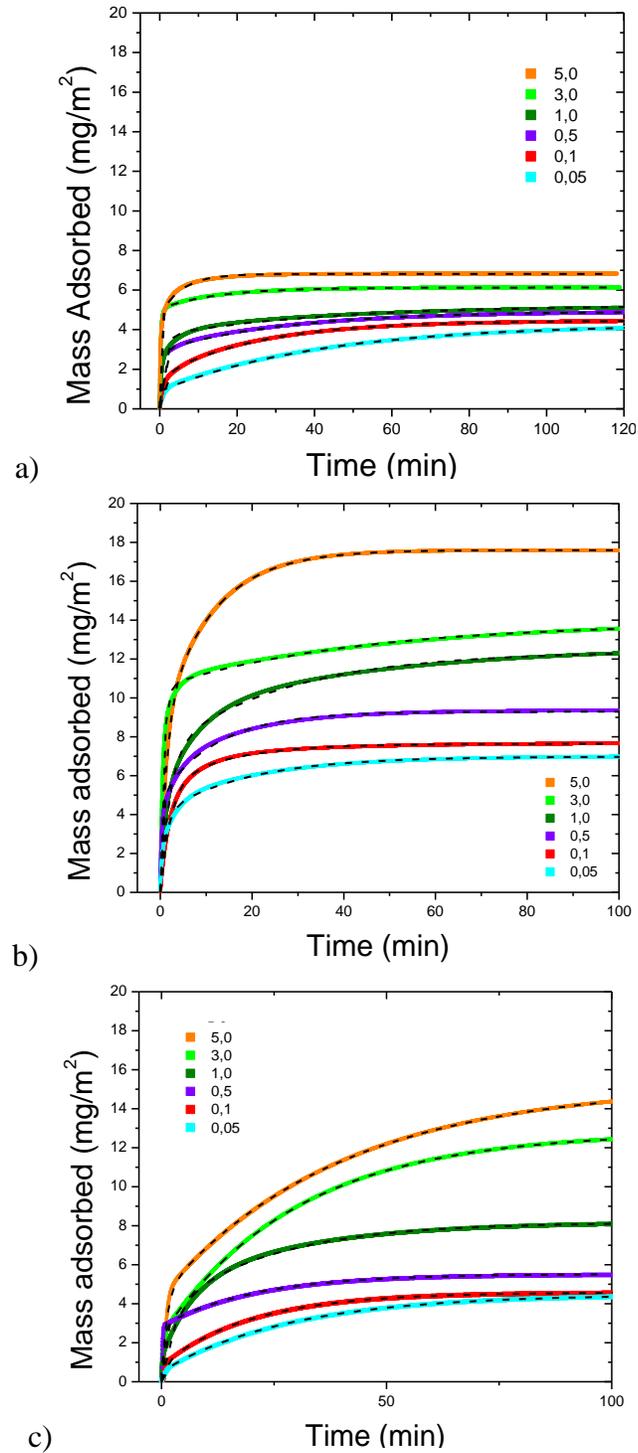


Figure 28. Real time mass trend of Bitumen A, B, C adsorption on SiO₂ surface at 25 °C, a), b), c) shows the mass trend obtained by Sauerbrey equation using 3rd overtone at concentration lower than 1g/L. 3rd,5th,7th 9th overtones were used in viscoelastic model to fit higher concentration. Dashed curves are fitted trend using double first order model.

up to 0.5 g/L of bitumen B, C and 1.0 g/L of bitumen A. Voigt model was used with Q-Tools (Q-sense software) for higher concentrations because the rigidity of layer decreased.

Table 11. Fitting parameters for two exponential kinetic model of bitumen adsorption on different mineral surfaces. Standard deviations are less than 1% and R^2 are higher than 0.99.

SiO ₂												
Bitume n (g/L)	SAMPLE A				Sample B				Sample C			
	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)
0.05					3.48	0.63	3.34	0.05	3.93	0.03	0.54	1.43
0.1	1.65	0.83	0.04	2.81	4.58	0.57	2.94	0.04	3.73	0.05	0.85	1.10
0.5	1.96	0.03	2.95	2.50	5.07	0.88	3.30	0.05	2.69	0.05	2.84	4.24
1.0	1.54	0.03	3.69	0.88	6.31	1.04	5.43	0.04	3.60	0.35	4.57	0.42
3.0	1.06	0.07	1.06	3.15	3.46	0.04	8.87	1.55	10.42	0.03	2.38	3.13
5.0	4.70	3.63	2.11	0.18	3.77	0.05	9.88	1.15	10.74	0.03	4.47	0.85
Fe ₂ O ₃												
Bitume n (g/L)	SAMPLE A				Sample B				Sample C			
	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)
0.05	1.86	0.06	1.86	0.84	2.74	0.34	3.41	0.03	2.02	0.04	1.83	0.30
0.1	1.56	0.04	2.94	0.49	2.53	0.05	4.54	0.34	1.74	0.40	1.50	0.05
0.5	0.74	0.06	3.98	1.94	2.16	0.07	6.29	1.22	1.52	0.07	3.06	0.54
1.0	1.20	0.08	4.56	2.15	7.94	1.85	3.76	0.03	2.19	3.80	2.96	0.15
3.0	5.06	1.18	1.83	0.16	9.80	0.04	8.62	2.43	3.15	0.05	5.12	2.40
5.0	6.82	1.78	2.34	0.04	9.48	2.10	13.16	0.04	5.78	2.40	5.41	0.04
AGGREGATE												
Bitume n (g/L)	SAMPLE A				Sample B				Sample C			
	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)	m ₁ (mg/ m ²)	k ₁ (1/s)	m ₂ (mg/ m ²)	k ₂ (1/s)
0.05	2.42	0.41	1.40	0.01	3.16	0.03	3.70	0.50	1.40	0.01	2.43	0.41
0.1	2.63	0.91	1.68	0.02	3.11	0.03	2.37	0.86	2.18	0.50	3.15	0.01
0.5	1.03	0.04	3.39	1.31	6.66	1.35	3.18	0.03	3.67	1.30	2.19	0.02
1.0	1.92	0.03	3.23	1.78	7.86	1.54	12.25	0.01	4.17	0.75	3.98	0.02
3.0	4.75	1.83	2.75	0.06	7.15	2.88	15.77	0.04	4.61	0.04	4.67	1.32

During the adsorption stages, an immediate sharp increase of adsorbed mass indicated the quick adsorption of bitumen to the surface. Previous studies showed this fast adsorption is related to oxygen containing group from asphaltenes, acidic and basic components in bitumen that form covalent, ionic or hydrogen binding to the silanol groups on SiO_2 surface as shown in Figure 29 (Fritschy & Papirer, 1978; Scott, 1978). Oxygen group in silica can act as a Lewis base sites for the adsorption of acidic bitumen. As the polar part of asphaltene adsorbs to the surface, nonpolar part of the compound oriented outward, this will cause further interaction with less polar hydrocarbons like saturates. This is why there appeared slow adsorption afterwards in QCM-D. The same trend was observed for bitumen adsorption on Fe_2O_3 and aggregate sample surface (AGC aggregate, SiO_2 content of 54.37 w/w %).

