Calorimetric investigations of asphaltene self-association and interaction with resins

Daniel Merino-Garcia

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CALORIMETRIC INVESTIGATIONS OF ASPHALTENE SELF-ASSOCIATION AND INTERACTION WITH RESINS



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VEJLEDER: SIMON I. ANDERSEN







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"Porque sueño, yo no lo estoy"

PREFACE

This Thesis is submitted as a partial fulfilment of the requirements for the Ph.D.degree at Danmarks Tekniske Universitet (technical University of Denmark). The project has been financially supported by the Danish Technical Research Council (STVF) under the Talent Program (Project 95-50107).

This PhD Thesis comprises the work carried out from October 2000 to February 2004 at the Institut for Kemiteknik. The topic was the state of asphaltenes in toluene solutions and the influence of model and native resins in the aggregation behaviour of this petroleum fraction, under the supervision of Associate Professor Simon Ivar Andersen, to whom I express my gratitude.

This Thesis has been divided into two parts: first, a comprehensive report in which the main aspects of the investigation are presented, together with the conclusions of the work. Second, several Appendixes have been included to give a more complete view of the work performed and to further explain some of the aspects that were just sketched in the first part of the Thesis.

A CD-ROM is as well provided, with some additional information and useful programs for future investigations.

Lyngby, 31 January 2004

Daniel Merino-Garcia

Abstract

Asphaltenes are a complex fraction of crude oil known to cause severe problems in petroleum extraction and refining. This PhD project deals with the investigation of the state of asphaltenes in toluene solutions and the interaction of this crude oil fraction with resins. Asphaltene research has been carried out for more than 60 years. Still, many fundamental questions are a matter of debate, such as the main mechanism of selfassociation and the average molecular weight of the fraction. This study is an attempt to shed some light on the aggregation behavior of asphaltenes in toluene, and the characterization of the interaction with another petroleum fraction, namely the resins. Resins are believed to act as natural inhibitors for asphaltene precipitation.

The objective was to establish a procedure to apply Isothermal Titration Calorimetry to obtain experimental values of some of the parameters that are used to model and predict asphaltene behavior. Other techniques, such as Fluorescence and Infrared Spectroscopy have been applied to support the conclusions drawn in calorimetric experiments. The work has been carried out with asphaltenes from different sources in an attempt to cover a wide range of origins and stability.

In Chapter 1, a brief overview of asphaltene science is presented, together with the main objectives of this work.

In Chapter 2, the techniques used in this work are described. The main advantages and drawbacks related to their application to asphaltenes are listed as well.

In Chapter 3, well-known substances are tested by ITC to get the patterns of selfassociation. These experiments would be used later determine which is the behavior of asphaltenes in organic solvents.

In Chapter 4, the state of asphaltenes in organic solutions is investigated, prior to the study of the interaction with other species, such as model and native resins. A comprehensive study with 10 asphaltenes has been performed covering a wide range of concentrations. Solvent and temperature effects have as well been studied. Several models have been used to fit the ITC titrations in order to get the average enthalpy of self-association. The behavior of asphaltenes fractionated with acetone-toluene mixtures is as well presented. In Chapter 5, asphaltenes have been treated to selectively block certain functionalities, in order to determine which type of functional group is more active in ITC experiments. The reactions carried out were: methylation, silylation, reduction and reductive alkylation. The altered samples were studied both by calorimetry and spectroscopy.

In Chapter 6, the interaction of asphaltenes with a well-known substance is investigated, prior to the study of mixtures with native resins. Several models have been applied in order to determine the enthalpy and the average number of sites in this interaction.

In Chapter 7, the study of the interaction of asphaltenes with resins is presented. The ultimate objective is to determine the enthalpy (Δ H) of interaction asphaltene-resin for several stable and instable crude oils, for which there are no available data in the open literature. With this information, it would be possible to determine if resins have a critical influence in the stability of the crude oil.

In Chapter 8, the interaction of altered asphaltenes with resins is discussed in terms of the variation observed in ITC experiments after the modification.

Conclusions and future challenges are collected in Chapters 9 and 10. The additional information is gathered in the Appendixes. It must be observed that these Appendixes do not only contain data but also explanations of some of the facts that were only cited inside the thesis because of reasons of space. They are not critical in the understanding of the work presented but they do help in the overall picture of asphaltenes that comes out of this study.

IV

Resume på Dansk

Asfaltener er en kompleks fraktion af råolie, der kan forårsage store problemer under indvinding og raffinering af olie. Dette Ph.D-projekt omhandler forskning om asfalteners tilstand i toluen-opløsninger og deres vekselvirkninger med en anden råoliefraktion: resinerne. Resiner antages at forhindre udfældning af asfaltenerne i olie. Forskning indenfor området har stået på i over 60 år. Alligevel bliver mange fundamentale aspekter stadig debatteret, f.eks. mekanismer bag selv-association og asfalteners molvægt.

Målet har været at bestemme eksperimentelle værdier for nogle af de størrelser ,der indgår i modellering af asfalteners faseligevægte vha. isoterm titreringkalorimetri. Fluorescens- og infrarødspektroskopi er blevet brugt til at understøtte de kalorimetriske resultater. Arbejdet er udført med prøver der dækker et bredt område af oprindelse og oliestabilitet.

I kapitel 1. gives et kort overblik over asfalteners egenskaber og samt de vigtigste formål i dette Ph.D. projekt. Kapitel 2 beskriver de brugte teknikker samt deres fordele og ulemper mht. undersøgelser af asfaltener. I kapitel 3 testes kendte stoffer vha. isoterm titreringskalorimetri (ITC) med henblik på bestemmelse af selvassociation. Disse erfaringer anvendes senere i tolkningen af ITC-resultater for asfalterne i organiske opløsninger. I Kapitel 4 undersøges asfalteners tilstant i organiske opløsninger vha. ITC. 9 forskellige asfaltener er undersøgt i et stort koncentrationsområde. Desuden undersøges effekter af temperatur og fraktionering af asfaltener. Flere modeller undersøges i tilpasningen af ITC-resultater så gennemsnitlige termodynamiske parametre kan udregnes for selv-association. I kapitel 5 undersøges asfalterne, der er kemisk ændrede, så bestemte funktionelle grupper er blokeret, for at påvise hvilke grupper, der er mest aktive. Disse reaktioner er metylering, silylering, reduktion og reduktion+alkylering. ITC og spektroskopi anvendes i undersøgelserne. I kapitel 6 undersøges vekselvirkninger mellem asfaltener og kendte enkelt sotffer. Såvel termodynamiske parametre som antallet af associationspunkter (sites) er blevet bestemt vha. forskellige modeller. I kapitel 7 undersøges vekselvirkninger mellem asfaltener og resiner. Det endelige mål er, at bestemme entalpier for vekselvirkningen mellem asfaltener og resiner for forskellige stabile og ustabile olier. Dette er ikke beskrevet i litteraturen. Med denne information er

det muligt, at bestemme om resiner har en kritisk indflydelse på stabiliteten af råolie. I Kapitel 8 måles vekselvirkninger mellem kemisk ændrede asfaltener og resiner vha. ITC.

Konklusioner og fremtidige udfordringer er samlet i kapitel 9 og 10. Yderligere information er samlet i Appendix. Dette indeholder ikke alene data, men også yderligere forklaringer af observationer og målinger præsenteret i selve afhandlingen. Dette er ikke kritisk i forståelsen af selve afhandlingen, men er ment som en hjælp i en videre forståelse af dette studie og som basis for fremtidigt arbejde.

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APPENDIXES

A. Acknowledgements

B. Materials: Chemical compounds used and their characteristics are listed.

C. Asphaltene and resin separation: The procedures are described.

D. VP-2000 ITC Calorimeter Optimization: *The ITC equipment has been optimized in experiments in water and toluene.*

E. ITC experimental procedure: The routine for ITC experiments is explained.

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M. Unresolved issues: The problems found during the investigations are listed.

N. Description of the CD-ROM attached: The files supplied are described.

O. List of publications, conferences and courses: *The articles published are gathered here, together with the conferences attended and the courses followed.*

P. List of abbreviations: The abbreviations used in the text are explained.

Q. References: The investigators quoted are listed.

1. Introduction

The basic principles to understand asphaltenes and resins are presented, together with a brief review of asphaltene research. The points discussed in this section are:

- 1.1. Petroleum: general aspects.
- 1.2. Asphaltenes: Definition and Properties.
- 1.3. Resins: Definition and Properties.
- 1.4. State of asphaltenes in crude oil.
- 1.5. Asphaltene issues.
- 1.6. Aim of this project.

1.1. Petroleum: general aspects.

Petroleum is a complex mixture of mainly organic compounds with a wide range of properties. Petroleum is the primary source of energy of the world, due to the large amounts of energy per unit of volume contained in this mixture. The consumption per day is estimated to be around 10 million cubic meters per day (Carbognani, 2002). The importance of crude oil in our world has driven an enormous amount of scientific work in order to get a better understanding of the composition and behavior of this mixture and the optimal procedure to extract it.

Petroleum is usually divided into four fractions: saturates, aromatics, resins and asphaltenes (Figure 1-1). A more complete description of the separation procedure is available in Appendix C. It is important to keep in mind that the crude is a continuum of chemical types. This implies that there may be a considerable overlap among the different fractions in terms of polarity, aromaticity and molecular weight.



Figure 1-1. The separation of a petroleum feedstock into four major fractions

The saturate fraction comprises the n-alkanes and their derivatives, such as methane, ethane and so on. Long-chain n-alkanes ($C_n > 20$) are known as waxes and they are the fraction of petroleum that causes the greatest economical losses in oil recovery because they tend to form crystalline structures upon cooling, leading to the clogging of pipelines. The aromatic fraction comprises compounds as benzene, toluene, naphtalene

and more condensed aromatic sheets. Saturates and aromatics account for the majority of the crude oil. The concentration ranges from 50 to 90 wt% (Speight, 1999). The products obtained from these fractions are countless: gasoline, all kinds of plastic material, lubricants, kerosene and so on.

Resins and asphaltenes are the most complex fractions of crude: most of the highboiling material and heteroatoms (N, O, S and metals) are present in these fractions.

1.2. Asphaltenes: Definition and Properties.

Asphaltenes are a solubility class, which means that the fractionation is based on the solubility properties of the mixture. They are defined as the fraction of crude that precipitates after the addition of an n-alkane (usually heptane) and that is soluble in an aromatic solvent (toluene), according to the IP143 standard (1985). Toluene has a solubility parameter (δ) equal to 18.2 MPa^{0.5}, which is closer to δ of asphaltenes (19-22 MPa^{0.5}) (Barton, 1983). Asphaltenes are insoluble in n-alkanes due to the large difference in solubility parameter (15.2 for n-heptane). Asphaltenes are also soluble in other liquids of high solubility parameter such as pyridine (23 MPa^{0.5}), carbon disulfide (20.5 MPa^{0.5}) and carbon tetrachloride (17.6 MPa^{0.5})⁴ (Yen, 1998).

The definition of asphaltenes is somewhat loose, which allows the presence of species of very different characteristics inside this fraction. The number of different compounds inside the asphaltene fraction is statistically estimated to be over 100,000. Asphaltenes have been compared to mammals: elephants and mice are both mammal species, but they are completely different from each other. It is a good analogy, as asphaltene molecules can be very different in terms of molecular weight and associating capacity. A more technical definition says that asphaltenes are "the heteroatom-rich macromolecular component of petroleum capable of self-association even at low concentrations" (Strausz et al., 1999).

It is usually the combination of high molecular weight, aromaticity and polarity that makes a substance be insoluble in n-heptane and thus become an asphaltene. Figure 1-2 depicts the region where asphaltenes are found in a crude oil in terms of polarity and MW (Long, 1981).



Polarity

Figure 1-2. The asphaltene fraction in terms of polarity and molecular weight, after Long (1981).

The complexity of the fraction makes asphaltenes from different crude oils be somewhat different. The amount of asphaltenes is crude oil varies in a wide range, from 0.1 to 17 wt% (Speight, 1999). The carbon and hydrogen amounts vary however in a very narrow range. The constancy of the H/C ratio, around 1.0-1.2 in weight percent, led to the belief that asphaltenes had a definite composition. The fraction is highly aromatic: 20 to 50% of the carbon atoms are in aromatic rings (Yen, 1998). The presence of alicyclic systems has also been reported (Ibrahim et al., 2003).

The heteroatom content is very significant but varies from crude to crude in almost one range of magnitude (Table 1-1). Asphaltenes consist, as an average, of around 1-10%wt heteroatoms. Sulphur is usually the one with the highest concentration.

	Wt% in ASP ¹	Functional Groups	Technique
0	0.3 - 4.9	Hydroxyl	Infrared Spectroscopy ²
		Carbonyl, Carboxylic	RICO ³
		Ethers	BBr ₃ Hydrolysis ⁴
N	0.6 - 3.3	Pyrroles and pyridines XANES ⁵	
S	0.3 - 10.3	Sulfoxides	RICO ³
		Sulfides and Tiophenes	RICO ⁶ , XANES ⁷

Table 1-1. Heteroatom content of asphaltenes. ¹Speight, 1999. ² Moschopedis and Speight, 1976. ³ Strausz et al., 1999. ⁴Peng et al., 1997. ⁵ Mitra-Ketley et al., 1993. ⁶ Strausz et al., 1992. ⁷ Sharma et al. 2002.

Asphaltene fraction contains acid, basic and neutral molecules. These fractions are separated by chromatography (Ramljak et al., 1977 and Khulbe et al., 1996). The first method gave a small amount of acidic material while the second gave more or less 50

%wt of each. Calorimetric experiments in coal fractions have shown that basic and acid asphaltenes act as electron acceptors and donors, respectively (Dietz et al., 1977).

Free stable radicals have also been found in asphaltenes by Electron Spin Resonance (ESR), and they are concentrated in the acidic fraction (Khulbe et al., 1996). Nevertheless, the energy involved in the interaction through free radicals is assumed to be much smaller than any of the other forces involved in asphaltene-resin interactions (Murgich, 2002). Kvostitchenko et al. (2003) investigated the presence of charges in asphaltenes by electrodeposition. It was necessary to apply a high potential (1000 V) to see the movement of some particles to one of the plates. This implies that asphaltenes do not contain naturally charged regions.

Metals in crude oil are concentrated in the asphaltene fraction. The concentrations are in the ppm range. The most important ones are Nickel, Vanadium and Iron. These metals bind to asphaltenes by the formation of metalloporphyrins complexes, which can be detected by SEC (Andersen, 1994) and by the bonding of metal ions to the center of an imperfect aromatic sheet (Yen, 1998). These metals are important in the self-association of asphaltenes, as the removal of these elements leads to an increase in the dissolution rate (Kaminski et al., 2000). Nalwaya et al. (1999) and Kilpatrick et al. (2003) showed in fractionation studies that Fe is related to the most problematic fractions of asphaltenes, suggesting the importance of this particular metal in aggregation. It is unknown whether these metals are an integral part of asphaltenes or just co-precipitated, as suggested by Andersen (1994b) based on chromatographic extraction and acetone fractionation by Buenrostro-Gonzalez et al. (2001c). Asphaltenes may co-precipitate together with many other diverse nanoparticles, including sulphur, quartz and NaCl (Cosultchi et al., 2002). Mineral matter has been reported (Carbognani et al, 1999 and references cited therein) to play an important role in deposit formation. However, these structures are not considered to be part of the asphaltene fraction.

The polarity and aromaticity make asphaltenes have a tendency to participate in intermolecular association by forces ranging from the quite strong to the very weak. Even if many researchers have said that the forces involved in asphaltene self-association are not "well-understood", they cannot be different from those observed in the organic and

organometallic species that compose this fraction (Murgich, 2002). These forces comprise mainly van der Waals, electrostatic, charge transfer and hydrogen bonding.

The complex behavior of the asphaltene fraction has made that some of the most critical properties, such as the distribution of molecular weights is still a matter of debate. This problem is very important, because the MW is critical in the correlation of physical properties with molecular structure. The current technologies are not able to give a conclusive result. Some techniques, such as Vapor Pressure Osmometry (VPO) suffer from aggregation issues (Moschopedis and Speight, 1976). The sensitivity of the equipment does not allow the use of very dilute solutions. Therefore, VPO measures the MW of the aggregates. Gel Permeation Chromatography (GPC) lacks from a good standard to compare with. The use of polystyrene as a "model" asphaltene is not very correct. Polystyrene is a linear chain while asphaltenes tend to have a more spherical shape. The hydrodynamic volume of this polymer may differ significantly from an average asphaltene molecule. This technique is also limited by the underestimation of MW due to the adsorption of molecules to the packing material (Andersen, 1994a) and the overestimation of MW due to the self-association (Artok et al., 1999). Mass Spectroscopy techniques are probably unable to ionize the whole sample. Boduszynski (1987) reported that up to 40% of asphaltenes are not volatilized. It can also fragmentize some of the molecules, leading to very low values of MW (Artok et al., 1999).

Fluorescence depolarization has been claimed to give the correct average MW (Groenzin and Mullins, 1999). The low concentrations used (ppm range) assured no self-association and there were not vaporization or ionization issues. It has been lately found, however, that a substantial fraction of asphaltenes may not fluoresce, limiting the validity of the results inferred by this technique (Ascanius and Andersen, 2002).

The molecular weight is directly related to the size of asphaltene molecules. The pioneer researchers believed asphaltenes were a huge aromatic sheet surrounded by alkyl branches (Figure 1-3a). This huge molecule would be in agreement with high molecular weight of around 10,000 units or more. This type of structure has been denominated *continental* asphaltenes, as the aromatic core is surrounded by alkyl chains. As the calculated average molecular weight decreased, the size of asphaltene molecules decreased significantly. The shape of the average model also changed, to be in agreement

with molecular simulation studies. These studies showed that asphaltene molecules were more flexible, so that they could migrate along with the rest of petroleum. This gave a picture of asphaltenes with some fused rings linked by alkyl branches (Figure 1-3b). This structure is called *archipielago* asphaltenes. This structure is supported by evidences by ruthenium-ion-catalyzed oxidation (RICO, Strausz et al., 1992) and pyrolysis of asphaltenes (McCaffrey et al., 2003). Continental asphaltenes are still considered possible, but they must have less condensed structures than those showed in Figure 1-3a.



Figure 1-3. Evolution of asphaltene average molecule (a) Highly condensed structure. (b) Archipielago type (Mushrush and Speight, 1995).

The divergences in molecular weight obtained by the different techniques determined the number of fused aromatic sheets of the average molecule. Researchers that believed in a MW of around 3000-5000 g/mol., presented molecules with several fused aromatic sheets connected by alkyl branches (McCaffrey et al., 2003). Investigators that used fluorescence and mass spectroscopy measurements presented smaller molecules, more in agreement with MW of around 500-700 g/mol (Groenzin and Mullins, 1999). They believe asphaltene molecules contain one or two aromatic sheets with an average of seven rings with short aliphatic chains (Groenzin and Mullins, 2000). The only difference between these two trends is whether the aromatic sheets are interconnected or not. Both types of molecule are likely to co-exist in asphaltenes, according to the polydispersity of the fraction.

Asphaltenes are also found in coal and other type of fossil fuel sources (Yen, 1998). Coal asphaltenes are smaller, more aromatic and with shorter alkyl chains than petroleum asphaltenes (Buenrostro-Gonzalez et al., 2001a). In this thesis, the attention has only been focused on petroleum asphaltenes.

1.3. Resins: Definition and Properties.

Resins are considered to be the transition between the highly aromatic and polar asphaltenes and the simpler fractions. Resin molecules have similar structures to asphaltenes but longer alkyl non-polar chains (Koots and Speight, 1975) and smaller aromatic rings (Figure 1-4). This increases their solubility in aliphatic solvents. The MW of resins is in the range 600-1000 units, according to VPO measurements (Speight, 1999). Resins are supposed to aggregate less than asphaltenes, allowing the use of this technique to determine the monomeric MW.



Figure 1-4. Hypothetical model resin molecules (Murgich et al. 1996).