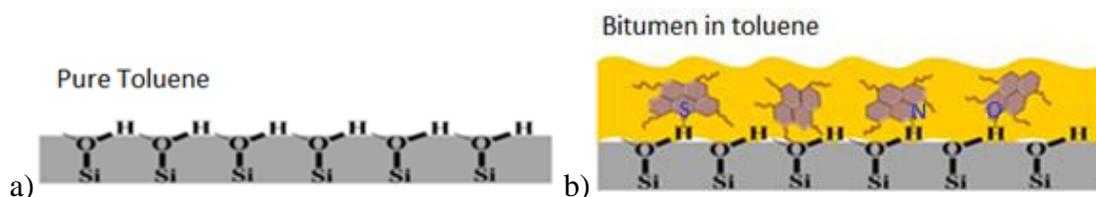


Figure 29. Adsorption of asphaltene molecules on SiO_2 surface. a) First step in study of adsorption with QCM is to establish a baseline with pure toluene. b) Adsorption of asphaltene molecules from bitumen in toluene solutions on SiO_2 surface. (adapted from (Yang et al., 2015)).

It was observed that higher equilibrium masses at higher concentration is due to high concentration of polar materials like resins and asphaltenes in the solution. For bitumens under analysis, the amount of resin and asphaltene in bitumen is $B > C > A$, thus the adsorbed equilibrium masses of bitumen B are highest in all concentrations. On the other hand, considering the slow adsorption amount from apolar component like saturates and naphthene aromatics which are the highest component in these bitumen, there is no obvious trend. Slow adsorbed masses are not only depended on the apolar amount in three bitumens, they also related to the previous adsorbed masses

from polar materials. Previous studies showed that adsorbed apolar material on SiO₂ will mask adsorption from polar component (Christine W. Curtis et al., 1993; Fritschy & Papirer, 1978). Thus, the total amount of slow adsorbed mass due to saturates and aromatics was from masses adsorbed on surface and masses adsorbed on polar material of bitumen.

4.3.2 Adsorption Isotherms of Bitumen on Mineral Surfaces with QCM-D.

Adsorption is usually described by isotherms. Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties, as well as the degree of affinity of the adsorbents such as minerals present in aggregates with adsorbates which in this case is bitumen. Therefore, the construction of isotherms for bitumen - aggregate will allow the study of physicochemical properties of the system.

When phase containing an adsorbate has been contacted with the adsorbent for sufficiently long times, adsorption equilibrium is established. Such an equilibrium is typically described by the ratio of the adsorbed amount to the adsorptive amount at sufficiently long times. One way to scientifically present such information is to use adsorption isotherms in which the amount of substance adsorbed (adsorbate) is plotted against the pressure or concentration in the external phase at constant temperature and under equilibrium conditions. Over the years, a plethora of models describing behavior of adsorption isotherms have been formulated. These models are based on either of kinetic considerations, thermodynamics, potential theory, or theories of capillary condensation.

For bitumen - mineral system, data for equilibrium adsorption was fitted to Langmuir and Freundlich models. Langmuir model assumes that the adsorbed layer is one molecule in thickness,

with adsorption occurring at a fixed number of localized equal sites. Freundlich adsorption isotherm is one of the earliest known model relating the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. This empirical model is not restricted to the formation of monolayer i.e. it can be applied to multilayer adsorption

Steady-state equilibrium masses, m_{eq} , of asphalt concentration ranging from 0.05 to 5.0 g/L were obtained from Eqn. 27 and Table 11, and plotted versus concentration to generate adsorption isotherms presented in Figures 30 to 32 for SiO₂, Fe₂O₃ and AGC aggregate, respectively. The data were fitted with Langmuir and Freundlich isotherms by using Eqns. 5.6 and 5.7 (Foo & Hameed, 2010):

$$m_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \quad (28)$$

$$m_e = K_F C_e^{1/n} \quad (29)$$

where q_e (m_{eq}) is the amount of bitumen adsorbed on surface at equilibrium (mg/m^2), C_e is the equilibrium concentration of bitumen (g/L), K_L is the Langmuir isotherm constant related to the affinity of adsorption (L/g), Q_{max} is the maximum amount of bitumen for monolayer coverage (mg/m^2), K_F is the Freundlich isotherm constant related to the adsorption capacity [$(mg/m^2)(L/g)^{1/n}$], and $1/n$ can be seen as heterogeneity index of the surface.