According to the model developed in the early 1940s (Pfeiffer and Saal, 1940) resins are the stability factor in asphaltene colloids. Upon changes in pressure or composition in oil recovery operations, resins are no longer able to peptize asphaltenes and precipitation occurs. It has been observed that the removal of resins causes the precipitation of asphaltenes (Koots and Speight, 1975). Murzakov et al. (1980) reported an increase of colloidal stability as the concentration of resins increased in gravimetric sedimentation analysis. Andersen et al. (2001b) proved by microcalorimetric titration that the addition of resins eliminates the change previously assigned to the Critical Micellar Concentration.

Carnahan et al. (1999) studied the influence of native and non-native resins on the flocculation point of Hamaca asphaltenes. The non-native resins (from Boscan) were more effective stabilisers. This indicates that resins from different sources may have different dispersive power. Hotier and Robin (1983) found that 1 cm³ of resins had the same dispersing power as 105 cm³ of benzene. The presence of resins also retarded the onset flocculation point of asphaltenes in Kuwaiti crudes (Al-Sahhaf et al., 2002). Goual

and Firoozabadi (2002b) observed the same effect: Resins increased the onset point but increasing as well the amount precipitated. The most polar resins were more effective in the stabilization of asphaltenes, stressing the importance of the polar interactions in the system asphaltene-resin.

Resins contain oxygen mainly in esteric and carbonyl functions, rather than hydroxyl (Moschopedis and Speight, 1976). Nitrogen is found in amine, pyrrole and indole functionalities. Chromatographic fractionation of resins shows that they are mainly basic in nature, with a predominance of pyridinic groups (Hammami et al., 1998). The ratio H/C is greater for resins than for asphaltenes, as it is usually above 1.4 (Speight, 1999). There is a tendency to have a greater ratio of heteroatoms in resins than in asphaltenes. Significant deviations from this trend are usually found for sulphur. The amount of resins in petroleum varies in a wide range from 3 to 38 wt% (Speight, 1999). The amount of resins has been found to be greater for crudes with high asphaltene content (Goual and Firoozabadi, 2002a). This suggests that there might be a relationship among the content of resins and asphaltenes and the stability of the oil. McLean and Kilpatrick (1997) reported a dependence of the stability of water-oil emulsions on the ratio between asphaltenes and resins (R/A). Islam (1994) claimed that a ratio R/A above 1 in %wt was an indication of the stability of the crude. However, a comprehensive study with more than 20 crudes has shown that instable oils can also have a ratio above one (Carbognani et al., 1999). The same observation has been reported for Mexican crudes (Buenrostro-Gonzalez et al., 2001b). These studies depend strongly on the method of separation of asphaltenes and resins, as the amounts obtained in the resin fraction can vary in one order of magnitude depending on the standard used (Andersen and Speight, 2001).

Resins are usually separated from the de-asphalted oil by adsorption on surfaceactive materials, but they can as well be obtained as the fraction of de-asphalted oil that is insoluble in liquid propane (Speight, 1999). In this work, silica gel has been used as the packing material of the chromatographic column. A more complete description of the separation procedure is available in Appendix C. Resins are sometimes further fractionated in two groups, one being more polar than the other. Flocculation onset measurements have given evidence that the polar fraction increases the stability of asphaltenes, while the less polar fraction has very little effect (Hammami et al., 1998). Resin interaction with asphaltenes is believed to be a combination of van der Waals, charge transfer, coulombic and exchange-repulsion forces (Murgich, 2002). Due to the polar functionalities and the aromatic rings, resins can interact with asphaltenes by means of hydrogen bonds or charge-transfer complex formation, as shown by IR-spectroscopy and Proton Magnetic Resonance (Moschopedis and Speight, 1976). It has however been claimed that even if hydrogen bonding may be an important factor in the stabilization, other forces should as well taken into account (Murgich, 2002). According to this point of view, polarity is relevant in the process of approach of asphaltenes and resins. Van der Waals (VdW) interaction would take over when the distance is close enough. At longer distances, VdW may be screened by other molecules.

It must be kept in mind that there is a considerable overlap among asphaltene and resin fractions. There is a group of compounds that can be considered either lowmolecular-weight asphaltenes or high-molecular-weight resins, in agreement with the concept of petroleum as a continuum. The separation procedure would determine to which fraction these compounds would go.

1.4. State of asphaltenes in crude oil.

In order to solve the problems asphaltenes cause, it is necessary to understand the structures these compounds form in crude oil. The research developed in the early decades of the 20th century had a great impact in the knowledge about asphaltenes. Some of the theories and qualitative studies developed at that time are still valid, even if they were done with much less equipment than what it is available nowadays.

It is generally accepted that asphaltenes exist as discrete or colloidally dispersed particles in crude oil, and resins are the transition between asphaltenes and the rest of the oil (Figure 1-5). Asphaltenes are considered to be the center of the colloids, surrounded by resin material. Pfeiffer and Saal (1940) proposed this scheme for asphalt (asphaltenes plus resins) and Ray et al. (1957) proved it was also valid for petroleum. The molecules with greatest MW and aromaticity would be in the core and the size and aromaticity would decrease towards the outer layer of the aggregate. Resins have a higher polarity than the rest of the dispersing media, and are easily adsorbed on the surface of the colloids.



Figure 1-5. State of asphaltenes in petroleum according to Pfeiffer and Saal.

They act as a peptizing agent by charge neutralization (Yen, 1998). It is still not clear if these heterogenic colloids contain only one or several asphaltene molecules (Andersen and Speight, 2001).

The question that arises is how asphaltenes get together and what kind of forces are involved. The answer has to be found in the composition of asphaltenes. The heteroatom content gives asphaltenes the potential to associate by means of hydrogen bonds: this association has been studied by several techniques, such as Calorimetry, Infrared Spectroscopy and Proton Magnetic Resonance (Dietz et al., 1977 and references cited therein). Asphaltenes have the capacity to interact with the acidic heads of amphiphiles (Chang and Fogler, 1994 and Al-Sahhaf et al., 2002), supporting the importance of the polar groups of asphaltenes in the self-association or at least in the important interaction with so-called asphaltene inhibitors and dispersants used in industry.

The aromatic content of asphaltenes is also important in self-association. Stacks are formed by means of charge transfer complexes between the π -orbitals of the aromatic rings. X-ray diffraction experiments (Dickey and Yen, 1967) support this theory, based on the existence of a 002 peak in the spectra assigned to graphitic material. This stacking theory requires very big aromatic sheets to create stacks of 5-6 molecules. The actual vision of an asphaltene molecule (see Figure 1-3b) is not compatible with an aggregate formed by layers of asphaltene molecules. Several studies have reported the presence of

alkyl chains in asphaltenes. These alkyl branches, as well as the presence of non-flat naphtenic groups (Seidl, 2003) create a steric effect that limits greatly the chances of stacking among aromatic sheets. However, it is still possible that the aromatic rings associate through the π orbitals, but in a lesser degree than what was suggested by Yen and co-workers. HRTEM (Electron microscopy) has shown that the degree of stacking is between 2-3 sheets per stack (Sharma et al., 2002). In any case, the discussion is still open between these two theories (Pedersen et al., 2002). A combination of both mechanisms seems to be a good approach to understand how asphaltenes self-associate.

Steric hindrance seems to be the limiting factor in the size of asphaltenes. The difference in size of petroleum and coal asphaltenes helps to understand this fact. Coal has considerably larger molecules than petroleum, but asphaltene molecules in coal are smaller than petroleum asphaltenes (Buenrostro-Gonzalez et al., 2002). Petroleum asphaltenes have alkyl chains that act as a sterical hindrance for the self-association (Carbognani, 2003). The absence of these branches in coal reduces the hindrance, increasing the association and decreasing the solubility of the molecules in toluene. To be considered asphaltenes, the molecules must be soluble in toluene, and this implies that only small coal molecules would be solvated by toluene and become part of the asphaltene fraction. The large molecules would stack and have low solubility in toluene. The steric hindrance of alkyl branches limits the number of sheets per aggregate in petroleum asphaltenes, allowing bigger molecules to be considered asphaltenes. This does not mean that other forces such as hydrogen bonding may not play a significant role in the final size of the aggregates.

In any case, once the concentration of aggregates becomes very large, forces such as VdW start to play a role and the aggregates interact with each other, leading to the precipitation of the fraction.

The understanding of asphaltene solutions in organic solvents is much easier than in pure crude oils because of their chemical simplicity. This adds a favorable feature in the calculation of several properties. Toluene solutions have been used in this study. The intention is to extend the work to petroleum in the near future. Even if toluene is a good solvent for asphaltenes, asphaltenes still keep their tendency to associate. Several techniques, such as light scattering (Liu et al., 1995) and dielectric spectroscopy (Pedersen, 2000) have shown that asphaltenes exist in toluene solutions as aggregates of nanometric size. The polydispersity of asphaltene aggregates was proved by filtration: the use of different pore sizes led to different amounts recovered (Savvidis et al., 2001). However, once they were dissolved in toluene, there were no differences among the solutions obtained, leading to the conclusion that the aggregates are polydispersed but formed by the same entities. Safaniya asphaltenes were fractionated by ultracentrifugation and assigned a distribution of sizes from 33 to 252 Å by SAXS measurements (Fenistein and Barre, 2001).

For several years, the concept of Critical Micellar Concentration (CMC) had a wide acceptance in asphaltene science. This concentration would determine the point at which asphaltenes start to associate. Several techniques were used to obtain values of CMC, including surface tension (Rogacheva et al. 1980 and Rogel et al. 2000), calorimetry (Andersen and Birdi, 1991), and onset flocculation points (Deo, 2002). A change in trend of all these properties was observed in the range 2-4 g/l, which was assigned to the beginning of self-association. However, recent studies by SEC (Andersen, 1994), thermo-optical techniques (Acevedo et al., 1999) and fluorescence depolarization (Groenzin and Mullins, 2000) have shown that asphaltenes may start to associate well before that range of concentrations. These evidences support a step-wise mechanism over the formation of finite-size micelles, which has been further investigated herein.

In any case, it has to be taken into account that the behavior of asphaltenes in toluene solutions does not necessarily need to be the same as in the live oil. The structures and behaviors observed may not be projected to the behavior in the oil. Besides, the asphaltenes obtained as a solubility class may differ from the ones separated in the oil recovery operations, which are precipitated by pressure drop (Roux et al., 2001).

The fact that only a small fraction of asphaltenes would precipitate complicates even more the investigations, as the link between the total asphaltene chemistry and that of the precipitating material is still unclear. As pointed out (Porte et al., 2003), aggregation and precipitation are controlled by different intermolecular forces: association is due to strong forces such as hydrogen bonding or stacking, while precipitation is basically due to dispersive forces among aggregates.

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There is a big effort focused on the modeling of asphaltenes behavior. The goal is to be able to predict when a field will have precipitation problems. Several models have been used in the past to model the behaviour of asphaltenes both in solution and in live oil from several approaches, including Peng-Robinson EoS (Ngheim et al., 1993), regular solution theory (Hirschberg et al., 1984 and Wang and Buckley, 2001), micellization (Victorov and Smirnova, 1999 and Pan and Firoozabadi, 2000) and lately applications of SAFT equation (Wu et al., 2000, Buenrostro-Gonzalez et al., 2002 and Ting et al., 2003). All these models include numerous parameters (up to 15 in some cases!) that require either estimation or fitting without knowledge of actual ranges or magnitudes.

Molecular simulations are also applied to shed light on the association behavior of asphaltenes. The capacity of self-association has been simulated (Rogel, 2002) as well as the solvation by organic solvents (Takanohashi et al., 2003). The interaction of two model asphaltene molecules from the Athabasca oil sand with a water molecule in a toluene solution was carried out (Murgich et al., 2002). It was found that water forms bridging H bonds between the heteroatoms of asphaltenes with a considerable span in energies. Murgich et al. (1996, 1999), Murgich and Strausz (2001) and Ortega-Rodriguez et al. (2001) performed molecular simulations of the interaction between asphaltene and resin model molecules. All these studies depend strongly on the assumptions made when constructing the hypothetical asphaltene molecules.

1.5. Asphaltene issues.

Asphaltenes are usually recovered in the residua of the vacuum distillation of crude oil. The applications of this fraction are very limited. It can be used as a geological clock to determine the age of the petroleum, together with the depth of burial (Yen, 1998). It is also used in paving materials. In general, the refineries try to upgrade asphaltic material into more profitable oil by thermal and hydrocracking processes.

The importance of asphaltenes is based mainly on the problems they cause, rather than the application as a product (Table 1-2). Plugging of pipes due to asphaltenes alone or together with waxes is one of the most frequent causes of production shutdown in light oil reservoirs. Waxes are long-chain alkanes (> C_{20}) that precipitate in a cristallinic form due to the decrease of temperature (Pedersen, 2000). Nevertheless, wax science is quite advanced (Azevedo and Teixeira, 2003) and the methods to inhibit wax precipitation are varied: from good insulation of pipes to addition of ethyl-vinyl acetate polymers (Machado and Lucas, 2001).

Asphaltene precipitation is more complex, because the problematic is not directly related to the total content as much as to the accumulation of material during operation. Some reservoirs present problems when the amount of asphaltenes is in the order of ppm, such as Ula field in North Sea, with 0.57 wt% asphaltenes (Thawer et al., 1990) and Hassi Messaud in Algeria, with 0.062% asphaltenes (Hasket and Tartera, 1965).

Process	Problem
Recovery	Well bore plugging, and pipeline deposition
Recovery	Decrease in refining yield due to entrapment of light compounds into asphaltene aggregates (Sheu, 2002).
Blending	De-stabilization in the mixing of crude oils.
Thermal Processes	Phase separation (e.g. Vis-breaking) and coke formation.
De-stabilization	Residual, fuel oil.
Poisoning of catalysts	Decrease in lifetime and yield (Sheu, 2002).
Transportation and Storage	Sedimentation.

Table 1-2. Issues due to asphaltene flocculation and sedimentation.

Nevertheless, reservoirs of Boscan oil are free of problems, even if the asphaltene content is 17.2%. In fact, asphaltene precipitation is usually reported as a trace phenomenon. Crudes with small percentages of asphaltenes are more prone to be instable, due to the large pressure drop that exists before the bubble point (de Boer et al., 1995), as explained below in Figure 1-6. Another important point is that the start of the aggregation may not be a bulk but a surface process. If it starts in the bulk liquid, the research should be focused on solution properties. If it is a surface process, the attention should be on adsorption properties of asphaltenes. The stability seems to be more related to the aromaticity ratio H/C, rather than to the heteroatom content. The length of the alkyl chains seems to be relevant in stability issues: the longer the resin chains are, the greater steric effect is created. The absence of long chains in resins has been proven to be consistently related to instable asphaltenes (Buenrostro-Gonzalez et al., 2001b). It has

been shown that unstable oils are quite rich in saturates and contain asphaltenes with high aromaticity (Carbognani et al., 1999). This suggests that these crudes do not have the capacity to stabilize asphaltenes due to the big difference in solubility parameter among asphaltenes and the majority of the dispersing media. In fact, asphaltene precipitation occurs when the quality of the solvent is decreased.

Gas injection also causes asphaltene destabilization, especially CO₂. CO₂ lowers the pH and alters the oil composition, in combination with the temperature drop (Thou et al., 2002). The decrease in pH leads to the formation of rigid asphaltene films in the water-oil interface (Tuttle, 1983). Stimulation treatment by acids has also been reported to trigger asphaltene precipitation (Thou et al., 2002). Asphaltene fouling is also enhanced by the addition of flocculants (Roux et al., 2001). The addition of paraffins to decrease the viscosity increases as well the chances of asphaltene precipitation (Yarranton et al., 2003), as the increase of concentration of n-alkanes would precipitate asphaltenes, by definition. Figure 1-6 shows the evolution of the amount of asphaltenes in the liquid phase as the pressure decreases in the recovery process. When pressure decreases, the relative volume occupied by the lighter species increases, making the solvent less favorable for asphaltenes. Precipitation begins at the upper pressure limit (Ponset) and continues until the bubble point is reached. At that point, the gases are released and the quality of the solvent is increases. That is to say, the solubility parameter of the crude becomes closer to the one of asphaltenes as the gases are released. After the bubble point, the absence of light n-alkanes makes the asphaltenes re-dissolve in the crude. When the lower pressure limit is reached, all the asphaltenes are re-dissolved.

Nowadays, the lack of understanding of asphaltene precipitation leads to remedial more than preventive measures to solve asphaltene problems. The usual methods to remediate asphaltene fouling are based on the injection of additives that disperse asphaltenes and reduce the onset pressure (Carbognani, 2002). Surfactants with long alkyl chains and a very polar head group have been shown to disperse asphaltenes (Chang and Fogler, 1994). Double branched alkyl compounds have as well been proposed (Wiehe and Jermansen, 2003). Compounds containing basic nitrogen are also reported to be good inhibitors (Van der Berg and Munsterman, 2003). By the addition of surfactants, the interval of pressures at which precipitation occurs is significantly reduced and in some

cases P_{onset} reaches the Bubble Point, avoiding totally the appearance of a solid deposit (Figure 1-7).

These additives are usually a combination of solvents and surfactants (Gonzalez and Middea, 1991 and Thou et al., 2002). The surfactant concentration is not very high, in the ppm range, but the process is still very expensive because the amounts of dispersing agents needed are enormous (Thou et al., 2002).



Figure 1-6. Amount of asphaltenes soluble in crude oil as a function of pressure.



Figure 1-7. Effect of a dispersant on asphaltene precipitation by depressurization. (- - -) No dispersant.

It would be more convenient to have a better understanding of the nature and mechanism of association of asphaltenes to be able to design more efficient synthetic inhibitors. The use of environmentally friendly surfactants could be implemented based on this approach. This work would also help in the development of more reliable models to predict whether a well would have problems or not, and the effective measures to avoid that precipitation.

1.6. Aim of this project.

Modeling asphaltene behavior is a very complicated task. To the best of our knowledge, a predictive tool that can determine if a field would present asphaltene deposition is not available. All the models available nowadays have a large number of assumptions and estimated parameters that decrease the reliability of their predicting capability. This is due to a big lack of experimental data on this topic. The energy involved in the self-association of asphaltenes and the interaction with resins (ΔH_a and ΔH_i , respectively) are critical parameters. If it is very high, it is necessary to separate the asphaltenes before they reach the refinery. If it is low, then there must be a process to upgrade them in a low-cost way. These variables are usually fitting parameters, as in SAFT model (Wu et al., 1998).

This thesis reports the capacity of Isothermal Titration Calorimetry (ITC) to study the interaction between asphaltenes and model and native resins. It also presents experimental values of the heats of self-association of asphaltenes and interaction with resins. The goal is to determine the number of sites and heat of interaction of asphaltenes and resins, for which there are no data available in the open literature. The experimental values provided by a technique such as ITC would be useful in order to decrease the number of estimations. These experiments also shed light on the association mechanism of asphaltenes. The final goal is to extend this study from organic solvents to crude oils, in order to help in the development of more effective synthetic inhibitors for asphaltene precipitation.

2. Technique description

The techniques used in this work are introduced in this section. The descriptions include the special matters of concern in the application to asphaltenes.

- 2.1. Isothermal Titration Calorimetry (ITC).
- 2.2. Infrared Spectroscopy (IR).
- 2.3. Fluorescence Spectroscopy (FS).
- 2.4. Karl-Fischer Titration (KF).

2.1. Isothermal Titration Calorimetry (ITC).

ITC is widely used in biochemistry in the study of ligand-protein interactions (Freire et al., 1990, Blandamer, 1998 and Tameet al., 1998). It has been used to measure the changes in enthalpy of a protein solution in a cell following injection of small aliquots of ligand solution from a syringe. By the use of a suitable model, it allows the determination of the number of sites of interaction in the protein molecule and the enthalpy of association. Moreover, it discriminates among modes of interaction: the data obtained in the titration look different if the binding in different sites is competitive or sequential (Terada et al. 1999).

It also has a wide application in the investigation of the micellar behavior of surfactants in water (Majhi et al., 1998 and Paula, 1995). The advantage of ITC above others is that it allows the determination of both the Critical Micellar Concentration (CMC) and the enthalpy of surfactant micellation in one single experiment. The determination of CMC at several temperatures allows the calculation of the free energy and also the entropy, giving a complete thermodynamic characterization of surfactant micellation. It has also been applied to the study of reversed micelles of AOT in organic solvents (Majhi et al., 1999). The intention is to transfer the knowledge from these two fields into asphaltene science, with the aim of getting a better understanding of the mechanism of interaction, as well as the energies involved in this process. Titration Calorimetry has never had an extended application to petroleum species. Dietz et al. (1977) and Tewari et al. (1978) used calorimetry to study the acidic and basic nature of coal asphaltenes, by reacting them with substances like phenols and quinoline. Andersen and Birdi (1991) used a LKB 2277 bio activity monitor microcalorimeter to study the aggregation of asphaltenes and calculate operative Critical Micellar Concentrations. The same equipment was used show the critical influence of water in the self-association of asphaltenes (2001).