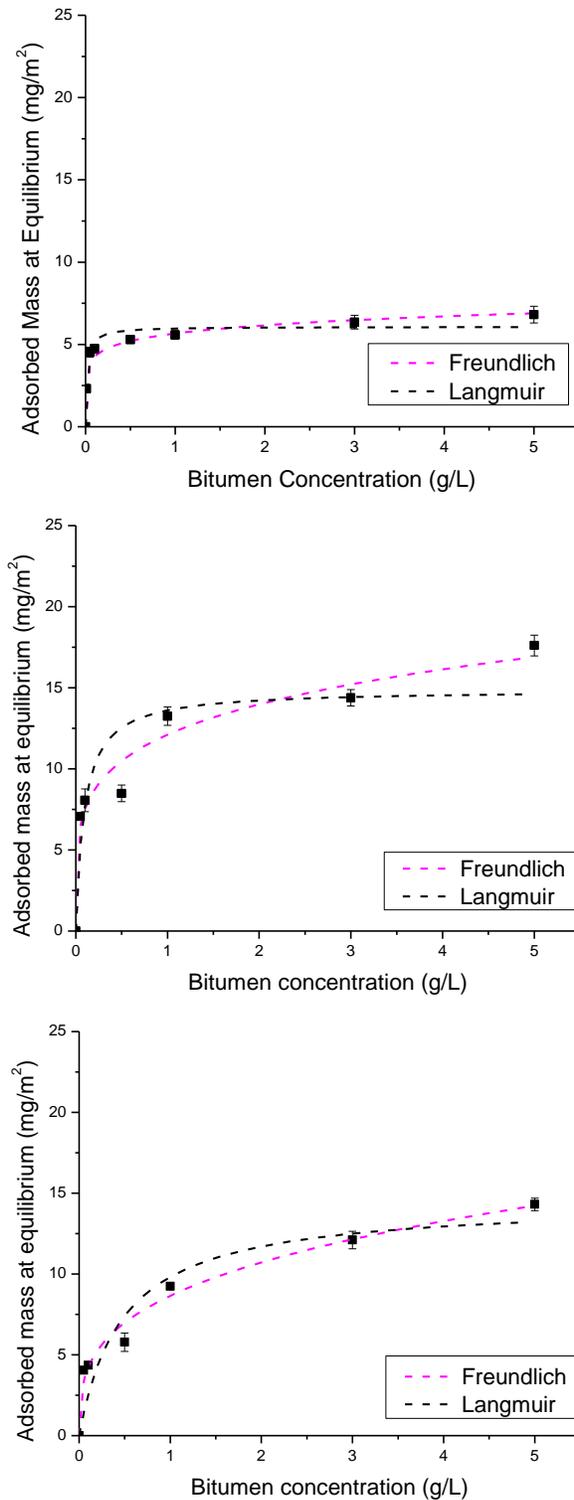


Figure 30. Bitumen adsorption isotherms on SiO₂ surface at 25 °C; black dashed line is fitted with Langmuir isotherm and pink dashed line is fitted with Freundlich. a), b), and c) adsorption of bitumen A, B and C respectively.

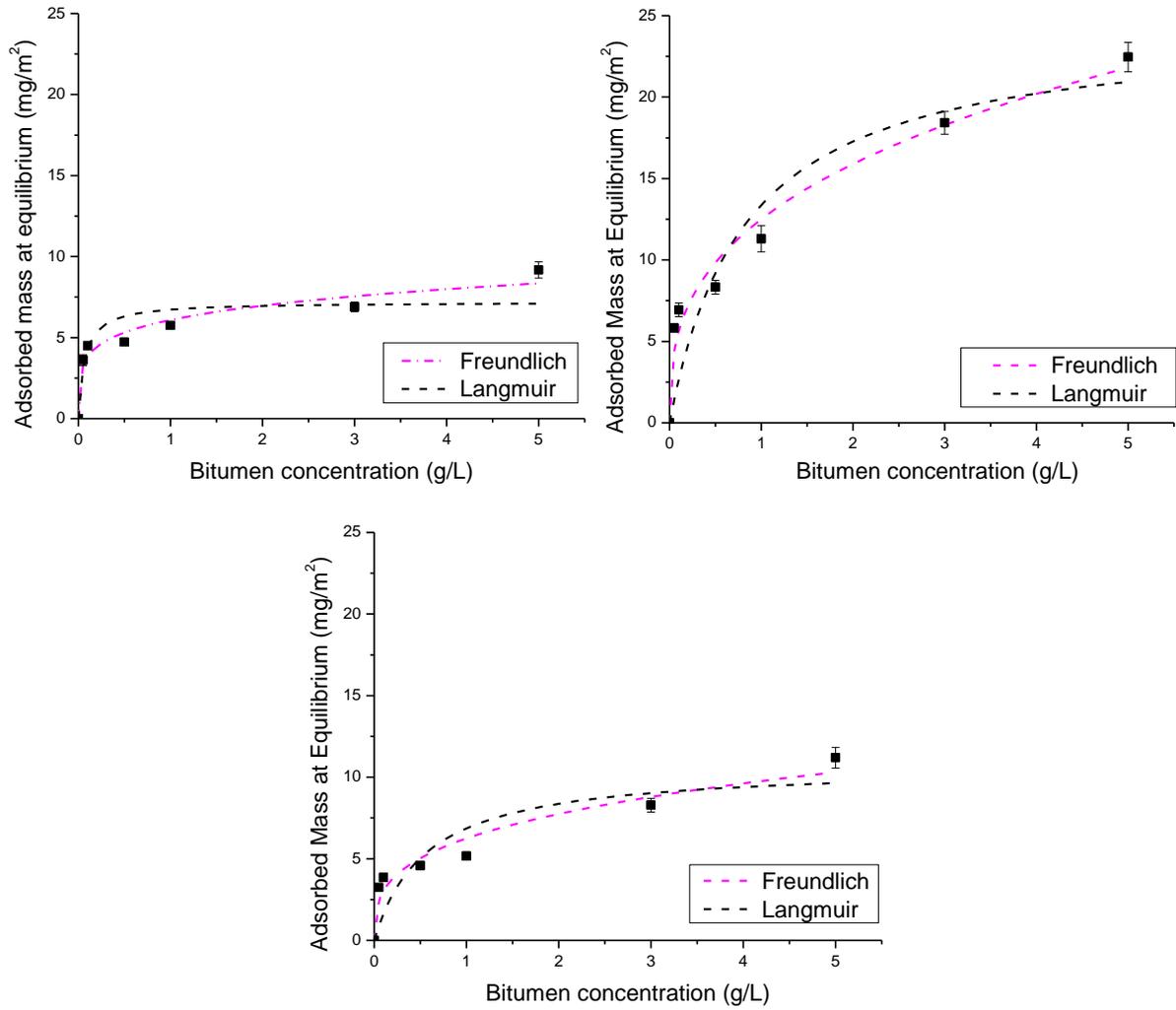


Figure 31. Bitumen adsorption isotherms on Fe₂O₃ surface at 25 °C; black dashed line is fitted with Langmuir isotherm and pink dashed line is fitted with Freundlich. a), b), and c) adsorption of bitumen A, B and C respectively.