In this work, experiments have been performed in a VP-ITC 2000 Microcal^{\odot} calorimeter (MicroCal, Inc., Northampton, MA). The experiments consist of the sequential injection of known volumes from a syringe into a cell (Figure 2-1). The volume of the cell is 1.4615 ml. The syringe is filled with a reactant. It has a capacity of 294 µl, and this solution is injected in steps of 3-10 µl. The number of injections per test

range from 30 to 100. The equipment is kept inside a glove box to minimize the influence of the external conditions. Silica gel is used to keep the atmosphere dry and reduce the effect of humidity.



Figure 2-1. Schematic view of the calorimeter.

ADVANTAGES	DRAWBACKS
It gives information about the mechanism	It provides only average properties, as it
of self-association of compounds by	is impossible to discriminate the
comparison with other molecules.	contributions from the different species
	of asphaltene fraction.
It allows the calculation of the enthalpy of	The idea is to provide experimental data
interaction among the species injected	to the models, but it is necessary to apply
from the syringe and the ones in the cell.	a model to get these values.
The average number of sites available for	
interaction can also be inferred.	
For surfactants, it allows the determination	Asphaltenes may not follow the same
of all the main thermodynamic properties	association mechanism as surfactants. A
(CMC, Δ H, Δ S and Δ G) in a single run.	new model approach should be used to
	calculate the thermodynamic properties.

Table 2-1. Advantages and drawbacks of ITC.

The cell can contain either pure solvent, when studying the self-association of a compound, or another reagent, when studying the interaction between different species. The calorimeter also has a reference cell that is filled with pure solvent. The sample cell has a stirrer that spins at 300 rpm to assure that the perfect mixing is accomplished fast enough to neglect diffusion issues. After each injection, the sensors in the calorimeter detect the temperature gradient between the reference and the sample cell and send a signal to the controller. This signal determines whether the heat transferred to the cell has to increase or decrease in order to maintain the isothermal conditions. The heat supplied by the control system is recorded and displayed in the screen of the computer.

The first injection point is not used in the treatment of the data, because the tip of the syringe has been in contact with the solution in the cell during the equilibration, prior to the injections, and it is possible that some asphaltenes have diffused into the cell solution, and vice versa. The optimization of the equipment is described in Appendix D. A complete description of the preparation of the experiments is available in Appendix E.

2.2. Infrared Spectroscopy (IR).

Spectroscopy is a very powerful technique that allows the identification and quantification of chemical species. It is based on the absorption of light by matter. Spectrophotometry consists of the measurement of the energy absorbed by a sample after a beam of light of a certain wavelength has passed through it.

This technique allows the identification of functional groups, based on the wavelengths at which energy is absorbed. Certain functional groups have bands in the IR spectrum at the same wavelength, independently from the structure of the rest of the molecule (Table 2-2).

The IR spectrum covers the wave number region between 4000 and 400 cm⁻¹. Wave numbers are the inverse of the wavelength. IR radiation only has an impact in the vibrational and stretching states of the molecules (Ewing, 1985).

The near-infrared region (NIR) covers from 780 to 2500 nm (12820 - 4000 cm⁻¹) and many of the bands observed arise from combinations of C-H stretching vibrations. Scattering from particles gives also raise to bands in the region 1300-1600 nm (Aske 2001), allowing the study of the aggregation state of the systems. Nevertheless, other

researchers have raised some doubts about this fact, as absorption seems to dominate over scattering (Mullins, 1990). The bands at these wavelengths did not decrease after strong dilution of crude even if the aggregates were believed to dissociate, pointing out that they were caused by absorption and not by the dispersion of light.

Wave number (cm ⁻¹)	Functional Group
3650-3500	Free OH
3500-3200	Hydrogen bond (-OH or -NH)
2950	CH ₃ Asymmetric Tension
2925	CH ₂ Asymmetric Tension
1750-1640	Carbonyl group (C=O) Tension Region
1034	Sulfoxide

Table 2-2. Location of some functional groups in IR spectra (Buenrostro-Gonzalez, 2002).

There have been many applications of IR to asphaltene research. Petersen (1967) started the application of IR in the study of hydrogen bonding in asphaltenes and concluded that both hyodrxyl and pyrrolic groups were present in a strongly hydrogen bonded form. A comprehensive hydrogen bonding study was carried out as well in Saudi Arabian asphaltenes (Siddiqui, 2003). Moschopedis and Speight (1976) used IR to prove that asphaltenes contain more hydroxyl groups than resins, while the carbonyl functionalities are more predominant in resins. Chang and Fogler (1994) studied the capacity of hydrogen bonding of asphaltenes with surfactants by monitoring the change in the free hydroxyl peak. Buenrostro-Gonzalez et al. (2001) compared the IR spectra of resins and asphaltenes to conclude that the absence of long alkyl chains in resins may be related to crude stability. Principal Component analysis of IR spectra of crude oils has been successfully used to determine the SARA distribution (Aske et al. 2001). High pressure NIR has been applied to the determination of the onset point of asphaltenes in reservoir conditions (Hotier and Robin, 1983 and Aske, 2002). NIR has also been used to study the dispersive effect of amphiphiles on asphaltene aggregates (Auflem et al., 2002).

ADVANTAGES	DRAWBACKS
It gives information about the degree of	The use of toluene as a solvent limits the
hydrogen bonding of asphaltene solutions.	information obtained, as all the aromatic
	peaks are contaminated and masked by
	the solvent. The use of CCl ₄ is preferred,
	but the degree of hydrogen bonding may
	be different in that solvent.
It gives information about what functional	Many asphaltene researchers believe that
groups are present in asphaltene fraction.	the information that can be taken out
	from IR studies is very limited. NMR is
	preferred over IR.
NIR allows the comparison of the	It is not clear that the bands in NIR are
aggregation state of asphaltenes in	due to scattering by aggregates or just by
solution.	absorption by the molecules (Mullins,
	1990)

Hydrogen Bond Index	$I_{Hbond} = \frac{A_{OH-,NH-,3500\to3100 \ cm^{-1}}}{A_{TOTAL,3500\to2740 \ cm^{-1}}}$
Methyl Index	$I_{CH_2/CH_3} = \frac{I_{at \ 2925 \ cm^{-1}}}{I_{at \ 2950 \ cm^{-1}}}$
Carboxyl-Carbonyl Index	$I_{C=O} = \frac{A_{C=O,1800 \to 1640 \ cm^{-1}}}{A_{C=O,1800 \to 1640 \ cm^{-1}} + A_{Carom,1640 \to 1533 \ cm^{-1}}}$
Sulfoxide Index	$I_{S=O} = \frac{A_{S=O,1060 \to 970 \text{ cm}^{-1}}}{A_{TOTAL,1800 \to 970 \text{ cm}^{-1}}}$

Table 2-3. Advantages and drawbacks of IR and NIR spectroscopy.

Table 2-4. Main IR indexes used in the qualitative study of asphaltenes (Buenrostro-Gonzalez 2002).

The equipment used is a Perkin-Elmer PARAGON 1000 FT-IR Spectrometer with a Specac cell of 0.5 mm path length and NaCl windows. The interest has been focused on the CH_2 - CH_3 region (3000-2900 cm⁻¹) and also the regions were the polar

functionalities appear (3700 to 3200 cm^{-1} for hydrogen bonding and 1800 to 1100 for other functional groups).

Several indexes can be calculated to determine the relative importance of these groups in asphaltene molecules (Table 2-4). In the Hydrogen bond index, the intensity in the hydrogen bond region is normalized by the area in the high frequency region of the spectra. Methyl Index measures the ratio between methyl and methylene groups, which gives an idea of the length of the alkyl chains. Carboxyl-carbonyl Index measures the polarity of asphaltenes in terms of the relative amount of oxygenated groups, while the Sulfoxide Index measures the contribution of sulfoxide group to the polarity of the fraction.

2.3. Fluorescence Spectroscopy (FS).

FS is a spectroscopic technique based on the re-emission of radiation after the absorption of energy. Once the electrons have been excited to higher energy levels, the energy is released. Some species re-emit this energy as heat, but polycyclic organic compounds emit it as radiation (Ewing, 1985). The wavelengths at which energy is emitted have been used to determine the population of small aromatic rings in asphaltenes. The absence of bands in the region 300-350 nm led to the conclusion that the population of these rings was small compared to more condensed structures (Ralston et al. 1996). The lifetime of the fluorescence depolarization of asphaltenes has been used to determine an average molecular weight of roughly 500-1000 units (Groenzin et al., 1999). This technique has been used in the past to investigate the degree of association of asphaltenes (Buenrostro-Gonzalez et al. 2002).

In synchronous fluorescence, the energy emitted by asphaltenes is recorded while varying the excitation and emission wavelengths at the same time. The difference between them ($\Delta\lambda$) is kept constant at 20 nm. Synchronous fluorescence allows an enhanced resolution between the different chromophores, as only the regions where the emission and excitation spectra overlap will give a signal. In principle, a solution containing a single compound will only give one peak if $\Delta\lambda$ is small enough, but asphaltenes will give a more complex spectrum. Figure 2-2 shows the luminescence of
four compounds. If either the emission or excitation wavelengths were fixed, not all the compounds would be observed. On the other hand, the variation of both wavelengths with a constant $\Delta\lambda$ gives a spectra that contains all the compounds with a good resolution among the peaks of each chemical (Figure 2-2b). Vo-Dinh et al. (1985) demonstrated that up to eight benzoquinilone isomers could be resolved by synchronous fluorescence.



Figure 2-2. Synchronous Fluorescence. (a) Total contour of four compounds. (b) Fluorescence spectra of a mixture of naphthalene, anthracene, perylene and tetracene (Ewing, 1985).

ADVANTAGES	DRAWBACKS		
It gives information about the degree of	Self-association is only one of the		
self-association of asphaltene solutions.	possible explanations for the behaviors		
	observed.		
It can give information about the size of	The alkyl branches shift the curves to		
aromatic rings that are present in the	he longer wavelengths, limiting the validity		
asphaltene fraction.	of the discussion of the population of		
	small rings.		
	A significant fraction of asphaltenes may		
	not emit fluorescence (Ascanius and		
	Andersen, 2002).		

Table 2-5. Advantages and drawbacks of Fluorescence spectroscopy.

The equipment used is a MPF-3 Perkin-Elmer Fluorescence spectrophotometer, with 1 cm-quartz cells. No temperature control was performed, and the experiments were carried out at room temperature (25 °C).

2.4. Karl-Fischer Titration.

The water content of the samples has been measured with the Karl-Fischer method, in a 756 KF-Coulometer (Metrohm). Iodine reacts with Water and forms the ion Γ^1 . The formation of Γ creates a potential that is directly proportional to the amount of water in the sample.

ADVANTAGES	DRAWBACKS		
It is a direct measurement of the amount of	Asphaltenes tend to adsorb onto the electrodes.		
water present in a solution.	The cleaning of the cell must be very frequent.		
The sensitivity limit is rather low, allowing	It only calculates the water that is in free state.		
the study of toluene solutions, which have	Water bound to asphaltenes or trapped inside		
a very low solubility of water (0.047 wt%)	would not react with the iodine.		
ppm at 20 °C ²⁹)			

Table 2-6. Advantages and drawbacks of Karl-Fischer titration.

3. Preliminary ITC tests

Preliminary tests were carried out in order to determine how well-known associating molecules behaved in the calorimetric titrations. The idea was to have patterns of behavior of molecules with different association mechanisms, which would be later compared with the enthalpograms of asphaltenes. This would help in understanding the self-association behavior of asphaltenes. The compounds studied in this section are:

3.1. Surfactants.3.2. Rhodamine 6G.3.3. Coronene.3.4. Pyrene.3.5. Nonylphenol.3.6. Conclusions.

3.1. Surfactants.

SDS (see Figure in Appendix B) is a standard surfactant that forms micelles in water. SDS has a polar head (the sulphate group) and a non-polar tail (dodecyl chain). In dilute water solutions, the strong hydrophobic nature of the alkyl chain makes the molecules stick to the interface with air, keeping the polar head in solution while the hydrophobic chain is airborne. When the concentration of surfactant is high, the molecules in the bulk liquid gather and form micelles with the polar heads on the outer surface of the aggregate to protect the non-polar alkyl chains. Equilibrium exists between monomeric and aggregated surfactant. These micelles have an aggregation number of around 50 molecules. This number decreases with temperature and increases with concentration (Majhi and Blume 2001).

The concentration at which these micelles are formed is called Critical Micellar Concentration (CMC). In ITC experiments, CMCs are easily calculated. The syringe is filled with a solution of SDS of high concentration (30 g/l) to assure that the surfactant is in micellar state. The solution is injected into the cell and the heat developed is recorded (See Figure 3-1a). The reproducibility of the results is very high. Experiments have been performed at 30 °C. Positive peaks represent endothermic processes, as the heat signal recorded is the heat supplied by the control system of the calorimeter. If the injection developed exothermic heat, the control system would have to remove heat from the cell and the heat signal recorded would be negative. The enthalpogram can be divided into three regions: first, a plateau of high heat developed, in which the micelles break because the concentration in the cell is below CMC. Second, a transition region appears, which corresponds to the CMC. Third, at cell concentrations higher than CMC, a plateau of low heat developed is observed, which is related only to the dilution of micelles. The inflexion point in the curve is assigned to the CMC and it can be calculated by the derivative of the curve (the minimum corresponds to the CMC, as shown by Garidel et al. 2000) or by the plot of the cumulated heat versus the concentration (the change in slope is assigned to CMC, as shown by Andersen et al., 1991). The second method was used and the CMC obtained was 2.4 g/l at 30 °C (Figure 3-1a). Paula et al. (1995) and Andersen and Christensen (2000) found a value of 2.5 g/l by ITC. The enthalpy of micellation is usually calculated as the difference between the two plateaus of the first and third region.





Figure 3-1. (a) Titration of 30 g/l of SDS in water at 30 °C. (b) Titration of 80 g/l of Sodium Cholate in buffered water (pH=7) at 40 °C.

Sodium Cholate is a more complex surfactant. It belongs to the family of bile salts. Classical surfactants have a hydrophilic polar head group clearly separated from the hydrophobic flexible aliphatic chain. On the other hand, bile salts have a hydrophobic surface, which is the convex side of the rigid steroid ring, and a hydrophilic surface, which is the polyhydroxylated concave side of the molecule (see Appendix B).

The structure of the molecule is more complex than that of SDS and therefore, more similar to asphaltenes. In any case, the calorimetric titration of 30 g/l at 40 °C in a pH=7 buffer displayed again the same three regions as SDS (See Figure 3-1b). The buffer is added to avoid the variation of pH during the titration. The calculated CMC is 6.11 g/l. The micellation energy is $\Delta H_{mic} = -1.91$ kJ/mol. In this case, the CMC region is broader due to the greater complexity of the molecule and the heat of micellation is lower because

the aggregation number of the micelles is also lower (Garidel et al. 2000). Paula et al. (1995) reported a CMC of 6.67 g/l and Garidel et al. (2000) of 7.13 g/l and ΔH_{mic} of -2.8 kJ/mol. The differences in ΔH_{mic} are maybe due to the fact that the final plateau is not totally reached in Figure 3-1b.

3.2. Rhodamine 6G.

Rhodamine 6G is a dye (See Appendix B). Dyes are substances used in paint industry and have been applied in fluorescence studies as model molecules for asphaltenes (Groenzin and Mullins, 1999). They are usually very aromatic and also contain a number of heteroatoms, which leads to a complex mechanism of selfassociation into aggregates of variable size. The influence of the ionic nature of the molecule in the self-association cannot be disregarded. They are supposed to follow a step-wise mechanism of association (Martin, 1996). This means that they do not need a certain concentration in the solution to start forming stable aggregates, as surfactants do. Instead, they form dimers, trimers and so on, with a higher aggregation number at higher concentrations.



Figure 3-2. (a) Titration of 6.86 mM Rodhamine 6G into water at 30 °C. (b) Coronene Tests.

In ITC experiments, it is observed that there is not an initial region of constant heat developed when the solution of Rhodamine 6G is injected into the cell (See Figure 3-2a). Li et al. (1996) presented a titration of a protein into a buffer and the shape of the curve was very similar to the enthalpograms of Rhodamine 6G. In the case of the protein, the titration was fitted successfully to a dimer model the simpler case of step-wise association. This confirms that this dye associate in a step-wise manner. The heat developed decreases gradually, as the concentration and the degree of self-association in the cell gets closer to those in the syringe.

Of the three regions observed with surfactants, only one is present in dye experiments. Figure 3-2a shows that the reproducibility of the experiments is very high. Tests with a concentration six times lower were also performed to check that the location of the CMC was not at much lower concentrations. The absence of the first plateau shows that this dye does not have a Critical Micellar Concentration.

3.3. Coronene.

Another calorimetry study was carried out with two model molecules: coronene and pyrene, which are two examples of aromatic molecules that stack in solid phase (Rubio et al., 1996 and Boeyens et al., 1969). In principle, these molecules will also stack by π - π interactions when dissolved in toluene. The first molecule investigated was coronene, which is a 7-ring aromatic sheet (See Appendix B). It is completely flat, and it would represent the core of an asphaltene molecule. However, the solubility is very low in toluene (less than 1 g/l) and the titration only gave small uniform exothermic peaks that were assigned to the friction losses of the injection process (Figure 3-2b). This fact reinforces the idea of alkyl branches limiting the association of asphaltenes. If there were no branches, they would not be soluble in toluene, as it happens with coal big molecules (Buenrostro-Gonzalez et al., 2001). Coronene would better represent a coal asphaltene molecule than an asphaltene molecule. The heat developed is too low, so the ITC equipment is not sensitive enough to measure it properly. The heat is in the range (-2,-4) μ cal/injection, while the reference tests where toluene is injected into toluene develop around -2 μ cal/injection.

3.4. Pyrene.

Pyrene, a substance more soluble in toluene, was investigated as well. ITC experiments show that pyrene has a complex enthalpogram (Figure 3-3). At low concentrations, an exothermic process dominates. At higher pyrene concentrations, there magnitude of the exothermic process grows, but a second peak (endothermic) appears and increases in size with increasing syringe concentration.

The assignment of the processes responsible for the peaks observed is not an easy task. In connection to the previous experiments, it is suggested that the positive peaks are due to the dissociation of bonds among pyrene molecules. Pyrene molecules can associate through the free electrons of the π orbitals. With respect to the exothermic peaks, it was first considered that it may be related to the frictional heat, as the enthalpogram resembles the one of pure toluene (See Appendix D). Nevertheless, the frictional heat is assumed to be constant and the exothermic peaks grow with increasing concentration.



Figure 3-3. ITC experiments. Injection of several pyrene concentrations into dried toluene. (a) Raw Data. (b) Integrated areas.

These experiments show that the combination of endothermic and exothermic processes hinders the discussion of the experimental results, as the total heat developed is a sum of both types of processes. For instance, when C=50 g/l, the total heat developed is almost zero because the two contributions compensate each other. The implications are even more relevant in the cases where only one peak is observed, for instance, the titration of Rhodamine 6G. Even if the peaks observed are all positive, there may as well

be exothermic processes ongoing in the cell, but of lower magnitude than the dissociation of bonds. This contribution is masked by the dominating endothermic heat, but has a significant influence on the total heat measured. This suggests that the heat developed in the dissociation of bonds may be underestimated.

3.5. Nonylphenol.

Nonylphenol was used as a model hydrogen-bonding molecule. These experiments have been used as reference data in the study of the interaction of asphaltenes and nonylphenol (See Chapter 6). Experiments were carried out in dried toluene (see Figure 3-4). The heat developed is endothermic, as expected. The dilution in the cell after the injections causes the dissociation of hydrogen bonds.



Figure 3-4. Titration of nonylphenol into dried toluene with two syringe concentrations (5 and 20 g/l). Experiments fitted with a simple dimer model (See Chapter 4).

A simple step-wise model was applied to model the titration. The model considers that nonylphenol can be present as monomers or dimers. Association is believed to occur through the hydroxyl groups. The good performance of the dimer model suggests that nonylphenol has only one interaction site. Therefore, nonylphenol cannot act as a bridge between two asphaltene molecules; that is to say, nonylphenol is able to block the growth of asphaltene aggregates. This fact will be later used in the development of the models to describe asphaltene-nonylphenol association.

3.6. Conclusions.

Several well-known compounds have been tested in the calorimeter to establish patterns of behavior of substances with known mechanisms of self-association. Surfactants present three distinct regions in the enthalpograms that are assigned to demicellization, CMC region and dilution of micelles, respectively. Substances that do not have a Critical Micellar Concentration, such as Rhodamine 6G, only show one region called step-wise dissociation.

Aromatic compounds were titrated as well, but the results were not satisfactory. Toluene is a very poor solvent for coronene, while pyrene displays a complex behavior that is not fully understood. Even if pyrene is a single and well-known molecule, the titration into toluene presents a combination of processes with different types of heat developed. If the exothermic contribution is small compared to the endothermic, the negative peak may not be appreciable. It will still have an influence in the actual size of the positive peak, though. This fact can lead to an underestimation of the heat developed in the self-association of asphaltenes. It is expected that the polydispersed asphaltenes will present this behavior as well or even magnified. The influence in the resin-asphaltene interaction is believed to be less important, due to the reference tests carried out that may take this effect into account.

At the present stage of the investigations, it is considered as a reasonable approach to neglect the underestimation of heat developed. The heat developed in ITC titrations is either due to formation or dissociation of bonds. For the sake of simplicity, it is assumed that each type of process always develops heat in the same direction (for instance, dissociation of bonds is always endothermic). Nevertheless, there are other processes such as tangling of alkyl chains, repulsion, solvation and others that may be relevant but are not taken directly into account.

4. Asphaltene Self-Association

In order to understand the mechanism of association of asphaltenes with resins in toluene, it is first necessary to get more insight on the state of asphaltenes alone in solution. The points discussed in this section are:

- 4.1. Concentration dependence of self-association.
- 4.2. Influence of water.
- 4.3. Influence of temperature.
- 4.4. Influence of solvent.
- 4.5. Fluorescence spectroscopy measurements.
- 4.6. Infrared spectroscopy measurements.
- 4.7. Discussion of experimental results.
- 4.8. Modeling self-association.
- 4.9. Asphaltene fractionation with a polar mixture.
- 4.10. Conclusions.

4.1. Concentration dependence of self-association.

Asphaltenes have been shown to have some similarities with surfactants: they had been reported to stabilize water-in-oil emulsions (Waarden, 1958 and Neumann, 1965) and present surface activity (Rogacheva et al., 1980). Concentrated asphaltene solutions exhibit some degree of colloidal behavior (Sachanen, 1945). For many years it was believed that asphaltenes in organic solutions had a well-defined CMC, as it is the case for surfactants. This hypothesis implies that asphaltenes remain in monomeric state in the solution until a certain threshold concentration is reached CMC. Above that concentration, asphaltenes arrange themselves into aggregates. Several techniques have been used in the past to obtain CMC values, such as Calorimetry (Andersen et al., 1991), Surface tension (Sheu et al. 1992, Rogel 2002) and Onset flocculation points (Deo 2002). Nevertheless, other researchers have supplied evidences by the same techniques that reject this approach. Christensen and Andersen (1999) claimed that the observed changes in the CMC-region may be due to the association of small aggregates into bigger ones. Yarranton et al. (2000) could not find a CMC for asphaltenes in toluene and 1,2-dichlorobenzene by surface tension measurements.



Figure 4-1. Titration of 15 g/l of LM2 asphaltenes with 10 µl/injection.

In agreement with the latter, the ITC titration of an asphaltene from Venezuela (Figure 4-1) shows a different enthalpogram from the model surfactants that were studied in the previous section (see Figure 3-1). There is not a first region in which the heat developed is constant. If there was a CMC in the concentration range studied (0.2–2 g/l), the first injections (when $C_{cell} < CMC$) should give a constant heat signal. As in the case of SDS and Sodium Cholate, the micelles would break and asphaltenes would exist in the cell only in monomeric state.

However, the chart looks more like the one of Rhodamine 6G: the heat developed decreases with increasing concentration in the cell, which means that the newly injected aggregates dissociate less and less as titration is carried out. This is more in agreement with a step-wise mechanism of association. Andersen and Christensen (1999) also found a continuous decrease in asphaltene titration but the absence of a clear change in tendency was believed to be caused by the low sensitivity of the apparatus. The sensitivity and signal-to-noise ratio of this new equipment allows rejecting that possibility (See Appendix D). The standard deviation is slightly greater than in water solutions, because the signals are one order of magnitude lower, leading to a greater signal-to noise ratio. Besides, toluene is more volatile than water. The time between tests allows a higher degree of evaporation that leads to an increase in concentration of the solution in the syringe. These effects are minimized by keeping asphaltenes in sealed vials and stored in a dark place.



Figure 4-2. Enthalpograms of the titration of asphaltenes into dried toluene. Csyringe = 30 g/l.

Nine asphaltenes were titrated to give a concentration in the cell in the region usually referred to as CMC (1-6 g/l, Andersen, 2003) (Figure 4-2). There is again a continuous decrease of the heat developed, without a first monomeric region. The behavior observed is the same as for LM2, giving more generality to the conclusions drawn. Tests with 50 g/l in the syringe that resulted in concentrations in the cell from 2 to 10 g/l were also performed with comparable results (See Appendix G and CD supplied).

The comparison of the behavior of SDS and Alaska 95 asphaltenes (Figure 4-3) in ITC experiments shows clearly the difference in aggregation mechanism of these two species.



Figure 4-3. (a) Enthalpograms of SDS and Alaska 95 (both Cs = 30 g/l) normalized by the heat developed in the first injection. (b) Cumulated heat of SDS and Alaska 95 asphaltenes. The cumulated heat of Alaska 95 has been multiplied by 6 to get a better comparison of both plots.



Figure 4-4. Influence of syringe concentration on ITC titrations. OMV asphaltenes.

Titrations with different syringe concentrations (from 5 to 50 g/l) show that the heat developed in cal/g injected increases with concentration. All concentrations used are above the previously reported CMC region. Following the micellization approach, the aggregates formed at all these concentrations would be similar. The increase in heat developed implies that the aggregation state of asphaltenes is different. This indicates again that the aggregation is concentration dependent and follows a step-wise mechanism.

So far, the attention has been focused on the region 1-10 g/l because that is where most of the values of CMC are found in the literature. The question that arises now is what happens at lower concentrations. Some surfactants of long chains (ammonium bromides with chains up to 16 methyl groups) have very low CMCs (around 10^{-3} M) (Chatterjee, 2002). Assuming a MW of 1000 g/mol. for asphaltenes, that value of CMC would imply a concentration of 1 g/l. The study of lower concentrations becomes necessary. Only the latest generation of calorimeters can reach these low concentrations.

Eight asphaltenes were tested in dried toluene with a very low syringe concentration (Cs = 5 g/l, Figure 4-5). The chart shows that, for all the asphaltenes studied, there is no break in the concentration region 0.07-1 g/l. The ITC enthalpograms are slightly distorted at these concentrations because the sensitivity limit of the apparatus is being reached, as the energies measured are in the range of 10 μ cal/injection.



Figure 4-5. ITC experiments of asphaltenes at very low concentrations (Cs = 5 g/l).

Another experiment was performed with MOT asphaltenes from Venezuela (Figure 4-6). The titration was made with injections of less volume (5 μ l instead of 10 μ l) to see if it was possible to reach the beginning of the self-association.



MOT Asphaltenes at 30 °C

Figure 4-6. ITC titration of MOT asphaltenes. Cs = 5 g/l and V_{inj} = 5 μ l.

It is observed that there is no plateau at the first injections even if the concentration in the cell is as low as 34 ppm. This implies that asphaltenes are already in aggregated state at such low concentrations. This is in agreement with results from other researchers and techniques. Andersen (1994) used Size Exclusion Chromatography (SEC) to conclude that there is association at concentrations lower than the usual CMCs. Absorbance measurements (Castillo et al., 2001) also showed self-association in toluene at 100 ppm. Groenzin and Mullins (1999) reported aggregation issues at around 60 mg/l in fluorescence depolarization studies. Thermo-optical techniques showed as well that the aggregation is step-wise and the aggregation stage was estimated to last from 0.05 g/l until 2 g/l (Acevedo et al., 1999). The variation in numbers is maybe due to the different nature of the asphaltenes used and also to the sensitivity of the technique applied. In any case, it is clear that aggregation begins in the ppm range.

In a different type of experiments, asphaltenes were titrated with pure dried toluene (Figure 4-7). This helps to illustrate the different heat contributions that are present in ITC titrations. The raw data shows that at low concentration of asphaltenes in

the cell, there are small exothermic peaks, just like when pure toluene is injected into pure toluene (See Appendix D).



Figure 4-7. Effect of the injection of dried toluene into KU asphaltene solutions.

These exothermic peaks are assigned to the friction losses of the injection process. When the concentration increases to 1 g/l, this peak is compensated by an endothermic contribution, namely the breaking of asphaltene-asphaltene bonds. At higher concentrations, this endothermic peak is the one that prevails over the heat developed in the injection process.

The conclusion of the ITC experiments is that asphaltenes present self-association prior to the region at which values of CMC are usually reported. The micelle concept seems to be no longer valid for this system in this solvent. In the light of the comparison with model molecules, a step-wise mechanism is suggested as a suitable approach.

4.2. Influence of water.

Water is present in most if not all crude oil reservoirs. Water is used in secondary oil recovery to displace oil and maintain the reservoir pressure. Its influence in asphaltene precipitation has been disregarded for many years. Similar-acting substances, such as phenol, have been more studied in relation to asphaltenes. Phenol and other alcohols have been shown to form hydrogen bonds with asphaltenes by IR spectroscopy (Barbour and Petersen, 1974) and to increase the stability of asphaltene dispersions in heptane (Chang and Fogler, 1994a). Czarneki (2003) reported that asphaltenes present more organized structures when precipitated in the presence of water. Alcohols have a hydroxyl group that can be bound to asphaltenes. Water, on the other hand, has two hydrogen atoms so it can act as a bridge between macromolecules. For instance, water has been found to play an important role in stabilizing the entire system ligand-duplex DNA by means of hydrogen bonds (Linjing et al., 1998), and water bridges play an important role in the recognition of DNA by a certain repressor (Suenaga et al., 2000). Water is expected to interact with asphaltenes in one of these three ways:

- Hydrogen bonding to the surface of the asphaltene aggregate.
- Inclusion into internal cavities of the aggregate.
- Chemical reactions by means of the free OH radicals of water (less probable).

The first study about water-asphaltene interaction (Andersen et al., 2001) was performed with a LKB 2277 bio activity monitor microcalorimeter. Water was found to be the driving force in establishing a measurable *operational CMC*. The authors called it *operational CMC* because they considered that it was related to the aggregation of small aggregates into bigger ones. The fact that asphaltenes aggregated at lower concentrations was already suggested in that work. This study also measured the water uptake of asphaltenes solutions in toluene by Karl-Fischer Titration. The saturation concentration reached was three times higher than in the absence of asphaltenes. This was a clear evidence of the interaction between water and asphaltenes. Vapor Pressure Osmometry showed that the increase in water content of the solution led to a sharp increase in the molecular weight of asphaltene aggregates (Andersen, 2001, personal communication). IR spectroscopy studies (Khvostitchenko and Andersen, 2002) showed that the ratio bound-water to asphaltenes is less than one. This implies that it is not possible to have water in the core of the asphaltene aggregate. It is more probable that water exists in the solution forming a network with the asphaltenes: water would be the bridge that *glues* asphaltenes together. The influence of water seems to be relevant mainly in the range from 0 to 5 g/l. Besides, molecular simulations show that the water molecule may generate additional mechanisms of aggregation of asphaltenes in toluene solution (Murgich et al. 2002). Therefore, it was of interest to continue the study of the effect of molecular water in the aggregation process of asphaltenes with the VP-ITC calorimeter.



Figure 4-8. ITC titration of Alaska 95 asphaltenes at 30 °C (Cs = 50 g/l).

The influence of water is very small in the tests with the VP-ITC calorimeter (Figure 4-8). Moreover, the heat developed in tests with dried solutions is higher than that of the tests with saturated toluene, even if the procedure had been in principle improved (see Appendix D).

In order to make a more comprehensive study, OMV asphaltenes were used to perform experiments with several water contents. The saturated toluene was substituted by a mixture 3:1 of saturated and dried toluene, to avoid possible problems of working in the limit of saturation, yet having a considerable amount of water in the system. A third water concentration (mixture 1:3 of saturated and dried) was as well tested. The influence of the water content (Figure 4-9) is again small; the increase in water concentration

causes a slight decrease in the heat developed. This seems to be the opposite as expected if water was the driving force of the association.



Figure 4-9. ITC titration of OMV asphaltenes with two syringe concentrations. (\Diamond) Dried Toluene. (O) 25% water-saturated toluene. (Δ) 75% water-saturated toluene.

According to that hypothesis, and the work carried out with the LKB equipment, the heat developed in the tests with dried toluene should be much lower because the lack of water would imply that there will be fewer aggregates to break and, therefore, less heat developed by dilution. Nevertheless, it has to be taken into account that water can form hydrogen bonds with asphaltenes both in monomeric and aggregated state. When the asphaltene solution is injected into pure toluene, the aggregates break, leaving the interaction sites free for the interaction with water. This asphaltene-water interaction is exothermic, and this new heat contribution "shifts" the curves to lower (less endothermic) heats developed. This process is more relevant at high water contents, and that is why the curves are shifted downwards as the content of water rises. Another possibility is to consider that the asphaltene aggregates are stabilized to some extent by water, and then the dilution effect is not strong enough to be a driving force for the dissociation. Therefore, the heat developed is lower. This suggests that water may play an important role but it is not the only driving force for self-association. In any case, this discussion is hindered by the fact that, even if toluene is dried with molecular sieves, the water content is not negligible, reaching sometimes 10% of the saturation value. The solubility of water in toluene at 25 °C is approximately 0.055% and the driest solutions have an average of 0.007% water, measured by Karl-Fischer titration. In the most unfavorable case (the highest concentration of asphaltenes in the cell is 8 g/l), the ratio water/asphaltene in moles in the cell is 0.4. This means almost one molecule of water per two of asphaltene. This means that the amount of water at a molecular level is very high. This fact has two important implications:

- The presence of traces of water cannot be neglected in the study of the association of asphaltenes because, even in such minute amounts, the mole ratio with respect to asphaltenes is higher than unity.
- The procedure to dry the toluene becomes a key factor in the study of the influence of water.

The use of a different desiccant, such as metallic Na or P_2O_5 , does not solve the problem, as they have a similar efficiency as the molecular sieves (Table 4-1).

	Dessicant		
Non-treated toluene	Molecular sieves	Sodium	P2O5
98.1 + 2.3	17.0 + 3.7	18.1 + 2.9	13.0 + 4.6

Table 4-1. Drying efficiency of several dissicants (water content in toluene in ppm).



Figure 4-10. Increase in water content after the addition of a certain amount of asphaltenes to toluene.

The water content in the dried toluene was lower than 0.02 g/l in all cases. The limit of solubility is 0.440 g/l at 25 °C (Kertes, 1989). However, the water content increased dramatically after the addition of asphaltene solid samples (Figure 4-10). This led to the conclusion that asphaltenes in solid state may contain an important amount of water. This increase did not follow a particular trend, limiting the conclusions that could be drawn out of this experiment.

In order to verify if this water was just adsorbed to the surface of the solids, or was internally bound to the asphaltenes, a solid sample of asphaltenes was put in the oven at 90 °C for 60 minutes and then dissolved in toluene.

The same quantity of asphaltenes was dissolved without the temperature treatment and the increase in water content in both samples was measured. The difference is very small (Table 4-2), and in both cases the increase after the addition of asphaltenes is significant. Therefore, the oven treatment did not remove any of the water attached to the solid asphaltenes.

	Dried	Asphaltene solution	Asphaltene solution
	toluene	no oven treatment	60 min. in oven 90 °C
Water content (ppm)	37.5 ± 0.7	85.0 ± 2.8	91.5 ± 4.9

Table 4-2. The oven treatment did not avoid the increase in water content.

It was considered that the increase might be a consequence of the ultrasound treatment: in this process, water and asphaltenes associate and then toluene is preferentially stripped off the solution, increasing the water content. Nevertheless, the Table 4-2 shows that the increase in water content occurs even without the ultrasound treatment. The conclusion is that water is more tightly attached to asphaltenes than just by adsorption; this hinders greatly the drying process, and consequently, the discussion about the influence of water in the association of asphaltenes.

To sum up, the interaction of water with asphaltene exists, but it has not been possible to quantify it or to assign it a critical influence on the self-association of asphaltenes.

4.3. Influence of temperature.

Precipitation of asphaltenes from live oil increases with temperature (Aske et al 2002). However, the opposite behavior has been reported upon n-alkane addition. VPO measurements in organic solvents showed a reduction in the MW of the aggregates with increasing temperature (Moschopedis and Speight, 1976). This phenomenon has also been reported by Yarranton et al. (2000). SANS studies by Roux et al. (2001) showed that the aggregate size was reduced from 70 to 50 Å after increasing temperature from 20 to 73 °C. In principle, weak forces governing self-association of asphaltenes such as like hydrogen bonds are known to decrease in intensity with temperature (Prausnitz, 1999). The kinetic energy of the molecules becomes high enough to break these weak bonds.

ITC experiments have been performed at several temperatures from 30 to 50 °C. The intention was to determine if the association degree of asphaltenes varied. Taking the previous evidences into account, it was expected to see a significant decrease in heat developed. At higher temperatures, the solution in the syringe would be less aggregated and less heat would be released upon dilution.



Figure 4-11. Influence of temperature. (a) Alaska 95; Csyringe = 5 g/l. (b) KU; Csyringe = 30 g/l.

Experiments with several asphaltenes show the opposite trend. The variation in heat developed is surprisingly small (Figure 4-11). The deviation is inside the standard deviation, hence no temperature effect is observed in ITC titrations.

4.4. Influence of solvent.

Up to this point, toluene had always been used as solvent. It was interesting as well to see how asphaltenes behave in other organic solvents. The strength of the solvent would determine the association degree of asphaltenes. Therefore, it was expected to see a variation in the heat developed from solvent to solvent. Experiments in Carbon Tetrachloride (CCl₄), Pyridine and Carbon Disulphide (CS₂) were performed and compared with toluene. Pyridine was selected because it has been claimed that asphaltenes always present a CMC in pyridine solutions by surface tension measurements (Sheu, personal communication). The experiments will as well been used to determine if the association mechanism is the same in all solvents.

Yagual asphaltenes were selected for these tests, and a 30 g/l solution was injected into the organic solvents, which had previously been dried over molecular sieves. Reference tests were again performed, in which the syringe is filled only with dried solvent. The heat developed in the first injection (ΔH_o) is collected in Table 4-3, together with the solvent solubility parameter and dipole moment.

	δ (MPa ^{0.5})	Dipole moment (D)	$\begin{array}{c} \Delta H_o \\ (\mu cal/inj) \end{array}$
Carbon Tetrachloride	17.6	0.0	191.5
Toluene	18.2	0.4	154.4
Carbon disulphide	20.5	0.0	228.8
Pyridine	23.0	2.2	139.0

Table 4-3. Comparison of ITC titrations of Yagual into several organic solvents and correlation with solubility parameters (Barton, 1983) and dipole moments.

Figure 4-12 shows the enthalpograms of Yagual in all the solvents used. It is observed that the heat varies considerably when the solvent is changed. Pyridine and toluene experiments develop less heat and these two solvents are the ones that present a dipole moment. This may indicate a greater dissolving power by interaction with the polar functionalities of asphaltenes. This leads, in turn, to a lower heat developed in the dissociation experiments, due to a reduction in self-association caused by the greater solvent-asphaltene interaction. The solubility parameter δ does not correlate in the same way with ΔH_0 . Hansen solubility parameters did not, either. All enthalpograms show a

continuous decrease in heat developed as the concentration in the cell increases. Once again, the three-region enthalpogram of typical surfactants is not found, even in pyridine. The mechanism of association is believed to be step-wise in all cases.