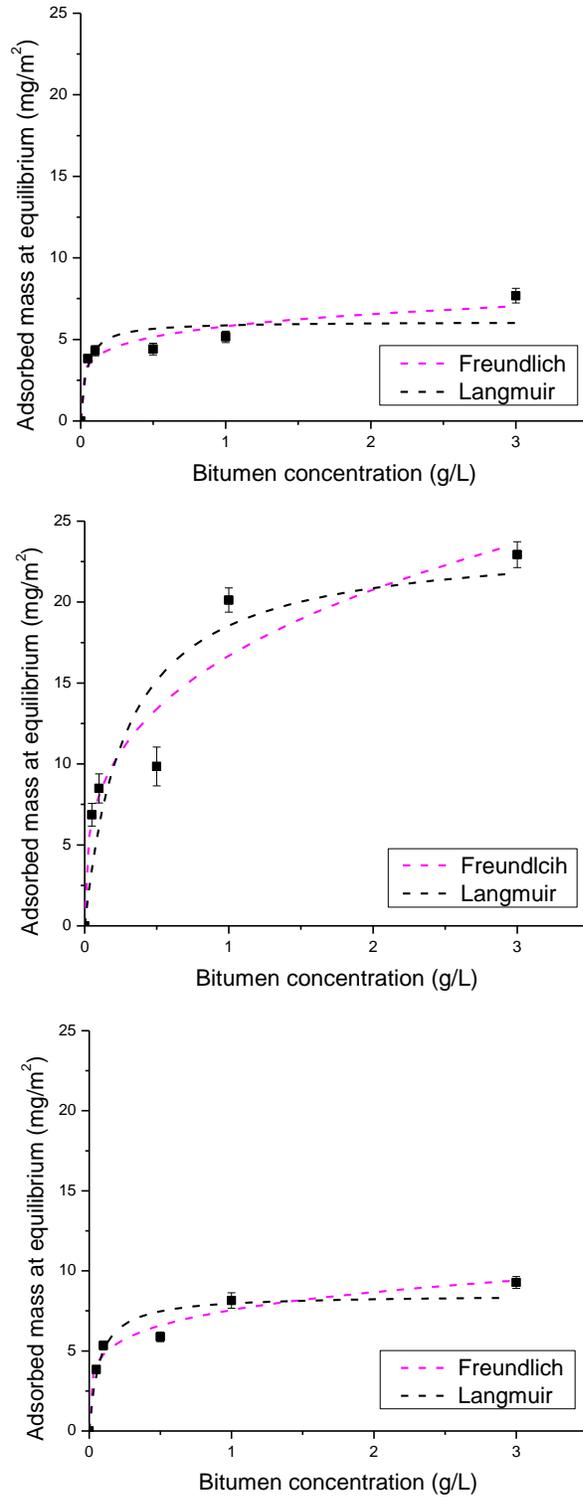


Figure 32. Bitumen adsorption isotherms on real aggregate surface AGC at 25 °C; black dashed line is fitted with Langmuir isotherm and pink dashed line is fitted with Freundlich. a), b), and c) adsorption of bitumen A, B and C respectively.

As seen in Figures 30 to 32, at different concentration, equilibrium adsorbed mass of bitumen is $B > C > A$ for each one of the surfaces studied. This is consistent to surface free energy of bitumen ($A > C > B$) presented in Chapter 2, that higher surface free energy cause less wettability. From Table 12, with higher K_L , higher Gibbs free energy of adsorption and there will be higher interaction with the surface which means lower activation energy. From Table 12 and Figures 30 to 32, A is biggest in K_L for adsorption on all surfaces which can explain the fast adsorption rate is highest in bitumen A excluding data for bitumen C – aggregate, taking into account that for this system the adsorption measurement was done up to 3 g/L instead the 5 g/L for other systems.

From R^2 in table 12, adsorption data fit well for both the Freundlich and Langmuir models. To compare the best fit model, the non linear analyses of the linear forms of isotherm models were conducted as per Eqn. 30 (Montgomery & Runger, 2006):

$$\chi^2 = \sum \frac{(q_{exp} - q_{model})^2}{q_{model}} \quad (30)$$

where q_{model} and q_{exp} are the amount of bitumen adsorbed at equilibrium obtained modeling and experimentally measured with QCM-D, respectively. Table 12 lists the calculated values from Langmuir and Freundlich isotherms with the standard error (SE), the smaller χ^2 value indicates the better agreement with the model. From χ^2 test analysis, is clearly visible that the fitting quality is much better for Freundlich than in the case of Langmuir isotherm with different accuracies and determination coefficients for each sample. It should be noted that Langmuir model is a simple model that assumes monolayer adsorption on the adsorbent surface, with adsorption only at a fixed number of identical an equivalent localized sites.

Table 12. Adsorption parameters for Langmuir and Freundlich isotherms

SiO₂						
FREUNDLICH						
Bitumen sample	K_f [(mg/m²)(L/mg)^{1/n}]	SE	1/n	SE	R²	χ²
A	5.661	0.004	0.129	0.006	0.882	0.457
B	11.893	0.016	0.199	0.020	0.917	0.649
C	7.381	0.022	0.176	0.029	0.905	0.357
LANGMUIR						
Bitumen sample	K_L (L/mg)	SE	Q_{max} (mg/m²)	SE	R²	χ²
A	5.927	0.014	6.831	0.006	0.992	8.362
B	5.786	0.006	13.717	0.003	0.994	9.061
C	3.519	0.016	10.604	0.007	0.975	7.411
Fe₂O₃						
FREUNDLICH						
Bitumen sample	K_f [(mg/m²)(L/mg)^{1/n}]	SE	1/n	SE	R²	χ²
A	6.055	0.021	0.173	0.028	0.906	0.340
B	12.844	0.028	0.279	0.036	0.937	0.975
C	6.282	0.032	0.246	0.042	0.862	0.711
LANGMUIR						
Bitumen sample	K_L (L/mg)	SE	Q_{max} (mg/m²)	SE	R²	χ²
A	2.840	0.026	9.074	0.011	0.955	9.005
B	1.695	0.010	23.981	0.004	0.950	15.064
C	2.421	0.020	9.606	0.008	0.971	7.881
AGGREGATE SAMPLE						
FREUNDLICH						
Bitumen sample	K_f [(mg/m²)(L/mg)^{1/n}]	SE	1/n	SE	R²	χ²
A	5.672	0.032	0.145	0.041	0.803	0.600
B	16.334	0.049	0.302	0.063	0.884	1.777
C	7.544	0.026	0.202	0.034	0.923	1.922
LANGMUIR						
Bitumen sample	K_L (L/mg)	SE	Q_{max} (mg/m²)	SE	R²	χ²
A	4.233	0.019	7.981	0.013	0.958	6.601
B	2.709	0.007	25.126	0.005	0.943	6.930
C	6.305	0.007	9.671	0.005	0.991	1.978

On the other hand, Freundlich model is an empirical relationship that can be applied to multilayer formation, with no-uniform distribution of adsorption heat and affinities on a heterogeneous surface. Moreover, Freundlich model could take into account factors such as lateral interaction, surface phase reorientation, multilayer formation, or aggregation of asphaltenes that could be present in bitumen adsorption over the surface (Arciniegas & Babadagli, 2014; da Silva Oliveira, Neto, Júnior, de Castro, & de Menezes, 2014; Subramanian, Wu, & Firoozabadi, 2015). This is also consistent with the high dissipation changes found during the monitoring of the adsorption process with QCM-D that suggested a reorientation over the sensor surface or a multilayer adsorption.