Figure 4-12. (a) ITC titration of 30 g/l of Yagual asphaltenes into dried solvents at 30 °C.



Figure 4-13. Titration of 5 g/l of Yagual asphaltenes in pyridine.

Storm and Sheu (1995) used surface tension measurements to find a CMC at 0.25 g/l for Ratawi asphaltenes. An additional experiment was carried out with a lower syringe concentration (5 g/l) to reach such low concentration in the cell. The heat developed is shown in Figure 4-13 and displays the same trend as the previous experiments. This indicates that Yagual asphaltenes do not have a CMC in that concentration region. The behavior of Ratawi asphaltenes may be different, but the ten asphaltenes studied in this project cover a wide range of origins and properties that allow the generalization of the conclusions drawn.

It has been pointed out already that the solvation of asphaltene molecules by toluene contributes to the total heat developed. In self-association studies, the dissociation of asphaltene aggregates implies a greater asphaltene-solvent interaction, as the solvent would occupy the sites previously involved in asphaltene-asphaltene bonds. It is not possible to quantify the solvation heat. Therefore, the enthalpies calculated in the section about modeling include a contribution from solvent-asphaltene interaction.

To sum up, solvent effects are observed and can be qualitatively correlated to the dipole moment. The greater the dipole moment, the less heat developed. This may indicate a lesser degree of self-association in polar solvents, due to a better solvent-asphaltene interaction.

4.5. Fluorescence spectroscopy measurements.

Synchronous fluorescence spectra of the asphaltenes were recorded. The active molecules that emit fluorescence (called *chromophores*) are the aromatic centers. The spectra were obtained at several concentrations in the range 0.01-0.5 g/l, with $\Delta\lambda = 20$ nm. Figure 4-14 shows the spectra of Yagual asphaltenes at very low concentrations (See the rest of spectra in Appendix K). The bands are mainly located in the region 400-500 nm, which indicates that the population of one-to three fused aromatic rings is small in asphaltenes (Ralston et al., 1996). This is in agreement with NMR studies that propose an average of 4-5 rings per aromatic sheet (Artok et al., 1999). The highest peak is located at around 470 nm. A five-ring compound like pervlene presents two peaks at 451 and 462 nm (Andersen, 1990). The substitution of functional groups such as alkyl branches, hydroxyl or amine groups directly on an aromatic ring would move the bands to longer wavelengths (red shift, as it moves the bands towards the red region of the spectrum) (Andersen, 1990). Hence, the distribution of asphaltenes would be centered on molecules with 4-6 rings per aromatic sheet. Groenzin and Mullins (2000) proposed 4-10 rings per aromatic sheet in the light of their fluorescence depolarization experiments. Strausz (1999) applied RICO to asphaltenes and concluded that 3-4 ring sheets are the most common in Boscan and Duri asphaltenes.



Figure 4-14. Fluorescence spectra of Yagual asphaltenes.

At higher concentrations (50-100 ppm), the emission does not increase proportionally as expected, but inner-filter effects start to appear (Figure 4-15). The

energy emitted by the chromophores is re-absorbed by the nearest neighbors, decreasing the energy that reaches the detector. This phenomenon, called *quenching*, may be assigned to the association of the chromophores. Groenzin and Mullins (1999) also reported the beginning of quenching in this concentration region. Dissolved oxygen is also an important quencher but the samples have been degassed with an ultrasound treatment. Another reported cause for quenching is the formation of excimers (Pesce, 1971). Excimers are instant aggregates that exist only in the excited state. Excimer formation gives structureless bands at wavelengths from 390 to 600 nm (Yokota et al. 1986), while the charts shown here still have well-defined peaks. Excimer formation is only observed at higher concentrations (0.5 g/l). It is reasonable then, to assume that if some quenching is observed, it is due to the self-association of asphaltenes. Besides, the bands experience a shift towards longer λ shift as the concentration increases. This effect is called *red shift*. This phenomenon was above attributed to branches, but it could also be due to the process of aggregation: the formation of a bond decreases the distance between energy levels, increasing the wavelength at which a molecule emits, if the functionality responsible of the bond is directly linked to an aromatic ring.



Figure 4-15. Fluorescence spectra of YAGUAL asphaltenes at high concentrations.

Figure 4-16a depicts the intensity at the maximum as a function of concentration. Initially, as the concentration increases, the amount of chromophores increases proportionally. Hence, the intensity emitted is linearly correlated to the concentration. However, it is observed that asphaltenes deviate from the linear behavior in the region 10-50 ppm, when the quenching effects start. As explained above, this may be related to aggregation of asphaltene molecules. ITC titrations also showed self-association at such low concentrations (See Figure 4-6). These two techniques agree on having self-association at concentrations lower than 1 g/l. The beginning of self-association would occur in the ppm range.



Figure 4-16. (a) Concentration dependence of maximum intensity. (b) Comparison of fluorescence spectra with saturated and dry toluene (Alaska 95, C = 0.025 g/l).

The influence of water has been investigated, as well. Saturated and dried toluene were used and several concentrations were tested. The variation of the spectra in the presence of water is negligible (Figure 4-16b). This is not what was expected, as water is known to associate with asphaltenes (Andersen et al., 2001). Association would lead to a *red* shift, as explained above. The presence of water-asphaltene bonds should shift the curve to longer wavelengths, as it happens with increasing asphaltene self-association.

This contradiction can be explained by a simple calculation: If the MW of asphaltenes is assumed to be 1000 g/mol, a solution containing 0.02 g/l of asphaltenes in dried toluene (0.044 g water/l) will have a ratio asphaltene/water equal to 0.0056, which means there are around 2 molecules of water per molecule of asphaltene when the toluene is supposed to be water-free. The presence of traces of water cannot be neglected in the study of the association of asphaltenes because, even in such minute amounts, the mole ratio with respect to asphaltenes is higher than unity.

4.6. Infrared spectroscopy measurements.

IR allows the determination of the main functional groups in chemical compounds. In the case of asphaltenes, the polydispersity in polarity and MW complicates the analysis. Numerous studies have been carried out to characterize asphaltenes by IR (Moschopedis and Speight, 1976, Chang and Fogler, 1994, Ralston et al., 1996, Buenrostro-Gonzalez et al., 2001, Ibrahim et al., 2003, among others). Figure 4-17 shows the spectrum of LM2 asphaltenes in CCl_4 . According to the general view about asphaltenes, the main bands correspond to the aromatic rings, the alkyl branches and the polar functionalities. It is observed that asphaltenes have the capacity of forming hydrogen bonds (region 3100 to 3600 cm⁻¹).



	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
LM2	0.40	0.061	1.82	0.029
A95	0.39	0.054	1.90	0.034
LM1	0.21	0.059	1.81	0.055
NM1	0.37	0.035	1.73	0.024
Yagual	0.37	0.038	1.95	0.005
Lagrave	0.31	0.024	1.87	0.028
Ca30	0.34	0.023	2.20	0.030

Figure 4-17. IR spectra of LM2 asphaltenes in CCl_4 . C = 5 g/l.

Table 4-4. IR indexes stable and instable (bold) asphaltenes.

IR indexes allow the determination of the relative abundance of the different functional groups in stable and instable asphaltenes. I (C=O) index is very similar in both cases, but it is observed that stable asphaltenes have a greater concentration of sulphoxide groups. Methyl and HB indexes are plotted in Figure 4-18. Stable asphaltenes have a greater capacity of forming hydrogen bonds. This may be related to their stability in crude oil in terms of enhanced resin-asphaltene interaction, as explained in the following chapters. Methyl index does not show a good correlation with stability. The length of alkyl chains has been claimed to be a key stability factor, as they create a steric hindrance for aggregation (Buenrostro-Gonzalez et al., 2001). Nevertheless, this index is not directly proportional to the length of alkyl chains, as bridges and naphtenic rings also carry CH_2 groups. Bridges make molecules more flexible and therefore more able to reach a suitable conformation for aggregation. The high value of this index in instable Ca30 may be related to this fact.



Figure 4-18. Methyl and HB indexes of stable and instable asphaltenes.

The behavior of asphaltenes in toluene may differ from the one in CCl₄. Spectra of LM1 and Alaska 95 asphaltenes in toluene were obtained in the region 3100-3500 cm⁻¹ to study their hydrogen bonding capacity. Toluene contaminates the aromatic peaks, and hinders greatly the discussion in other regions. Concentrations from 1 to 15 g/l were used

and the intensities in the H bond area are shown to increase proportionally with concentration of asphaltenes (Figure 4-19). The intensities obtained in this study are rather low, compared with other IR studies of asphaltenes in different solvents (Moschopedis and Speight, 1976) but the toluene used herein had been dried, limiting the influence of water in the formation of hydrogen bonds by asphaltenes.



Figure 4-19. (a) LM1 spectra at several concentrations. (b) Area below the spectra in the H bond region.

The increase with concentration of the area of the bands is linear for both fractions (Figure 4-19b). This shows that none of them presents a specific inflexion in this range of concentrations that can be assigned to a CMC, which means that the association of asphaltenes begins at much lower concentrations. If hydrogen bonding was the driving force for the formation of micelles, the intensity in this region would be zero until the CMC was reached and then it would increase. The absence of a zero region supports the previously discussed evidences by fluorescence spectroscopy and ITC.

4.7. Discussion of experimental results.

To sum up, the techniques presented here do not show any evidence that can be assigned to a Critical Micellar Concentration at which association begins. The heterogeneity of the system suggests that it would be too optimistic to assume that the self-association would occur in a narrow concentration range when the asphaltene fraction is composed of around 100,000 molecules with a wide range of polarity and MW. Besides, the concept of asphaltene micelles in toluene does not make much sense because they are very aromatic and the solvent is aromatic so there is no need to "protect" anything from the solvent. Surfactants arrange into micelles in water to isolate the nonpolar hydrophobic part of the molecules. Dipole moment calculations (Murgich, 2002) have shown that asphaltene model molecules do not have such a big difference in polarity as surfactants have between head and tail. Andersen (1994) also presented evidences by SEC that could not be explained by a micellization approach. The results presented in this work suggest that self-association begins at very low concentrations, in the range of ppm in toluene solutions. On the contrary, there are many evidences reported in the literature that show that there is a break in the values of many magnitudes when plotted versus concentration in the range 1-10 g/l. Techniques applied include interfacial tension (Storm and Sheu, 1995 and Rogel et al. 2000), onset flocculation points (Deo, 2002), to calorimetry (Andersen, 1991 and 2001, see Appendix H). Interfacial tension is a surface property that may not be necessarily related to bulk association. As Sheu (1995) pointed out, self-association may have begun before the break observed in the plot of surface tension versus the logarithm of the concentration. Besides, a large aggregation number is needed to observe a break in the charts of surface tension (Andersen, 2003). No sharp break is observed if the aggregation number is in the range 3-6, as expected for asphaltenes (Yarranton et al., 2000). It is important to consider that the break is only observed in aqueous solutions of very pure surfactants. Reported experiments show that the addition of 0.05% impurities to SDS in water change completely the usual shape of the surface tension vs. log C (Evans and Wennestrom, 1999). Asphaltenes are very complex fractions and some substances may act as surfactants but there are many others that do not. The percentage of impurities in asphaltenes, in terms of surface activity, is considerably higher than 0.05%. Even if there was a change in association state, it would not be possible to observe it by surface tension measurements. This has no connection with the aggregated state of asphaltenes in the bulk, as association probably occurs before the surface is saturated. It seems more probable that the reason why the surface tension reaches a constant value is that the surface gets saturated of asphaltene molecules. Aggregation seems to stop at a certain concentration. The aggregate size in toluene obtained by SANS is constant in the range 3 to 40 g/l (Roux et al., 2001). Deo (2002) observed that the amount of n-heptane needed to precipitate asphaltenes reached a constant value after a concentration around 3 g/l. This means that the aggregates are stable entities and keep the same structure even at these dilute concentrations in toluene. Asphaltenes do not start to form big clusters until high concentrations, as seen in i.e. viscosity data of asphaltic solutions (Briant and Hotier, 1983, Escobedo and Mansoori, 1994 and Mohamed et al., 1999). This formation of stable aggregates in dilute solutions cannot be considered a micellization. The key concept in micelle formation is that this special structure is developed in order to protect part of the molecule from the solvent (the hydrophobic tail in water and the polar groups in an organic solvent). The formation of aggregates is not influenced by the solvent, but the driving force has to be found in the aromatic and polar nature of the molecules. In a surfactant micelle, the aggregation number is kept in a narrow range, as the micelles are approximately all of the same size. Savvidis et al. (2001) showed by filtration with different pore sizes that asphaltene aggregates are very polydispersed. The limiting factor in aggregate growth may be the alkyl effect. Carbognani (2002) presented a model in which asphaltene molecules were surrounded by alkyl chains. This would explain that after a certain size is reached, it is not possible to expect more growth because of the sterical hindrance against interaction. Some of the sites may become unreachable due to the presence of alkyl branches. This is in agreement with photon correlation spectroscopy data that showed a change from diffusion- to reaction-limited aggregation at that range of concentrations (Yudin et al., 1998). This change in kinetics was as well used to explain the asympthotic behavior of MW in VPO measurements towards a constant value (Yarranton et al., 2003). Only when the concentration becomes very high, aggregate-aggregate interactions will begin. This would explain the changes observed in viscosity measurements when particle aggregation occurs.

4.8. Modeling self-association.

All the experimental evidences suggest that asphaltene aggregates have a stepwise growth. These results led to the development of a model in agreement with these evidences. This model would be fitted to the experimental data for the asphaltenes to obtain the enthalpy of self-association of asphaltenes (ΔH_a). The approach followed is based on the chemical equilibrium theory (Martin, 1996). It assumes that the molecular aggregates are in equilibrium among themselves and with the monomers, following the same type of reaction as in polymer growth and in the aggregation/stacking of aromatic molecules:

$$A_n + A_1 \leftrightarrow A_{n+1} \qquad \Rightarrow \qquad [A_{n+1}] = K_{n+1} [A_1] [A_n] \tag{1}$$

After subtraction of the friction losses, all the heat developed in the experiments is assigned to the formation of new species. After each injection, the concentration of the molecular aggregates changes and a new equilibrium has to be reached. The differences in concentration between the moment after the injection and the equilibrium allows the calculation of the number of association sites broken and the total heat developed in each injection, according to the equation:

Heat developed = Number of association sites broken (mol) $* (-\Delta H_a)$ (2)

The parameters of the models are optimized by means of a non linear least square fitting of Eq. 2. Four models have been used to fit the experimental data, all of them incorporating the step-wise growth mechanism. The first model is based on dimer formation. It only considers the formation of dimers (P₂), so the experimental data are fitted with one equilibrium constant (K) and the enthalpy of self-association (ΔH_a). The second model (EQUAL K or EK) allows the formation of compounds of higher aggregation number. To simplify the approach, it is assumed that the equilibrium constants and the enthalpies are the same for all the reactions (Martin, 1996):

$$K = K_2 = K_3 = \dots = K_{n+1}$$
(3)

$$\Delta H_a = \Delta H_{a2} = \Delta H_{a3} = \dots = \Delta H_{an+1}$$
(4)

The equilibrium concentration of the monomer is obtained by means of a mass balance analysis (See Appendix J for a more detailed description). The third model (ATTENUATED K or AK) (Martin, 1996) considers that the equilibrium constant
decreases as the number of components of the aggregates increases, as a result, i.e., of steric effects. The ratio between the values of the K is the following:

$$K = K_2/2 = K_3/3 = \dots K_i/i$$
 (5)

Again, ΔH_a is assumed to be the same for all reactions. Therefore, these three models are fitted with only two parameters: ΔH_a (kJ/mol) and K (l/mol). The last model (Terminator model) includes a third parameter: It is assumed there are two species in the asphaltenes, one with multiple interaction sites (*Propagators*, which can continue the growth of the aggregate) and the other one with only one interaction site (*Terminators*, which would stop the growth). The ratio between terminators and propagators (T/P)_o is used as a fitting parameter. This latter model assumes that the equilibrium constants of the termination reactions are also equal to the propagation constants. It was successfully applied in the modeling of molecular weight distributions of asphaltenes in toluene solutions obtained from VPO experiments (Agrawala et al., 2001).



Figure 4-20. Comparison of the fit of the models to LM1 asphaltenes (Cs = 30 g/l).

Figure 4-20 shows the fit of the four models applied to the titration of LM1 asphaltenes. The MW assumed in the calculations is 1000 g/mol for all samples. The four curves represent the same experiments, and they have been shifted to have a clearer view of the fits. All the models showed an excellent fit above 1 g/l for the LM1 asphaltene.

Nevertheless, only the dimer model showed an excellent fit over the entire rage of concentration studied, as seen in Figure 4-20.

Experiments with asphaltenes from nine different sources were fitted with equally satisfactory results. Table 4-5 displays the optimized parameters of two of the asphaltenes tested (see Appendix J for the parameters of the rest of asphaltenes).

		KU asphaltenes								
		C syring $e = 5 g/l$				C syringe = 30 g/l				
	ΔHa	K	(T/P)o	SS	ΔHa	K	(T/P)o	SS		
DIMER	-3.2	1006.3		0.19	-4.6	267.7		0.54		
EK	-1.9	416.0		0.58	-2.4	102.0		3.88		
AK	-2.4	810		0.56	-3.1	200		3.53		
TERM	-0.6	264.8	0.18	0.67	-0.7	59.7	0.16	5.08		
			L	M1 asph	altenes					
		C syring	ge = 5 g/l			C syring	e = 30 g/l			
	ΔHa	K	(T/P)o	SS	ΔHa	K	(T/P)o	SS		
DIMER	-5.5	482.9		0.19	-7.6	118.7		0.60		
EK	-4.1	196.3		0.37	-4.3	61.4		5.08		
AK	-3.4	930		0.35	-5.6	120		4.93		
TERM	-1.2	141.7	0.2	0.486	-1.5	33.6	0.19	6.02		

Table 4-5. Results of model fitting for the four asphaltenes at several syringe concentrations in dried toluene. Δ Ha is the heat of self-association in kJ/mol and K is the association constant in l/mol.

The goodness of fit, expressed as the sum of the square errors (SS), shows that the dimer model is usually the one with the best fit. The trend among the more complex models is such that the AK has the best fit, closely followed by the EK. The TERM model showed the poorest fit. The calculated values of Δ Ha are small, a bit smaller than the usual hydrogen bond magnitudes (-8 to -40 kJ/mol) (Prausnitz et al., 1999) and also smaller than the stacking of some pure aromatic compounds, such as pyrene (-15 kJ/mol) (Martin, 1996). It is not possible to determine which is the main driving force for association based on these experiments, as both mechanisms suggested (stacking and hydrogen bonding) present values of the same order of magnitude and would compete with each other (Murgich, 2002). Moreover, taking the heat of interaction between phenol molecules as a reference value (Δ H_{formation} = -16.6 KJ/mol), the heat developed in these

experiments is rather low, suggesting that a fraction of asphaltenes do not participate in these tests. This is to be expected considering the non-specific forces involved in the precipitation of asphaltenes by n-alkane solvents. SEC analysis of heptane-toluene fractions of asphaltenes also indicated that a substantial fraction could be inactive in self-association. They would precipitate after the addition of n-heptane because of the size difference, not because of aggregation issues (Andersen, 1994). The underestimation of the enthalpy of self-association may as well be related to all the processes involved in the association that are not taken into account explicitly, such as de-solvation of aggregates, solvation of monomers, tangling of branches and conformational changes.

The values of $(T/P)_0$ indicate that around 85% of asphaltene molecules are propagators. According to this model, they have more than one interaction site.

The values of the equilibrium constants found in this work are also low, in the order of 100. This means that the concentration of aggregates (n-mers) of n>5 is negligible.



Figure 4-21. Polydispersity predicted by the models in LM1 30 g/l titration.

Figure 4-21 shows the concentration profile predicted by the models at the syringe concentration of 30 g/l and also the profiles in the cell after the last injection. The concentration of trimers after the last injection ($C_{cell} = 5$ g/l) is much lower than that of monomers and dimers, which may explain why the dimer model works so well. The average aggregation number would be between 2 and 3 molecules at 30 g/l for our asphaltenes. Agrawala et al. (2001) suggests that the average aggregation number of

Athabasca asphaltenes would be between 4 and 10, based on the MW of the aggregates by VPO. This discrepancy suggests again that maybe not all molecules are active in these experiments, or that not all bonds are broken by dilution.

The values of ΔH_a (Figure 4-22) are very depending on the model used as well as the asphaltene concentration investigated; the variation is higher than 100% when passing from the DIMER to the EK model, for example. The values of ΔH_a are also extremely dependent on the average MW used in the fitting. The value of ΔH_a doubles when the average MW is changed from 800 to 1600 in the EK model, for instance, showing a linear dependence between enthalpy and MW.



Figure 4-22. AHa values obtained in optimization of polymerization models (LM1 asphaltenes).

This shows that these simple models cannot account for all the complexity of asphaltenes, as only one value of ΔH_a is as incomplete as trying to characterize asphaltenes with only an average MW. The choice of the range of molecular weights is also critical in the performance of the models and the final values of the enthalpy of self-association. It is known that in asphaltenes, the MW distribution is complex and multimodal and covers a wide range (Selucky et al., 1981 and Andersen, 1994). A polydisperse model would likely provide more consistent results. However, at the present stage of the investigations, the use of a polydispersed model with a distribution of MWs would imply extensive research to determine the relationship between mass fraction and

the MWs. This type of approach is left for a future work because there is no information available about the true MW distribution of asphaltenes.

Finally, a step-wise model of polydispersed asphaltenes, regardless of the conformity with the true nature of the material, would become very complex. For the time being, one may conclude that simplistic approaches may help in understanding phenomena observed for these very complex systems. The heats of dissociation measured by ITC contain contributions of the dissolution of aggregates containing all (or most of) the molecules that form the asphaltene fraction. Its measured value is actually a weighted average over the many different types of aggregates formed by the great variety of molecules of the asphaltene fraction.

Therefore, the heats of interaction displayed in Table 4-5 only provide an estimate of the order of magnitude and should be judiciously used. In any case, it is interesting to mention that the comparison with molecular simulations is quite satisfactory. The interaction between nitrogen atoms in asphaltene molecules with water was simulated and the ΔH_a obtained was -8.8 kJ/mol (Murgich et al., 2002).

The association constants obtained from these models decrease with asphaltene concentration, and increase with decreasing water content at fixed concentration (See Table J-3b in Appendix J). Both effects can be explained by the same mechanism: as the concentration of asphaltenes increases, the relative water content on a molecular level decreases, hence favoring the dissociation. When more water is present at fixed asphaltene concentration, we observe that the association constant increases as the water bridges keep asphaltene molecules together. No transition from one mechanism to another can be determined as the heat of dissociation is almost independent of concentration.

Again, we have to warn that the above results are more of a qualitative than quantitative nature because they are based on simple dissociation models. Concentration effects on the value of the equilibrium constants were expected, as the solutions have been considered as ideal, for the sake of simplicity. K should be based on activities, and activity coefficients (γ) should be included in the equations. The approach followed considers that the activity coefficients are equal to one, as the solutions are in the mM range of concentrations. This approach was as well applied by Yarranton et al. (2002).

The K presented in this work are considered as *apparent*, and include the activity coefficients, thus allowing a variation with concentration, as the activity coefficients are not the same as 5 and 30 g/l. Complex mixtures like asphaltenes are probably non-ideal even in the dilute regime, due to the great tendency to associate of the molecules involved. For instance, a dimerizing compound like propionic acid has a change in γ_i from 5 to 2 when the mole fraction is increased from 0.05 to 0.2 (Prausntiz, 1999). Carboxylic groups are known to exist in asphaltenes (Speight, 1999). Hence, variations in K are expected if the activity coefficients are included in it.

		Cs =	5 g/l			$\mathbf{Cs} = \mathbf{c}$	30 g/l	
	ΔHa	K	ΔSa	ΔGa	ΔHa	K	ΔSa	ΔGa
KU	-1.9	416.0	43.9	-15.2	-2.4	102.0	30.5	-11.7
Alaska 95	-4.0	284.0	33.8	-14.2	-4.3	69.0	21.0	-10.7
Yagual	-2.9	591.4	43.5	-16.1	-3.8	98.7	25.6	-11.6
Lagrave	-2.5	571.4	44.5	-16.0	-3.3	84.5	26.0	-11.2
LM2	-3.0	137.0	31.0	-12.4	-3.9	52.9	20.1	-10.0
Ca30	-1.8	662.9	48.1	-16.4	-2.8	73.0	26.4	-10.8
OMV	-3.9	349.9	35.8	-14.8	-3.2	66.0	24.3	-10.6
LM1	-4.1	196.3	30.4	-13.3	-4.3	61.4	20.0	-10.4

Table 4-6. Thermodynamic characterization of asphaltene self-association. ΔH and ΔG in kJ/mol, ΔS in J/molK and K in l/mol.

Table 4-6 gathers the calculated entropies and free energies of the selfassociation. ΔG has been calculated from the equilibrium constant K as:

$$\Delta G = -RT \ln K \tag{6}$$

 ΔG is related to the enthalpy through Eq. 7:

$$\Delta G = \Delta H - T \Delta S \tag{7}$$

It is observed that the contribution of ΔS to the total free energy is greater than that of ΔH . This indicates that the process is entropically driven. The conformation seems to play a significant role in the process of self-association. This may be connected to the influence of sterical hindrance in the limited size of asphaltene aggregates, as suggested in the previous section. To sum up, the modeling of the heat evolved during isothermal titration calorimetry shows that the step-wise growth mechanism is a good description for asphaltene self-association. The choice of the model, however, is critical in the final value of ΔH_a and the value used for the average MW is also very important. The heats of interaction obtained are low, suggesting that a part of the asphaltenes is not active in the titration experiments.

4.9. Asphaltene fractionation with a polar mixture.

The molecular complexity of the asphaltene fractions greatly hinders the investigation of their aggregation processes. A simple way of separating the different contributions to these processes is to fractionate asphaltenes and study the behavior of each of the separated parts. Toluene mixtures with n-heptane have been widely used to fractionate asphaltenes (Andersen, 1994 and Andersen et al., 1997). Also studies where the fractionation is carried out with polar solvents have been performed (Hillman and Barnett, 1937), particularly with acetone (Acevedo et al., 1997 and Buenrostro-Gonzalez et al., 2001) and CH₂Cl₂ (Nalwaya et al., 1999 and Wattana et al., 2003). Of these fractionation methods, the one using the mixtures of heptane and toluene gives the least chemical compositional variations within each of the resulting fractions (Andersen et al, 1997 and Buenrostro-Gonzalez et al., 2002). The fractionation into a predominantly polar fraction and a much less polar one allowed the study of the contribution of polarity to the molecular aggregation processes. It is therefore expected that the electrostatic forces will make a larger contribution in the more polar fraction. In particular, hydrogen bonding should be an important mechanism for the molecular aggregation in the more polar fraction of these asphaltenes. In both fractions, it is expected that the stacking of the aromatic regions of the asphaltene molecules will also contribute noticeably to the formation of the aggregates if the aromatic regions are large (Murgich, 2002).

In principle, the soluble fraction in acetone would contain most of the polar compounds of asphaltenes; acetone is polar and it is safe to assume that "like dissolves like". Takanohashi et al. (1998) showed that the fractionation of coal asphaltenes with acetone and pyridine gave the least aromatic fraction when acetone was used. Strausz et al. (2002) showed that the extraction of the acetone fraction from pentane-asphaltenes gives substances with lower molecular weight.

The liquid mixture was mixed with asphaltenes and treated with ultrasound for about 60 minutes. The samples were left overnight, and then centrifuged for 5 minutes at 3000 r.p.m. and then the insoluble (INS) and soluble (SOL) fractions were separated and the solvent was evaporated. It was observed that around 10% of the INS fraction of KU was not totally soluble in toluene. A fact that has been observed in previous experiments on asphaltene extraction (Andersen and Speight, 1992 and Acevedo et al., 1997). It is

expected that, after fractionation, some asphaltenes are not soluble in toluene, as we remove some of the molecules that may act as co-solvents. This particular insoluble fraction in toluene corresponds by definition to the carboid and carbene of the ultra heavy parts found in some crude oils (Speight, 1999). This solubility behavior was not observed in any of the two fractions of the LM1 asphaltenes, which were totally soluble in toluene.

A mixture 70:30 of toluene and acetone was used to fractionate KU asphaltenes. For LM1 asphaltenes, the ratio used was 60:40. Although affecting the distribution of species, the intention was to obtain an approximately 50-50 weight % fractionation, and hence the ratio of acetone was changed depending on the origin of the asphaltene. The fractionation of LM1 gave 40.7 weight% in the INS fraction. The elementary analysis did not show significant differences between the diverse fractions of LM1 in terms of heteroatom content and aromaticity (Table 4-7).

	N	С	Н	S	0	RATIO H/C
LM1 SOL	1.61	83.36	7.91	4.67	3.03	1.14
LM1 INS	1.79	83.06	7.57	4.57	2.99	1.12

Table 4-7. Elemental analysis of LM1 fractions.

Then, this rough estimate of the global (macroscopic) composition did not explain the solvent selectivity and fractionation. Besides, metal content was not analyzed. Recent studies have shown that metals such as iron are usually found in the most polar fractions (Nalwaya et al., 1999).

The heat developed in the titration of SOL and INS fractions is endothermic (Figure 4-23a). That means, in principle, that SOL (the most polar fraction) has a greater number of bonds broken per mass than INS fraction. The titration curves obtained are compared with the one of the original LM1 asphaltenes, which lies between the two fractions, as expected. A fourth experiment was carried out, in which SOL and INS were mixed in the same proportion as in the original asphaltenes. The titration curve of that experiment using a recombined asphaltene (INS + SOL in weighted proportion) lies on top of the curve of the original LM1 asphaltenes. This shows that the fractionation procedure does not modify the asphaltenes in the time scale used in the experiment, and that the differences observed in the calorimetric experiments are due to the difference in

the nature of the fractions, not to modifications due to its dissolution in acetone or any oxidation process that may have taken place during the preparation of the sample.



Figure 4-23. (a) Raw data of the titration of LM1 fractions (C syringe = 30 g/l) in dried toluene. (b) Integrated heat developed in LM1 titrations.



Figure 24. (a) Integrated heat (C syringe = 30 g/l) in dried toluene. (b) Heat developed in KU titrations (C syringe = 30 g/l) in 3:1 sat/dried toluene.

The titrations of KU asphaltenes showed the same behavior (Figure 4-24). SOL develops more heat than INS; it is also observed that the heat developed in the tests with INS fraction has a bump that diverts the signal from the usual exponential shape. This is assigned to the heat of solubilization of some of the insoluble particles during the test. With respect to the water content, 31SD solutions have consistently less heat developed than dried solutions. This implies there is another process, exothermic, that shifts the curves to lower heats. This process may be the interaction of water with asphaltenes, confirming previous studies that show that water may play an important role in the self-association of asphaltenes (Andersen et al. 2001).

So far, the results indicate that the fraction soluble is the one responsible for most of the heat developed. This proves the importance of the polar nature of asphaltenes in their self-association in toluene. In another type of experiments, dried toluene was injected into a 10g/l solution of asphaltenes (Figure 4-25). This concentration was much higher than those used in the other experiments, in which the maximum concentration in the cell was around 5 g/l. The titration gave endothermic peaks for the SOL fraction, as expected. This means that the dilution effect of toluene breaks some asphaltene molecular aggregates. This is also the behavior observed with the original asphaltene sample. On the other hand, the toluene dilution titration of the INS fraction only gave exothermic heats associated to the friction during the injection process, which suggests that the dilution effect cannot break the molecular aggregates of this fraction at high concentrations.



t (sec) Figure 4-25. Injection of dried toluene into 10 g/l of KU fractions.

It should be emphasized that the two types of experiments asphaltene-in-toluene and toluene-in-asphaltene represents two very different scenarios of high dilution and very weak dilution, respectively. Hence one may note that SOL is much more prone to dissociation than INS fractions, as shown in Figure 4-25, where the concentration is changed from about 10 to 8 g/L.

The question that arises now is why the insoluble fraction showed no heat changes upon dilution. Three possibilities may be considered to explain this result. First, that the INS fraction has a much lower degree of association than the SOL fraction. Polar fractions of asphaltenes have been reported to have a greater tendency to precipitate (Leon et al., 2001). The INS fraction could be formed by large non-associating molecules which due to size could become insoluble. Then, there would be less intermolecular binding so when the INS solution is injected, much less heat is evolved. However, it was observed that around 10% of this fraction was not soluble in toluene. Due to the belief that there is continuity not only in the composition but also in the degree of aggregation of the asphaltenes, it suggests that these asphaltenes could be strongly associated. This, however, remains speculative at the moment. The second hypothesis is that the INS fraction forms stronger molecular aggregates that are not broken in the titration. It has been reported that the polar fractions are better dissolved in toluene than the insoluble after fractionation with CH₂Cl₂ (Kaminski et al., 2000). Therefore, no heat from the dissolution of the aggregates will be produced. The third hypothesis considers that the aggregates formed in the INS fraction are much weaker than in the SOL fraction. Therefore, the heat evolved is much lower upon dissolution. If the amount of heat evolved in this case is sufficiently small, it may escape detection. These hypotheses are based on a model where the dissolution of the aggregates of asphaltenes is instantaneous.

It should also be noted that the fact that SOL develops more heat than INS may be related to the capacity of the molecules to adapt to the surroundings. SOL fraction may be more easily adapted in terms of changing their conformation and therefore develop more heat in the dissolution and solvation process. INS may remain more aggregated due to its lower capacity to be solvated by toluene.

In order to find some evidences that will help us to understand the complex dissolution processes observed, a spectroscopic study was performed on the same asphaltene fractions employed in the calorimetric measurements.

The hydrogen bonding capacity of LM1 fractions was studied in the concentration range from 1 to 10 g/l by IR spectroscopy. The formation of hydrogen bonds gives bands in the region 3100-3500 cm-1 of the IR spectra, which grow with increasing concentration of asphaltenes and degree of H-bonding (Figure 4-26a). The increase with concentration of the area of the bands is linear for both fractions (Figure 4-26b). No significant differences were found between the two fractions. IR did not give substantial differences in the spectra of CH_2Cl_2 fractionated asphaltenes, either (Nalwaya et al., 1999). This implies two things: first, the linear increase for both fractions shows that

none of them presents a specific inflexion in this range of concentrations that can be assigned to a CMC, which means that the association of asphaltenes begins at much lower concentrations.



Figure 4-26. (a) IR bands of LM1 SOL fraction in dried toluene in the H bonding region. (b) Integrated area of hydrogen bond bands of LM1 fractions.

Second, the INS fraction has the same degree of association in terms of H bonding as the SOL fraction. It is assumed that H bonding is a significant factor in the selfassociation of asphaltenes (Moschopedis and Speight, 1978 and Murgich, 2002) although one may not preclude other interactions such as π - π . This rules out one of the hypothesis proposed, as the INS seems to have a comparable degree of self-association through H bonding as the SOL fraction. Therefore, the differences in heat evolved upon dissolution are not due to a different degree of H bonding in the fractions. Hence, other factors influencing the formation of aggregates of asphaltenes, such as aromaticity, should be considered.

The synchronous fluorescence spectra were obtained at several concentrations in the range 0.025-0.2 g/l. Figure 4-28 shows the spectra of the whole, SOL and INS fractions of LM1 asphaltenes. The band of the whole asphaltenes lies between those for the SOL and INS fractions. The SOL fraction is the one with the highest intensity. It was first assumed that the INS fraction would be predominantly aromatic. However, the acetone-toluene fractionation could include both polar and aromatic molecules in the SOL fraction. No evidence was found from H/C of LM1 fractions suggesting any predominance of aromaticity (Table 4-7). However the H/C magnitude covers an average of many different molecules which on average leads to the similarity. Considering a similar aromaticity of the two fractions, this suggests that the band of INS fraction is quenched, either because the molecules have large aromatic rings that re-absorb the emitted energy, or because the energy is absorbed by the aggregates formed.



Figure 4-28. Fluorescence bands of LM1 fractions.

This is in agreement with SEC experiments, which showed that the acetoneinsoluble fractions of Maya asphaltene had higher apparent MW (or hydrodynamic volume) than the SOL fractions (Buenrostro-Gonzalez et al, 2002). The energy emitted by these large molecules may be re-absorbed before reaching the detector.



Figure 4-29. Normalized intensities at 469 nm in fluorescence spectra. (a) LM1 fractions. (b) KU fractions.

Figure 4-29 shows the variation with concentration of the intensities at the maximum (469 nm). The amount of chromophores increases with concentration, but the

fluorescence intensity does not increase linearly with concentration for any of the asphaltene fractions. In fact, it decreases for all the fractions but the INS of KU. This quenching phenomenon may be assigned to the association of the chromophores. Dissolved oxygen is also an important quencher but the samples have been degassed by an ultrasonic irradiation of 50-minutes. Besides, the bands showed a red shift as the concentrations increases, which could also be due to the formation of the molecular aggregates of asphaltenes (Figure 4-30). This also supports the hypothesis of having extensive molecular association in INS fraction.



Figure 4-30. Normalized intensities of KU INS at 469 nm at different concentrations.

4.10. Conclusions.

- + The comparison between the ITC enthalpograms of asphaltene and model molecules shows that the step-wise mechanism is a better approach than micellization for asphaltene self-association in toluene. Other techniques, such as Fluorescence and IR spectroscopy also give evidences of association at low concentrations (in the ppm region), which are in disagreement with the existence of a CMC in the 1-5 g/l region.
- + The aggregates may end up having a definite size, but the many different compounds present in asphaltene fraction would finish this aggregation at different concentrations, giving an enthalpogram with only one region (aggregation). The final size is probably not due to a solvent-phobic effect but to the presence of alkyl chains surrounding the aromatic cores.
- + The influence of temperature in the degree of self-association has been found to be negligible in the range 30-50 °C. This was unexpected, and a satisfying explanation has not been found yet.
- + It has been observed that the heat developed depends on the solvent used. Solvents with a dipole moment different from zero showed a reduction in heat developed, due to a better solvent-asphaltene interaction that leads to a decrease in the degree of self-association.
- + Water may play a role in the association, but it is not the only driving force. A small difference in self-association was found between dried and saturated samples. It was found that water is tightly bound to asphaltenes in solid state, limiting the capacity of obtaining ultra-pure toluene.
- + The application of polymerization models that are in agreement with the step-wise approach was successfully carried out. The heats of interaction obtained are low, suggesting that a part of the asphaltenes is not active in the titration experiments, or that there are other processes that develop heat and are not directly taken into account. The choice of the model, however, is critical in the final value of ΔH_a . The value used for the average MW is also very important.
- + These simple models cannot account for the complexity of asphaltene fraction. This leads to significant variations in some of the parameters such as the equilibrium

constants when the syringe concentration is changed. Nevertheless, state of the art models for asphaltenes are usually based as well on a monodispersed approach. The goal is to provide data to these models; hence, the data provided in this work are of utility.

- + Asphaltenes have been separated by acetone-toluene fractionation giving fractions of highly different behavior in solution, which have been analyzed regarding association propensity using ITC. The experimental work shows that the soluble fraction develops more dissociation heat when the samples are injected into pure toluene. The experiments left open the question about the reason why this fact was observed; several hypothesis were considered, and fluorescence spectra of the fractions confirms that INS fraction also associates, and that the aggregates of INS may be stronger than or different from those of SOL fraction.
- + The picture that comes out of these experiments is an aggregate of asphaltenes formed by the combination of polar and a non-polar (probably stacking) interactions: The strengths of the molecular interactions cover a wide spectrum, from the weak (broken in the calorimetric titrations) to the very strong (present in INS fraction), which are not broken by dilution. The aggregation process would begin at very low concentrations and the size of the aggregates is limited by steric hindrance.