As mentioned before, Freundlich constants K_f and n correspond to adsorption capacity and heterogeneity of the surface, respectively. Additionally, values of $1/n$ below one indicate a normal adsorption and have been widely applied to correlate sorption data where $1/n$ is a heterogeneity parameter, becoming more heterogeneous as its value gets closer to zero (Jeppu & Clement, 2012). If n lies between one and ten, this indicates a favorable sorption process ("Adsorption Energetics, Models, and Isotherm Equations," 2005). However, K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting; whereas linear regression is generally used to determine the parameters for isotherm models. From the data in Table 12, the values for $1/n$ and K_f indicate that the adsorption of all bitumen samples minerals surfaces are heterogeneous and favorable. Bitumen sample B with the highest K_f for all mineral samples showed the highest adsorption capacity. All samples showed heterogeneous adsorption as its $1/n$ values are closer to zero.

4.3.3 AFM Surface Characterization and Multilayer Adsorption. To compliment the QCM study of bitumen deposition on minerals surface, AFM images of sensors surface in tapping mode were recorded to verify the heterogeneity of adsorbed mass (Figure 33). In the present study, height measurements were made for all systems following adsorption of each bitumen sample on mineral sensor with QCM-D.

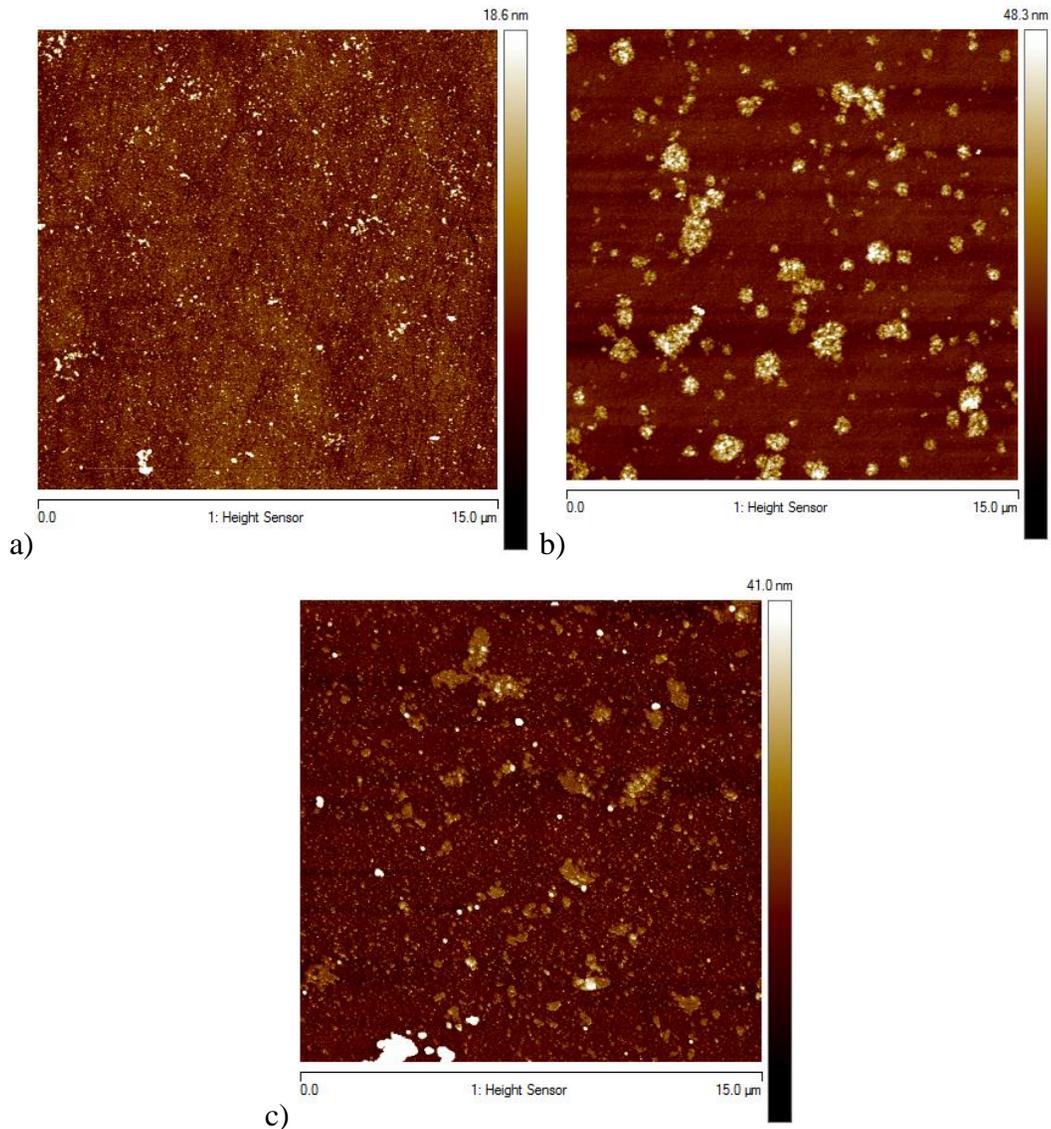


Figure 33. AFM images of sensors after adsorption of 5 g/L bitumen samples. a) Bitumen sample A on Fe₂O₃ surface, b) Bitumen sample B on aggregate surface, c) Bitumen sample C on SiO₂ surface.

The z -scale varies from image to image to highlight surface features. The films on each image revealed peaks (white spots) less than 50 nm size and a roughness (average difference between peaks and valleys) in the range 2–12 nm. Surface roughness tended to be greater for sample C (between 12 and 6 nm) than samples B (between 9 and 5) and A (between 5 and 2 nm). These observations confirm the formation of multilayer adsorption at 5 g/L of bitumen over the all sensor surfaces measured. The combined use of QCM-D and AFM has provided new information on the structure of bitumen multilayer adsorption.

4.4 Conclusions

The QCM-D was successfully used to monitor and measure the bitumen adsorption on SiO_2 , Fe_2O_3 and a sample of a real aggregate surface. The adsorption was fast in the first seconds followed by a slow approach to equilibrium. A viscoelastic film was build up for high concentrations behavior expected due to bitumen properties. The adsorbed amounts of bitumen over different mineral surfaces are in the range 17.6 – 26.7 mg/m^2 for bitumen B, 11. 2-14.3 mg/m^2 for bitumen C and 6.8 – 12.4 for bitumen A this suggest a relationship between adsorption and asphaltene content in bitumen $B > C > A$, however only three bitumens were studied. More bitumens and different mineral surfaces are suggested to validate the findings of this study. Freundlich and Langmuir isotherms were used to fit the experimental adsorption data. The better fit was observed with Freundlich model with no-uniform distribution of adsorption heat and affinities on a heterogeneous surface. This was also consistent with the high dissipation changes found during the monitoring of the adsorption process with QCM-D that suggested a reorientation over the sensor surface or a multilayer adsorption. Multilayer adsorption suggested by Freundlich isotherm

was confirmed with AFM images of the sensor surface after adsorption process that revealed characteristics of this model of adsorption such as peaks to result in roughness in the surface.

5 General discussion

Surface free energy, adhesion at macro and nano scale, and adsorption of bitumen on aggregates as present in asphalt mixtures were exposed in previous chapters. Chapter 2 presents surface free energy of bitumen and general assessment of some properties of bitumens that are related to this property. Also, the bitumen bond strength test was introduced to evaluate cohesion and adhesion in bitumen-aggregate systems at macroscopic scale. Chapter 3 dealt with adhesion at the nanoscale. Atomic force microscopy was used to characterize bitumen surface and morphology at nanoscale such as to measure the force of adhesion between bitumens and probes modified with silicon dioxide and calcium carbonate, which are the main components of aggregates used in asphalt mixtures. Finally, in chapter 4 a methodology to the study adhesion in real time of bitumen - aggregate systems using a QCM-D was proposed. In this chapter, the main advantages and drawbacks of each method are summarized and the relationship between the results obtained at macroscopic and nanoscopic scale is analyzed.

Failures occurred due to the lack of a strength adhesion is one of the forms of pavement distresses that results in high maintenance and rehabilitation costs of pavements. Therefore, it is important to identify and eliminate materials or material combinations during the mix design

process that can render the asphalt mix susceptible to induced damage due to poor adhesion. Several methods to assess the adhesion properties between bitumen and aggregates at macroscopic scale have been used during the last years. Moreover, different methodologies to calculate the surface free energy using contact angles are exposed by several researchers, however its applicability to estimating the surface feature is questionable because the lack of an ideal surface required in the measurement (Bonn, Eggers, Indekeu, Meunier, & Rolley, 2009). It should be pointed out that only the experimental contact angles on smooth and homogeneous solid surfaces can be meaningful in the determination of solid surface tensions in the context of Young's equation (Tavana et al., 2004).

Table 13 resumes the results obtained for the evaluation of bitumen surface free energy (by Fowkes and van Oss models) and adhesion (POTS) at macroscopic scale presented in Chapter 2. The standard deviation (SD) of surface energy components is a measure of the precision of this technique. Standard deviations of the surface energy components were typically a small percentage of the total magnitude of the component. Not significant differences between results for surface free energy obtained with two models were observed. The main difference was observed for the surface free energy of bitumen C between both Fowkes and van Oss methods, obtaining values of 32.2 mJ/m^2 and 26.5 mJ/m^2 respectively. However, as explained before a good correlation in results obtained by Fowkes model and bitumens chemical properties was observed.

Table 13. Results for Bitumen – aggregate adhesion at nanoscale.

Bitumen	Contact angles				PATTI			
	γ_{Fowkes} (mJ/m ²)		$\gamma_{\text{van Oss}}$ (mJ/m ²)		POTS (psi)			
	Avg.	SD	Avg	SD	AGC	AGI	AGE	AGM
A	33.4	0.5	32.3	0.7	196.1 4	200.4 7	157.7 0	144.4 7
B	27.5	1.7	29.0	1.1	326.7 8	478.5 4	495.1 9	471.3 9
C	32.2	2.6	26.5	1.2	220.8 6	226.9 3	197.6 4	183.1 6

In Figure 34, it was plotted values of Pull off Tensile Strength versus surface free energy obtained by Fowkes model. Note that bitumen B present of highest value of tensile strength measures with PATTI and the lowest value of surface free energy indicating that these coat better the aggregates surface leading to less weak points.

In addition, Figure 34 was found a good correlation between the surface free energy obtained with Fowkes model and POTS measured with PATTI with correlation coefficients higher than 0.97. This is supported by the fact that liquids with the lower surface energy wet better the solid surface which is also related to the adhesive properties of the system. For a given aggregate surface, bitumen with greater wettability has a stronger affinity to coat the aggregate surface than a bitumen with lower wettability. Better coating of an aggregate surface results in fewer “weak points” or locations for the initiation of failures.

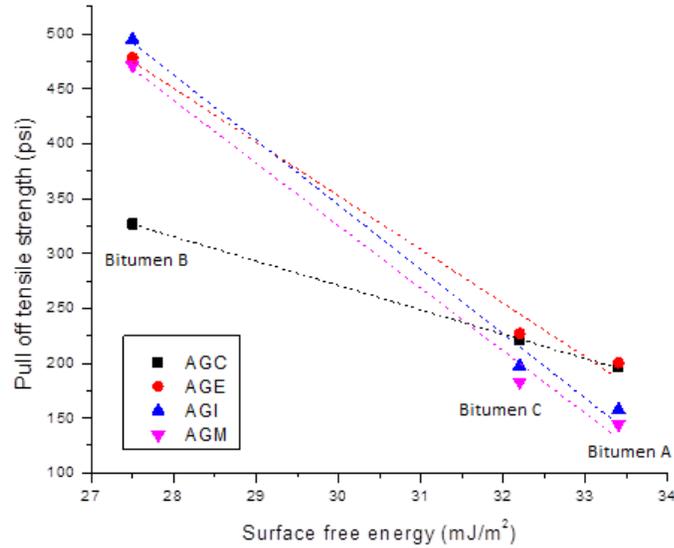


Figure 34. Surface free energy and POTS relationship

Surface energy of asphalt binders and aggregates can be used to select materials that promote better performing asphalt mixtures. The relationship between surface energy of these materials with the moisture sensitivity of the asphalt mixture is straightforward and also well established in the literature. Surface energy is a fundamental material property that can also be combined with other material properties using principles of fracture mechanics and mechanistic models to predict the crack growth and healing characteristics of asphalt mixtures. An energy parameter is recommended as independent measures of moisture sensitivity for any combination of asphalt binder and aggregate in asphalt mixtures. This parameter can be determined using the surface energy components of bitumen, aggregate, and water using the following equation (D. Little et al., 2006):

$$ER_1 = \left| \frac{W_a^{LS}}{W_{wet}^{LSW}} \right| \quad (31)$$

were W_a^{LS} is the work of adhesion between bitumen and aggregates and W_{wet}^{LSW} is the work required to displace bitumen from its interface with aggregate by water, and are described by:

$$W_a^{LS} = 2\sqrt{(\gamma_l^{LW})(\gamma_s^{LW})} + 2\sqrt{(\gamma_l^{AB})(\gamma_s^{AB})} \quad (32)$$

$$W_{wet}^{LSW} = \gamma_{SW} + \gamma_{LW} - \gamma_{SL} \quad (33)$$

were, γ_{SW} is the interfacial energy between aggregate and water, γ_{LW} is the interfacial energy between bitumen and water, and γ_{SL} the interfacial energy between aggregate and bitumen. The ER_1 parameters calculated for bitumens with different minerals and are shown in Figure 35.