5. Chemical Alteration of Asphaltenes

Chemical derivatization of asphaltenes has been carried out to study the influence of polar functionalities in self-association and the effect of addition of alkyl branches. The points discussed are:

5.1. Introduction5.2. Methylation.5.3. Silylation.5.4. Reduction.5.5. Reductive alkylation.5.6. Conclusions.

5.1. Introduction.

Understanding the molecular structure and concentrations of different oxygen, nitrogen and sulfur species is especially important in asphaltenes, as these have been implicated in oxidation, degradation and molecular associations (Speight and Moschopedis, 1981, and Snape, 1989). They affect properties of asphaltenes by participating in intermolecular associations through hydrogen bonding and formation of secondary structures (Leon et al., 1999, Murgich et al., 1999, Fotland et al., 1996 Acevedo et al., 1985 and Xu et al., 1995). Consequently such intermolecular associations may increase average molecular mass and tendency to flocculate. It is foreseen that modification of the chemical structure of these polar functionalities will have some impact on molecular interaction. Four different reaction chemistries have been used (Figure 5-1). Two of them alter the material without changing the bulk of hydrocarbon structure (Methylation and Trimethylsilylation) while the other two are more drastic and involve chemical degradation of the core structure as well (Reduction and Reductive Alkylation).



Figure 5-1. Schematic representation of the reactions carried out.

Methylation (MET) affects polar functionalities (-OH, -COOH, -NH and -SH) and substitutes the acidic hydrogen by a methyl group. This addition would decrease the acidity of asphaltenes and, therefore, the capacity of hydrogen bonding is expected to be diminished.

Silylation (SY) has the same effect but only affects oxygen functionalities. NH and SH groups have been reported to remain unreacted. By combining SY and MET, it is possible to determine the relative importance of oxygen groups in hydrogen bonding.

Reduction (RH) increases the acidity of asphaltenes. It causes fragmentation of core structure due to cleavage of bridging C-O and C-S bonds, followed by hydrogenation of aromatic rings and appearance of hydroxy (-OH) and thiol (-SH) groups. Removal of material is expected, as some of the newly formed molecules may be significantly volatile, hence lost during the process.

Reductive alkylation (RA) also leads to the cleavage of C-O and C-S linkages and it is accompanied by alkylation, leading to formation of ethers (-OR) and thioethers (-SR). The alkyl chain used in this study is butyl (C₄). The intention was to study the effect in asphaltene self-association of the addition of alkyl chains.

The alteration of asphaltenes was not part of this project; additional information about the reactions is provided in Appendix I. The aim of this work was to characterize and study the altered samples by several techniques: Elemental analysis and IR spectroscopy have been applied to characterize the resulting asphaltenes. These altered asphaltenes have subsequently been evaluated in terms of enthalpy changes by Isothermal Titration Calorimetry, which gives an idea about the self-association capacity. MET and SY samples are expected to show less heat developed, as the hydrogen bonding capacity has been reduced. RH asphaltenes are expected to show an increase in self-association, due to the fact that the acidity of the fraction is increased. R-A asphaltenes should present a reduction in self-association due to steric hindrance. Fluorescence spectra have as well been obtained to further understand the ITC results. Five asphaltenes from different sources have been used in this study: LM2 (Venezuela), Alaska95, Ca30, Lagrave (France) and Yagual (Venezuela). The last three oils have been reported to present significant asphaltene precipitation. The ITC cell initially contains dried toluene and a dilute asphaltene solution (10 g/l) is added into it in steps of 10 µl.

5.2. Methylation

Elemental analysis is only available for LM2 asphaltenes (DBLab, Odense, DK). It is assumed that the rest of crude oils follow the same trends. Methylation only affects acidic hydrogen and substitutes them by a methyl group. An increase in the weight percent of H and C is observed, as expected, as well as a decrease in weight percent of O, N and S (Table 5-1). The aromaticity decreases after methylation, due to the addition of new alkyl branches, as expressed by the ratio H/C.

	RATIO H/C	RATIO N/C	RATIO O/C	RATIO S/C	wt% C
LM2 RAW	1.15	0.017	0.029	0.017	84.30
LM2 MET	1.23	0.014	0.025	0.017	84.00

Table 5-1. Elemental analysis of raw and methylated LM2 asphaltenes.

IR indexes of altered asphaltenes were calculated and the percent variation with respect to raw asphaltenes is shown in Table 5-2 (see description of indexes in Chapter 2). It is observed that Alaska95 and LM2 are the asphaltenes that present a greater reduction in hydrogen bonding capacity. They were also the ones with the largest peaks in this region for the raw asphaltenes, which means that Ca30 and Yagual show less reduction because hydrogen bonding (HB) was not so relevant in the original asphaltenes.

	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
Alaska 95	-30%	172%	0%	-74%
Yagual	8%	7%	-12%	-9%
Ca30	-2%	56%	-15%	-43%
LM2	-15%	27%	0%	-75%
Lagrave	11%	23%	2%	-62%

Table 5-2. Variation of IR indexes of methylated with respect to raw asphaltenes.

Figure 5-2 shows the hydrogen bonding region of LM2 altered asphaltenes. The decrease in HB index is followed by a decrease in size of the H bonding bands. The ratio CH_2/CH_3 tends to decrease due to the addition of CH_3 groups. Alaska and LM2 do not show this effect. This may be attributed to the reagent that may not have been removed from the sample. It contains butyl groups that would increase the amount of CH_2 in the

samples. The polar indexes S=O and C=O are difficult to analyze due to the several contributions that appear in those regions. Sulphoxide Index increases probably due to oxidation and Carbonyl Index tends to decrease but shows a large variation in behavior from one asphaltene to another.



Figure 5-2. LM2 asphaltenes (Raw, Silylated and methylated) in the IR region of hydrogen bonding.



Figure 5-3. (a) ITC titration of LM2 raw and MET asphaltenes. (b) Ca30 asphaltenes.

ITC experiments show that the methylation of asphaltenes leads to a significant decrease in the heat developed. The blockage of potential hydrogen bonding sites decreases very significantly the capacity of self-association of asphaltenes. This decrease is more significant in the asphaltenes that presented a larger decrease in the hydrogen bond capacity, such as LM2, as expected after the IR experiments (Figure 5-3a). The reduction in Ca30 asphaltenes is significantly smaller (Figure 5-3b) because the reduction in HB observed by IR was also smaller. In order to quantify this reduction, the difference in heat developed between raw and methylated samples was calculated and expressed in average percent reduction (Table 5-3).

	LM2	Yagual	Ca30	A95	Lagrave
Methylation	-62%	-27%	-27%	-52%	-26%

Table 5-3. Variation in self-association of methylated with respect to raw asphaltenes from ITC.

Fluorescence spectrum of methylated Alaska95 shows an increase in intensity at shorter wavelengths with respect to raw asphaltenes (Figure 5-4a). The same behavior is observed in LM2, but not in Ca30 and Yagual (Figure 5-4b), whose spectra are significantly the same. Emission at shorter λ would in principle imply the presence of smaller aromatic rings (Ralston et al., 1996), but the reaction does not alter the core of asphaltene molecules. If some molecules emit at short wavelengths in the methylated samples is because they did as well in the raw asphaltenes. These small molecules that emit at short λ would be bonded through hydrogen bonding in raw asphaltenes, as association is believed to move the bands to longer wavelengths (red shift, Pesce, 1971). Yagual showed a very small decrease in hydrogen bonding tendency, therefore, this effect is not observed in the fluorescence bands.



Figure 5-4. Fluorescence spectra of MET and Raw asphaltenes. (a) Alaska 95. (b) Yagual.

To sum up, hydrogen bonding is a significant contribution to the self-association of asphaltenes and the blocking of acidic sites by methylation decreases significantly the heat developed in ITC experiments. This contribution is more important in the *stable* asphaltenes, such as LM2 and Alaska95 than in two of the *unstable* asphaltenes tested (Yagual and Ca30). Hydrogen bonding was also more prominent in the RAW asphaltenes of *stable* crudes, as expected. Lagrave shows a significant reduction in HB index that was not followed by a reduction in self-association by ITC. The explanation is found in the fact that the contribution of HB in the RAW samples was insignificant, as the band of HB was very small. This suggests that polar functional groups may be related to the stability of asphaltenes in crude oil, possibly due to enhanced resin-asphaltene interactions.

5.3. Silylation

This reaction attacks only the acidic oxygen, while sulphur and nitrogen functional groups remain unaltered (See Appendix I). The reaction substitutes hydrogen atoms by a trimethylsilyl group. Elemental analysis shows the expected decrease inaromaticity after silylation (Table 5-4). The sum is less than 100% due to the presence of silicium that is not analyzed. Sulphur content increases quite unexpectedly, probably due to the error in the analysis of RAW asphaltenes. It is a common problem in these analyses to get a sum greater than 100%.

	RATIO H/C	RATIO N/C	RATIO O/C	RATIO S/C	wt% C
LM2 RAW	1.15	0.017	0.029	0.017	84.30
LM2 SY	1.18	0.016	0.016	0.019	82.44

	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
Alaska 95	-22%	0%	-5%	69%
Yagual	5%	38%	-7%	149%
Ca30	-19%	61%	-19%	354%
LM2	-22%	7%	-5%	-10%
Lagrave	-21%	11%	-2%	55%

Table 5-4. Elemental analysis of raw and silylated LM2 asphaltenes.

Table 5-5. Decrease in IR indexes of silylated with respect to raw asphaltenes.

IR data (Table 5-5 and Figure 5-2) shows the expected decrease in hydrogen bonding in LM2 asphaltenes. Nevertheless, the rest of fractions show an increase in the hydrogen bonding capacity. This cannot be due to the asphaltene molecules, as the reaction is supposed to block hydrogen bond sites. The explanation can be found in the nature of the reagent, which is a secondary amine that boils at 127 °C. In spite of all the precautions taken, it is possible that some of the reagent can invariably remain entrained or adsorbed on to the asphaltene. Figure 5-5 shows that SY samples have broader bands in the region 3200-3100 cm⁻¹, usually assigned to -NH groups. The ratio CH_2/CH_3 decreases after the addition of numerous methyl groups in all asphaltenes, as expected. It was speculated that this index would help in the determination of the yield of reaction, as

there are three methyl groups added. If that was the case, the yields would be low. Besides, it has not been possible to correlate the variation of this index with the results of ITC experiments. Again, sulphoxide and carbonyl indices give quite confusing results, due to the abundance of peaks in those regions, and the probability of having traces of reagents in the sample. LM2 asphaltenes are the only ones with a reduction in hydrogen bond capacity. Therefore, a reduction in heat developed in ITC titrations is expected.



Figure 5-5. Hydrogen bond IR region of Yagual SY and RAW asphaltenes.

As shown in Figure 5-6a, silulation reduces the capacity of self-association of LM2 asphaltenes.



Figure 5-6. (a) ITC titration of LM2 raw and SY asphaltenes. (b) Ca30 asphaltenes.

	LM2	Yagual	Ca30	A95	Lagrave
Silylation	-19%	-4%	+1%	+35%	+5%

Table 5-6. Decrease in self-association of silylated with respect to raw asphaltenes.

According to IR indexes, the rest of crudes should show an increase in selfassociation with respect to the original asphaltenes. However, the IR magnitude of H bonding of Ca30 and Yagual is much lower than that of Alaska95. Therefore, the increase is greater for Alaska95 asphaltenes (Table 5-6). In any case, the change in molecular weight in silylated samples must be taken into account. The addition of a trimethylsilyl group increases the MW by 73 units. Therefore, if the test is performed at the same mass concentration (10 g/l), the number of molecules in the silylated sample is lower. Thus, even if the heat developed by Ca30 and Yagual asphaltenes is not varied significantly, the heat "per mol" is greater in SY samples. The expectations are then fulfilled, as these SY samples were shown to have more H bonding by IR than the original asphaltenes, due to the probable presence of reagent.

Fluorescence spectroscopy confirms ITC experiments. LM2 is the only asphaltene that presents a decrease in hydrogen bonding capacity, which is related to the shift of the band to shorter λ (blue shift). Some molecules that were active in hydrogen bonds have now been blocked for association and emit energy at shorter λ (Figure 5-7). Asphaltenes with increased HB capacity like Yagual do not show a significant change in the spectra.



Figure 5-7. Synchronous fluorescence spectroscopy of LM2 and Yagual raw and silylated asphaltenes. Spectra normalized by the intensity the maximum at 470 nm.

In LM2, the contribution of acidic oxygen to self-association is important and the reaction succeeds in blocking its capacity to form hydrogen bonds. Alaska95 should show the same behavior than LM2; its tendency to form hydrogen bonds is high, as seen by IR. However, the sample is probably contaminated by the amino groups of the reagent, so the expected decrease in self-association is not observed. Yagual, Lagrave and Ca30 had originally a small capacity of hydrogen bonding, and the variation in heat developed in ITC experiments is very small. The general conclusion is that –NH and –SH groups are more active in these asphaltenes, since the samples respond to methylation but not to silylation.

5.4. Reduction.

Reduction leads to an increase in the acidic content of asphaltenes. Ethers (-O-) and thioethers (-S-) are transformed into alcohols (-OH) and thiols (-SH), respectively. It was observed, mainly in LM2 and Ca30, that the solubility in toluene was considerably reduced after the reaction. The creation of acidic groups leads to a greater capability of H bonding that causes the aggregation of asphaltenes above the flocculation point. Appendix I has a more complete description of the alteration procedure.

The reaction adds hydrogen atoms to the asphaltene core, but the elemental analysis shows that, opposite to what was expected, the amount of H decreases and the aromaticity ratio increases (Table 5-7). The oxygen content increases very significantly in both asphaltenes. Reduced samples seem to be more prone to be oxidized than the original asphaltenes. Elemental analysis does not give any information about the yield of the reaction, and the errors in the total sum are quite big (2% in Ca RAW) so this analysis should be interpreted with caution, as the variations observed are very small compared to the errors.

	RATIO H/C	RATIO N/C	RATIO O/C	RATIO S/C	wt% C
LM2 RAW	1.15	0.017	0.029	0.017	84.30
LM2 R-H	1.11	0.016	0.032	0.018	83.95
Ca30 RAW	1.13	0.010	0.016	0.035	84.25
Ca30 R-H	1.16	0.010	0.026	0.035	81.20

Table 5-7. Elemental analysis of raw and reduced LM2 and Ca30 asphaltenes.

The cleavage of ethers and thioethers that connect the aromatic centers leads to the formation of smaller organic molecules that may be volatile. Desulphurization was found to be more important in Yagual and Ca30. During the processing, the particular smell of sulphur groups was identified. Sulphur content has not decreased significantly because the volatile compounds also contain the other heteroatoms.

	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
Alaska 95	26%	142%	3%	0%
Yagual	23%	7%	-6%	138%
Ca30	41%	76%	10%	-25%
Lagrave	21%	54%	0%	55%

Table 5-8. Variation of IR indexes of reduced with respect to raw asphaltenes.

Table 5-8 gathers the variation of IR indexes. HB index should increase, due to the protonation of asphaltene molecules, but this effect is only observed in Yagual and Lagrave. Alaska 95 did not show a variation, while Ca30 shows a decrease in this index. LM2 asphaltenes were difficult to analyze by IR because of the low solubility of the fraction in CS_2 and toluene. All asphaltenes have an increase in the Sulphoxide and Carbonyl indexes. It seems probable that after the reduction, some of the newly created hydroxyl and thiol groups are further oxidized by the oxygen in the air, as the samples are not stored in vacuum.

With respect to ITC experiments, the altered asphaltenes that were only partially soluble in toluene were expected to show a decrease in self-association. Those molecules that precipitated were the ones most prone to association. Yagual shows an increase in HB index, but desulphurization was very significant and this removal of volatile compounds may decrease the self-association capacity. It is important to remember as well that the molecules have been fragmented and it is assumed that the MW has decreased. 10 g/l of Reduced asphaltenes contain more molecules than 10 g/l of RAW. This means that the capacity of self-association per mol of reduced samples is overestimated if the two fractions are compared in gram basis. No information about the MW of the altered asphaltenes is available at the moment.



Figure 5-8. Difference in heat developed between Raw and Reduced asphaltene samples in ITC experiments.

	Lm2	Yagual	Ca30	A95	Lagrave
Reduction	-34%	-29%	-43%	+9%	-20%

Table 5-9. Decrease in self-association of reduced with respect to raw asphaltenes.

LM2 shows a significant decrease in the self-association capacity (Table 5-9). The creation of new acidic groups made a fraction precipitate and the removal of this material is responsible for the reduction in heat developed. The self-association capacity of Yagual is also reduced (Figure 5-8). The hydrogen bond capacity was increased, according to IR data, but the desulphurization seems to compensate that increase. The reduction in self-association is probably not related to hydrogen bonding but to other structural changes and mechanisms active in the volatile material eliminated, together with the low solubility effects. Ca30 asphaltenes show the same trend. The reduction in heat developed is assigned to the removal of volatile material. The solubility of this altered asphaltene was also low, as in the case of LM2. This is also a possible cause of the reduction in heat developed. Alaska95 shows a small increase in the self-association capacity. However, due to the change in molecular weight, the capacity expressed per mol is decreased, as in the rest of asphaltenes. The change in hydrogen bond index is small in this asphaltene, so

the change in self-association was expected to be small. To explain this fact, it is suggested that the amount of ether groups in this particular asphaltene is small.

Fluorescence spectra of LM2, Alaska 95 and Ca30 show a large increase in emission at short wavelengths. The aromatic sheets are not affected by the reaction, but the emission centers are probable less surrounded by other groups after the cleavage of bridges, resulting in less re-absorption of energy (quenching). Yagual does not follow this trend (Figure 5-9), probably due to the increased hydrogen bonding capacity. Hydrogen bonding compensates the blue shift, as explained previously.



Figure 5-9. Synchronous fluorescence spectroscopy of Ca30 and Yagual raw and reduced asphaltenes. Spectra normalized by the intensity the maximum at 470 nm

To sum up, reduction increases the capacity of self-association of asphaltenes by the creation of new acidic groups. Fluorescence spectroscopy indicates that the cleavage of bridges results in the appearance of new bands at shorter wavelengths, which are related to molecules that were previously quenched. ITC experiments showed an unexpected and generalized decrease in the heat developed, due to the side reactions after reduction. In the case of LM2 and Ca30, reduction leads to the insolubility of a fraction of the altered asphaltenes, due to its great tendency to self-associate. Removal of organic volatile material was observed, which seems to compensate the increase in hydrogen bonding capacity. Oxidation seems to be also important, as the hydroxyl groups are easily transformed into carbonyl or carboxyl, reducing the tendency to self-associate.

5.5. Reductive alkylation

This reaction takes a step forward with respect to the reduction explained in the previous section. The cleavage of C-O and C-S linkages is followed by alkylation resulting in the formation of ethers (O-R) and tioethers (S-R). The chain R added is a butyl group. This reaction also affects the acidic oxygen and sulphur of the original asphaltenes (See Figure 5-1 and Appendix I). Two effects are expected: first, the capacity of forming hydrogen bonds is reduced, and second, the butyl chains provoke a steric impediment to self-association.

	RATIO H/C	RATIO N/C	RATIO O/C	RATIO S/C	wt% C
LM2 RAW	1.15	0.017	0.029	0.017	84.30
LM2 R-A	1.20	0.015	0.030	0.017	84.24

Table 5-10. Elemental analysis of raw and alkylated LM2 asphaltenes.

Oxidation is supposed to be enhanced upon reductive alkylation but the elemental analysis shows that the oxygen content does not increase significantly (Table 5-10). The variation in weight percent of all atoms is very small, and whithin the error. The aromaticity of asphaltenes is decreased after the alkylation, and that is shown in the increase in the ratio H/C.

	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
Alaska 95	12%	139%	0%	-53%
Yagual	10%	-12%	-10%	7%
Ca30	-15%	43%	-14%	-42%
LM2	-39%	7%	-8%	-64%
Lagrave	2%	30%	2%	-11%

Table 5-11. Decrease in IR indexes of alkylated with respect to raw asphaltenes.

As expected, IR data shows that hydrogen bonding is reduced in most cases (Table 5-11). Only Yagual shows the opposite trend. The CH_2/CH_3 Index decreases unexpectedly. This would imply that the average length of the chains is decreased, when alkylation increases it.



Figure 5-10. Raw data of ITC experiments with Ca30 Asphaltenes. Csyringe = 10 g/l in both cases.