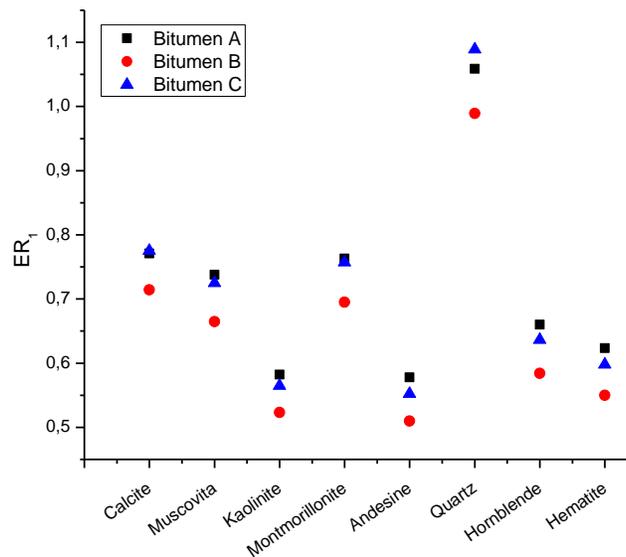


Figure 35. Moisture sensitivity for bitumens with different minerals

A higher value of ER_1 indicates better resistance to moisture damage. Typically this value can range from 0.3 to 10.0 depending on the surface energy components of the asphalt binder and the aggregate. In this case, the values of ER_1 for the combination of all bitumens with quartz are higher

than with other minerals. Based on this parameter the bitumens analyzed are likely to have better resistance to moisture damage with quartz or aggregates with high quartz content.

Subsequent to the study of materials and system properties at macroscopic scale using surface free energy and bitumen bond strength respectively, properties of bitumens and bitumen – aggregate systems were evaluated at the nanoscale with AFM and QCM.

The work of adhesion obtained with AFM in this research for bitumens with SiO_2 and CaCO_3 suggests that adhesion at nanoscale is influenced by more issues than only chemical composition and surface free energy of materials. This based on results that show for bitumen C a higher adhesive force than for bitumen B and A. However, the difference between bitumen B and C with SiO_2 was not much significant, opposite to the adhesive force measured for same bitumens with CaCO_3 which double the value obtained for B.

It seems that there is no correlation between results for work of adhesion calculated using Gibbs free energy in Chapter 2 and the work of adhesion measured with AFM in Chapter 3 for bitumen and SiO_2 combination. At nanoscale, specific molecular interaction counts for the adhesive force, instead of the representative average of interactions used for other test methods at macroscopic scale. However, if the purpose of measured surface energy of materials is to study the fracture mechanics of the system a larger scale is necessary and the advantage to study the interactions at nanoscopic scale becomes a drawback (D. Little et al., 2006). Nevertheless, the possibility to study the interaction of bitumens with different materials at molecular scale provide valuable information that can be used to identify minerals which enhance the adhesive force between materials and allow to obtain bitumen-aggregate systems with higher resistance properties. Likewise, bitumen morphology, its relationship with chemical composition and its effect on

properties of bitumen and asphalt mixture can also be studied with AFM (R. Grover Allen et al., 2014; Yu et al., 2015).

Further improvement in AFM methodology is needed to avoid the tip contamination and modify tips with extracted minerals from real aggregates. Nowadays, the companies which provide tips are not able to extract molecules from aggregates to modify tips with them, or to modify tips with bitumen samples. Future work with more minerals and real aggregates samples have to be conducted to improve and compliment the selection of materials for asphalt mixtures. This will also help to reduce the main distresses presents in pavements.

The correlation between the experimental data obtained for work of adhesion with AFM and chemical composition of bitumen samples was also investigated in Chapter 3. Results suggest that there is a good correlation between the nitrogen content in bitumen and the strength of the bonds formed with minerals. These findings help to better understand the adhesion phenomena between bitumen and different minerals present in asphalt mixtures.

QCM-D was successfully used in Chapter 4 to monitor and measure the bitumen adsorption process on SiO_2 , Fe_2O_3 and a sample of a real aggregate surface in real time, for the first time. A methodology was carefully developed to assure de reliability of results obtained. Due to the complexity of the systems and the sensitivity of the tests, several test were run to identify the operational parameters such quantity of sample needed, sample preparation, flow rate, sensors cleaning, such as the main issues that affect results.

Adsorption data for bitumen on minerals surfaces were acquired and analyzed. From dissipation values can be concluded that a viscoelastic film over the surface of different minerals was deposited, behavior expected due to viscoelastic properties of bitumen. Adsorption isotherms were constructed from adsorption data and fitted to Freundlich and Langmuir models. A better fit was

observed with Freundlich model which is based on a no-uniform distribution of adsorption heat and affinities on a heterogeneous surface. Different trends for the mass adsorbed at equilibrium as shown in Figure 36 were observed for each bitumen sample. If adsorption for pure minerals such as SiO_2 and Fe_2O_3 is compared, it can be observed that bitumen C adsorbs better on SiO_2 while bitumen A and B on Fe_2O_3 , this was supported by the adsorption capacity obtained from Freundlich isotherms.

Data for aggregate sample AGC cannot be compared with the aforementioned minerals, because the aggregate sample is a mixture of different minerals that would affect the adsorption process. This aggregate is composed of SiO_2 (52.37%), Al_2O_3 (15.76%), Fe_2O_3 (9.93%), CaO (8.34%), MgO (4.58%), Na_2O (3.92%), TiO_2 (1.35%) and less quantity of K_2O , P_2O_5 , MnO , Cl , Cr , V , Ba , Sr , Zr , and S . Although the last components are in quantities less than 1 % (wt/wt) can influence adsorption either in positive or negative ways. Additionally data for aggregate sample – bitumen systems were studied only to concentration of 3 (wt/wt)% of bitumen in toluene solution. Mass adsorbed on aggregate AGC from higher concentrations of all bitumen in toluene solution is expected to increase, however, at this bitumen concentration it can be observed from Figure 36 that bitumen B is better adsorbed on aggregate sample AGC followed by bitumens C and A, and the same trend was obtained for all bitumens on each surface analyzed.

Furthermore, Freundlich parameters K_f and n were plotted with different properties of bitumens. It is expected that systems with higher adsorption capacity adsorbed higher mass at equilibrium which will cover better the aggregate surface and lead to reduce weak sites on the system that can be susceptible to failures. It was found that there is a good correlation between the asphaltene content and K_f ($R^2 = 0.9$) as shown in Figure 37, however, coefficients correlation with n were as low as 0,6 because it is not shown. Also, it was observed that adsorption capacity, K_f , for bitumens

A and C were closed while for bitumen B a higher value when adsorbed on aggregate AGC surface was obtained.

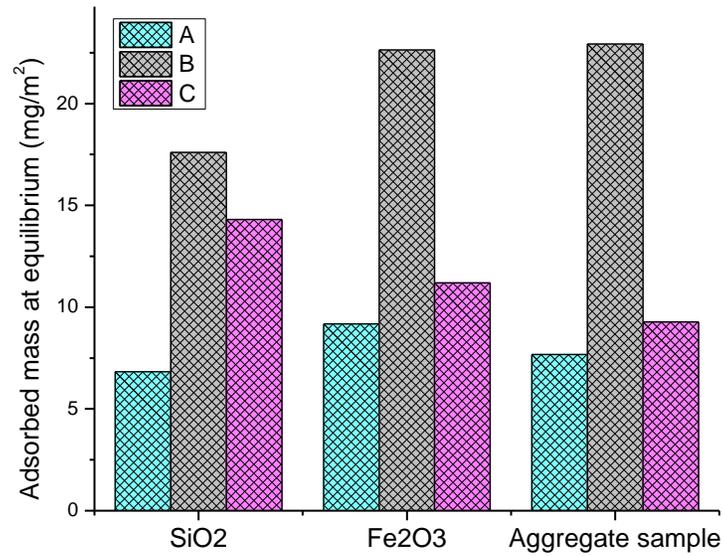


Figure 36. Bitumen adsorption on mineral surfaces

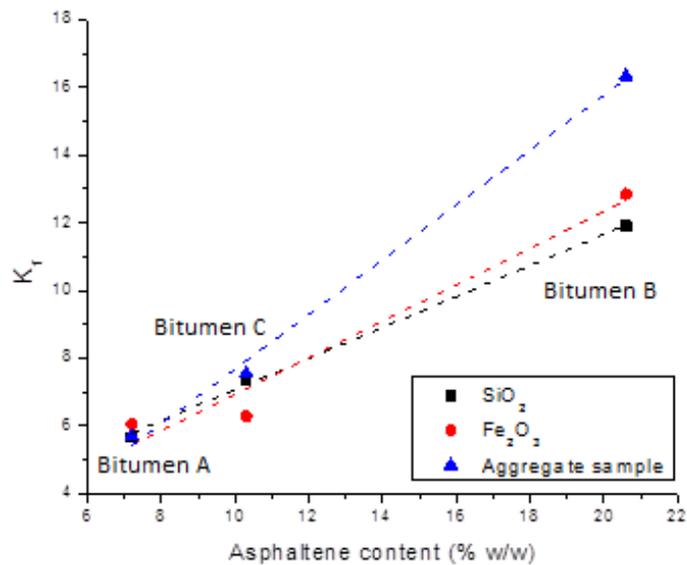


Figure 37. Freundlich adsorption capacity vs Asphaltene content

Finally, it was observed that higher adsorption of bitumen samples on aggregate AGC is related with higher pull off tensile strength measured with PATTI. In other words bitumen sample B with the higher mass adsorbed and adsorption capacity showed higher resistance to tensile strength measured at macroscopic scale, followed by bitumen samples C and A.

In general, it was observed that work of adhesion obtained at macroscopic scale differs from the measured with AFM. Materials properties such as nitrogen content of bitumen, could influence the adhesive properties of system generating interfaces with higher adhesive resistance. This was observed for bitumen C with the higher nitrogen content which showed the higher adhesion forces with both SiO_2 and CaCO_3 surfaces. Additionally, QCM-D was successfully used to follow the adsorption process of bitumen on different mineral surfaces. Adsorption isotherms for bitumen-aggregate surface in real time were obtained for the first time. The use of QCM - D allows the study of materials to promote adsorption and enhance the adhesive properties of the system, this enables the construction of higher resistant pavements. Further research to relate the adsorption capacity with bitumen content in asphalt mixtures is strongly recommended. Higher adsorption capacity and adequate wetting of the mineral surface would reduce the quantity of bitumen needed to cover the aggregate surface.

6 Conclusions

This dissertation attempts to contribute to the better understanding of adhesion phenomenon between bitumen and aggregates as present in asphalt mixtures. Wettability, adsorption and adhesion, were studied for three bitumens and different minerals and aggregates samples at macroscopic and nanoscopic scale. The main insights that were identified with the present research are the following:

- From the study at macroscopic scale of thermodynamic properties of asphalt mixtures, a good correlation between surface free energy calculated with Fowkes model and chemical composition of bitumens was observed. Higher resins content in bitumen caused higher polarity and thus higher surface free energy, contrary to the asphaltene content, a high content of asphaltenes will cause a low polarity and therefore lower surface free energy.
- Results for surface free energy and pull of tensile strength correlates well with high correlation coefficients. Bitumens with lower surface energy wet better the aggregates surface leading to less weak points which is reflected in higher resistance to tensile strength measured with PATTI. But it is important to highlight that all failures with PATTI were cohesive, therefore the work of adhesion for each system were not measured.
- Adhesion force measured at nanoscale with AFM showed different behavior than work of adhesion calculated using the surface free energy. It was observed that bitumen A and B showed a higher work of adhesion with SiO_2 while the opposite behavior was observed for bitumen C, which developed a higher work of adhesion with CaCO_3 . However, higher values for work of adhesion were obtained for bitumen C with high surface free energy.
- At nanoscale a good correlation between the nitrogen content in bitumen and the strength of the bonds formed with minerals was observed.

- A methodology to directly monitor and measure the bitumen adsorption process on aggregate surfaces in real time using QCM was successfully developed. Adsorption data allows a more reliable and accurate study of physicochemical properties of bitumen-aggregate systems.
- Adsorption data obtained with QCM support the observed trend at macroscopic scale. A higher mass adsorbed at equilibrium was obtained for bitumens with lower surface energy. A viscoelastic film was deposited on mineral surfaces, which is consistent with the viscoelastic nature of bitumen.
- The presence of some minerals on the aggregate surface promotes adsorption even in lower amounts. Iron oxide developed a higher adsorbed mass with bitumens A and B, while bitumen C with silicon dioxide. This finding helps to identify minerals which enhance adsorption with bitumen and therefore adhesion in bitumen-aggregate systems.
- Although the measurement of adsorption on real aggregate using QCM was performed up to 3 g/L, the same behavior as in minerals was observed. This proves the ability and reliability of the methodology developed to study complex systems such as the one formed by bitumen and aggregate surface.
- Adsorption phenomenon was satisfactorily described by Freundlich isotherm for heterogeneous systems, a fact that demonstrates the influence of physicochemical heterogeneity on adhesion between bitumen and mineral aggregates.

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