It is expected that asphaltene self-association is significantly reduced by butylation. This would in turn lead to a reduction in the heat developed in ITC experiments. The first effect observed was that the peaks of the titrations had a different shape. The peaks became broader than those of the original raw asphaltenes (Figure 5-10). This is assigned to the steric effect created by the butyl chains, that difficult both association and dissociation. The tangling of asphaltene molecules is more probable and it leads to a slower dissociation. LM2 asphaltenes show the expected decrease in associating capacity (Figure 5-11a). The effect is smaller than in methylation (Table 5-12), which leads to the conclusion that the butylation may affect predominantly to the ether groups. Hydroxyl groups are more affected by methylation than by reductive alkylation. Yagual and Alaska also show a slight decrease, but the variation is smaller than what was expected after the reduction in hydrogen bonding observed by IR. Moreover, altered Ca30 develops slightly higher heat than raw asphaltenes (Figure 5-11b). The tangling of alkyl branches may create a new associating force. This is a van der Waals type of interaction that is weaker than hydrogen bonding, but if there are enough branches it may be a contribution to take into account and that would counteract the expected decrease in associating capacity.



Figure 5-11. (a) ITC titration of LM2 raw and R-A asphaltenes. (b) Ca30 asphaltenes

	Lm2	Yagual	Ca30	A95	Lagrave
Red. Alkylation	-25%	-7%	+4%	-2%	-1%

Table 5-12. Decrease in self-association of alkylated with respect to raw asphaltenes.

The change in MW may have an influence as well. In this case, the variation of MW is not as clear as in reduction. The cleavage of bridges reduces MW but butylation increases it. It is assumed that the first process is more significant. Thus, an overestimation of the association capacity per mol is expected when comparing raw and altered samples in a mass basis. The combination of all these facts may explain why the ITC results are not conclusive.

The time dependence of self-association was studied in Yagual asphaltenes. Consecutive tests in different days show an increase in heat developed (Figure 5-12). The heat in the last experiments is five times greater that in the first one. This can be explained by the effect of butyl chains: they create a steric hindrance to self-association and that leads to more heat developed in the last tests. They have had longer time to form bonds and reach equilibrium. Thus, the more time between sample preparation and the experiment, the greater the heat developed because there are more bonds dissociated. Changes with time in associating behavior have also been observed by other researchers (Strausz et al., 2002).



Figure 5-12. Heat developed in ITC experiments with 10 g/l reductive alkylated Yagual asphaltenes.



Figure 5-13. Fluorescence spectra of Yagual and Ca30 alkylated and raw asphaltenes. C = 2 ppm.

Fluorescence spectra of alkylated asphaltenes do not fit the previously discussed results. Alkylated Yagual shows increased HB and increased heat developed by ITC but the spectrum shows a blue-shift that was previously assigned to a reduction in association (Figure 5-13). Small molecules are more prone to suffer from quenching, as explained in Chapter 7. The cleavage of bridges may decrease the re-absorption of energy by the neighbors. Ca30 does not show a rise in emission after the reduction in hydrogen

bonding. Hydrogen bonding in the original asphaltenes was small so the decrease in quenching cannot be important.

To sum up the results of this section, the expected reduction in self-association capacity is only observed in LM2 asphaltenes. The reduction is lower than in methylation. Reductive alkylation was supposed to act as well on the acidic groups that were blocked in methylation, but butylation seems to be more effective on the newly formed acidic hydrogen. The rest of butylated asphaltenes have a similar tendency to aggregate as raw asphaltenes, according to ITC data. MW reduction and tangling may cause an overestimation of the association of altered asphaltenes. Nevertheless, the steric effect of butyl branches is successful in slowing down the self-association.

5.6. Conclusions.

Asphaltenes have been altered in order to study the contribution of several functionalities to the self-association. Reactions such as methylation and silylation block polar functionalities and were expected to decrease the self-association. More severe treatments like reduction and reductive alkylation alter the core of the molecules and were foreseen to have a more complex response in the calorimetric titrations.

Methylation is the reaction that follows better the behavior expected. The reaction is accompanied by a reduction in hydrogen bonding by IR, and a reduction in heat of association by ITC. Fluorescence spectroscopy shows the appearance of new bands at short λ that are assigned to previously associated molecules.

Silylation is less effective than methylation in reducing the capacity of selfassociation. Silylation only affects oxygen groups, while methylation also attacks nitrogen and sulphur functionalities. This emphasizes the importance of nitrogen and sulphur in the aggregation of asphaltenes. In any case, trace amounts of reagent may still be present in silylated samples and these amino groups may increase artificially the capacity of self-association. This implies that the difference between the two reactions is probably smaller than what has been found in this study. It must be remembered that ITC may not be able to break all asphaltene aggregates. The changes observed in selfassociation capacity may only affect the outer layer of asphaltene aggregates, while the core may remain unaltered.
Stable asphaltenes have shown a greater response to these two reactions. The greater polarity of these asphaltenes may be related to the stability of the fraction in terms of an enhanced resin-asphaltene interaction.

Reduction increases the capacity of self-association of asphaltenes by the creation of new acidic groups. Nevertheless, in some cases it makes that some of the asphaltenes are no longer soluble in toluene. This resulted in lower heats developed by ITC. Besides, loss of material by desulphurization may have a significant impact in the behavior observed.

Reductive alkylation should decrease the capacity of self-association but this is not observed by ITC. Secondary effects, such as tangling and the variation in MW may explain why the heat developed is not significantly reduced.

The two reductions are difficult to analyze due to the lack of information about the reduction in MW achieved. This hinders greatly the discussion of results when the samples are prepared in a mass instead of in a mole basis.

Fluorescence spectroscopy has shown that self-association of asphaltenes at very low concentrations (2 ppm) shifts the bands to longer λ . The decrease in self-association in some altered samples allows the detection of smaller aromatic units. It is important to remember that the absence of emission in the range 300-400 nm was used as a conclusive proof (Ralston et al., 1996)⁸ to reject the presence of aromatic structures with less than four rings in asphaltenes. This work shows that there are small molecules that emit in that range of λ , but the bands are shifted to longer λ due to self-association. This discovery has a significant impact in the use of fluorescence spectroscopy to derive asphaltene properties such as MW (Groenzin and Mullins, 1999).

6. Asphaltene Interaction with a Model Compound

Preliminary tests with a well-known alkyl-phenol were carried out to characterize the interaction of asphaltenes with a compound that is often used as an asphaltene dispersant. An experimental protocol has been developed to be further applied in the study of the interaction with petroleum resins. The points discussed in this section are:

- 6.1. Introduction.
- 6.2. ITC measurements.
- 6.3. Modeling ITC experiments.
- 6.4. Maximum number of sites available for interaction.
- 6.5. Thermodynamic characterization.
- 6.6. Toluene-acetone fractions of asphaltenes and nonylphenol.
- 6.7. Conclusions.

6.1. Introduction.

In order to remediate asphaltene fouling, the concentration of resin-like material is increased by adding chemicals such as alkyl-phenolic surfactants. These molecules act as synthetic resins that enhance the stabilization of asphaltenes. However, to be able to optimize the performance and cost of operation, knowledge of the mechanism of interaction between asphaltenes and other oil fractions or additive chemicals is of great importance.

Alkyl-phenolic compounds have been reported to be good stabilizers of asphaltenes. The addition of nonylphenol delays the onset point of the flocculation of asphaltenes (Clarke and Pruden, 1998). Moschopedis et al. (1977) proved that the addition of phenol decreased the measured molecular weight of asphaltenes, as if they broke the aggregates and dispersed the asphaltene molecules. Chang and Fogler (1994a) showed that 7 wt% of nonylphenol was able to completely solubilize 1 wt% asphaltenes in n-heptane. The viscosity of xylene solutions was as well decreased by the presence of nonylphenol (Pierre et al., 2003). Lian et al. (1994) and Leon et al. (2002) showed, however, that the capacity of stabilizing asphaltenes is higher for native resins than for amphiphiles, even if they adsorb in lower quantities. Chang and Fogler (1994b) showed that nonylphenol aggregates with asphaltenes are slightly bigger than asphaltene aggregates, but resins do decrease the size of asphaltene aggregates (Leon et al., 2002). This suggests that nonylphenol does not disperse asphaltenes in the same way as native resins do. Other substances are as well able to stabilize asphaltenes, such as benzensulphonic acids (DBSA) and amines. The stabilizing power is higher for DBSA and lower for the amines (Wiehe and Jermansen, 2003). The stabilization of asphaltenes with surfactants depends on the polarity of the head group (Chang and Fogler, 1994a); this shows again the importance of the polar nature of asphaltenes in their stability and aggregation behavior. In this section, the study of interaction of nonylphenol (NP) with asphaltenes is presented. This was taken as a preliminary study to develop a procedure that would be later applied to the study of the interaction with native petroleum resins. The use of a well-known single molecule as model resin would simplify the experiments. These experiments would as well help in the understanding of the interaction between asphaltenes and alkyl-phenolic compounds.

6.2. ITC measurements.

Tests consist of the injection of a solution of nonylphenol into a solution of asphaltenes. The solvent is toluene in both cases. Asphaltene concentrations in the cell range from 0.25 to 10 g/l, in order to cover different associated states of asphaltenes. Nonylphenol (NP) concentrations in the syringe ranged from 5 to 100 g/l.

There are four processes going on in the cell in this type of experiment: The injected toluene causes a decrease in asphaltene concentration that leads to a rearrangement of the equilibrium between free and aggregated asphaltenes. The solution of nonylphenol in the syringe is also in equilibrium between the free molecules and the ones associated by hydrogen bonding. The injection of this solution into a greater volume causes as well the dissociation of nonylphenol bonds. The injection process has associated some friction that develops some heat. Finally, nonylphenol interacts with the asphaltenes by means of the formation of hydrogen bonds.



Figure 6-1. Effect of asphaltenes in the raw data of nonylphenol ITC titrations.

Figure 6-1 shows the effect of asphaltenes on the heat developed. It is clear that, as the concentration of asphaltenes in the cell increases, the exothermic contribution (interaction NP-ASP) becomes more and more significant and takes over the endothermic process of breaking of hydrogen bonds between nonylphenol molecules.



Figure 6-2. LM1 10 g/l asphaltenes and nonylphenol at several concentrations.

The acid-base interaction between asphaltenes and amphiphiles seems to be quite complex and involves different mechanisms. Raw data (Figure 6-2) show that there are at least three processes ongoing in the cell. Each peak represents the heat developed in one injection as a function of time. The negative peaks (2) represent an exothermic process, which is believed to be the interaction between free sites in asphaltene aggregates and nonylphenol (NP). As the sites available for the interaction become saturated, this contribution decreases in magnitude as the titration goes on. Once the heat developed in the interaction NP-asphaltene becomes small, there is another endothermic peak (3) that appears, which represents the breaking of the H bonds among nonylphenol molecules (see the titration of nonylphenol into dried toluene, C asp = 0 g/l in Figure 6-3). This heat contribution is more significant at high nonylphenol concentrations.

There is another endothermic peak (1) that appears in the first injections, which varies in magnitude among the different asphaltenes. The origin of this peak is not fully understood. This peak is not observed in the absence of nonylphenol. It cannot be assigned to the dilution of nonylphenol because the positive peaks disappear after a certain number of injections and then appear again. If these two sets of peaks corresponded to the same process, the peaks would be there in all injections. It was speculated as well that it could be caused by the control system. The action of the control system could be too strong and create a second order response. Nevertheless, similar experiments with other substances gave peaks of the same magnitude or even higher and

this second order response was not observed. Since the nonylphenol-asphaltene interaction has been shown to be exothermic, it is assumed to represent the dissociation of asphaltene-asphaltene bonds due to the presence of nonylphenol.

The work of Chang and Fogler (1994) cited in the introduction that reports the incapacity of nonylphenol to disperse asphaltenes is not in disagreement with this statement. That study was performed on asphaltene colloids in n-heptane, while the present experiments are in toluene, where asphaltenes only form aggregates of 4-6 molecules that cannot be considered colloids. Nonylphenol may have enough dispersing power to substitute an asphaltene molecule in an interaction site.

The nonylphenol-asphaltene interaction is more evident at high asphaltene concentration (Figure 6-3). At low asphaltene concentrations, the peaks are positive, which means that the main process in the cell is the breaking dissociation of nonylphenol associates bonds.



Figure 6-3. Injection of nonylphenol into Alaska 95 asphaltenes. (a) 5 g/l NP. (b) 20 g/l NP.

The amount of asphaltenes present is very low and the peak of the interaction nonylphenol-asphaltenes is masked by the big contribution of the breaking of NP-NP bonds. As the concentration of asphaltenes increases, the negative peak of the interaction ASP-NP starts to grow and at high asphaltene concentrations it masks the endothermic breaking of NP-NP bonds. As expected, the heat developed with 20 g/l of nonylphenol is greater than that with only 5 g/l, as there are more sites available for hydrogen bonding.

The integration of the peaks gives the heat developed in each injection. ITC experiments with Cs = 20 g/l nonylphenol show that the heat developed is different for each asphaltene (Figure 6-4a). LM1 and Alaska95 show an abrupt change in slope at

around 1 g/l. This may be related to the end of the dispersive effect of NP on asphaltene aggregates (process 1 in Figure 6-2). The fact that the total heat developed has an abrupt change in slope does not mean that the process 1 ends abruptly, as shown in Figure 6-4b. Process 1 has a faster decay than the processes 2 and 3, which are included in TERM model, as explained in the following section.



Figure 6-4. (a) Titration 20 g/l of NP into 10 g/l asphaltenes. (b) A95 Asphaltenes. Fast decay of Process 1.



Figure 6-5. Nonylphenol solutions into 1 g/l ASP: (a) 5 g/l of NP. (b) 20 g/l of NP.

It is observed in Figure 6-5 that *stable* asphaltenes such as Alaska95, LM1 and LM2 interact more with nonylphenol than the *instables* (Lagrave, Ca30, NM1 and Yagual). KU is a stable crude but does not interact with NP as much as the other stable asphaltenes. There are several processes that may contribute to the heat developed,

including solvation, de-solvation, repulsion, tangling of branches and so on. For the sake of simplicity, it is assumed that the one with the highest heat developed is the one with more interaction with nonylphenol. The effect of the dilution with toluene on the aggregation state of asphaltenes is also relevant, but the volume injected is small and the heat developed in this process would be smaller than the interaction NP-ASP. This suggests that Alaska 95 is the asphaltene with greater capacity of interaction with NP.

6.3. Modeling ITC experiments.

In order to obtain the enthalpy of interaction between NP and ASP (Δ H), it is necessary to apply a model and fit the experimental data. The method followed is based on the chemical theory (Prausnitz et al. 1999), and it considers that all the heat developed is due to the formation of new species, as in the self-association experiments.

In the first approach (Model 1), the titration is modeled with three equations. Each of them has two parameters: the equilibrium constant (K) and heat of interaction (Δ H).

- $1. \qquad \text{Interaction NP}-\text{ASP:} \qquad A_2+N \ \Rightarrow \ A_2N \qquad \{K, \Delta H_i\} \qquad (1)$
- 2. ASP-ASP aggregation: $A + A \Rightarrow A_2 \quad \{K_A, \Delta H_A\}$ (2)
- 3. NP-NP aggregation: $N + N \Rightarrow N_2 \quad \{K_N, \Delta H_N\}$ (3)

It must be noticed that nonylphenol is assumed to react with asphaltene aggregates (A_2) . A model in which NP reacts with the monomer A was as well proposed with very poor results. After each injection, the concentration of the different compounds changes and a new equilibrium has to be reached. The difference in concentrations between the moment after the injection and the equilibrium allows the calculation of the number of physical intermolecular bonds formed and broken. The total heat developed q in each injection is:

$$q = n_{A-N} (mol)^{*} (\Delta H_{i}) + n_{A-A} (mol)^{*} (-\Delta H_{A}) + n_{N-N} (mol)^{*} (-\Delta H_{N})$$
(4)

 n_{N-A} is the number of ASP-NP bonds formed and n_{A-A} and n_{N-N} are the number of ASP-ASP and NP-NP bonds broken, respectively. The parameters of the models are

		C asp cell = 10 g/l								
	I	LM1 A	sp.	ŀ	KU Asp.			A95 Asp.		
C NP (g/l)	ΔH_i	Ki	SS	ΔH _i	Ki	SS	ΔH _i	Ki	SS	
5	-3.5	400	-12.3	-3.9	300	0.8	-9.2	125	-1.4	
20	-1.7	450	73.2	-5.9	125	3.1	-3.1	125	-0.7	
40	-7.0	175	211.0				-5.6	175	182	
				C asp	cell = 1	l g/l				
	I	LM1 A	sp.	ŀ	KU Asj	p.	A95 Asp.			
	ΔH_i	Ki		ΔH _i	Ki	SS	ΔH _i	Ki	SS	
5	-1.0	700	5.8	-0.9	700	4.3	-8.0	250	-1.5	
20				-10.7	275	122.0				

optimized so that the heat calculated with Eq. 4 is as close as possible to the experimental heat. The results are gathered in Table 6-1.

Table 6-1. Results of model 1 with asphaltenes. ΔH in kJ/mol, K in l/mol and SS is in µcal/injection.

Six parameters are too many to be optimized in only one run. It is necessary to perform reference tests to calculate some parameters. The values of {K_A, Δ H_A} are taken from the titrations in which asphaltenes are injected into pure dried toluene (See Chapter 4). In order to obtain {K_N, Δ H_N}, nonylphenol was injected into dried toluene (See Chapter 3). With respect to the friction losses, the reference test was the injection of toluene into toluene. The heat obtained (-2 µcal/injection) was subtracted from the raw data prior to any further treatment.



Figure 6-6. Fit of Model 1 to the titration of 10 g/l Alaska 95 Asp with 5 and 40 g/l of NP. The dots represent the experimental data and the lines represent the model.

Once these parameters are fixed, the fitting of the model to the experimental data is done by means of the enthalpy of NP-ASP interaction (Δ H_i) and the equilibrium constant (K).The application of Model 1 to the titration of asphaltenes with nonylphenol is not very satisfactory (Figure 6-6). The figures have the x-axis in reverse order due to the fact that the concentration of asphaltenes decreases as the titration goes on. The optimal { Δ H_i, K} are shown (Table 6-1), together with the values of the sum of squares SS. Some of the experiments present good fits, but some have too large values of SS. Tests with 40 g/l of NP give much larger SS values than lower NP concentrations. Besides, the values of Δ H vary significantly from test to test.

The second model (TERM) applies a much simpler approach. The heat developed in the nonylphenol reference data was subtracted from the raw data. The remaining heat was assumed to be due to the interaction ASP-NP and also to the effect of toluene on the aggregation state of asphaltenes.

Asphaltenes are believed to associate step-wise, and in the previous sections the self-association of asphaltenes has been successfully modeled with polymerization-type reactions:

$$A_n + A_1 \leftrightarrow A_{n+1} \qquad \Rightarrow \qquad [A_{n+1}] = K_{n+1} [A_1] [A_n] \tag{5}$$

The equilibrium constants and enthalpies were considered to be the same for all the reactions. ΔH_{ai} and K_i are the enthalpy and equilibrium constant of the formation of imer:

$$K = K_2 = K_3 = \dots = K_{n+1}$$
(6)

$$\Delta H_a = \Delta H_{a2} = \Delta H_{a3} = \dots = \Delta H_{an+1} \tag{7}$$

In the asphaltene-resin experiments, asphaltenes are again modeled with polymerization reactions, while the ligands are considered to act as terminators of the polymerization type reaction.

$$A_n + N \leftrightarrow A_n N \qquad \Rightarrow \qquad [A_n N] = K_{Nn} [N] [A_n] \tag{8}$$

$$K = K_2 = K_3 = \ldots = K_{n+1} = K_{N1} = K_{N2} = \ldots = K_{Nn}$$
(9)

$$\Delta H_a = \Delta H_{a2} = \Delta H_{a3} = \dots = \Delta H_{an+1} \tag{10}$$

$$\Delta H_i = \Delta H_{i1} = \Delta H_{i2} = \dots = \Delta H_{in} \tag{11}$$

To simplify the approach, it is considered that the equilibrium constants are the same as those of the propagation reactions, but the NP-ASP interaction is modeled with a different value of Δ H. Δ H_i and K_{Ni} are the enthalpy and equilibrium constant of the formation of aggregates of NP with the i-mers. The values of Δ H_a are taken from Table 4-6 and the Δ H_i of the interaction asphaltene-ligand is used as a fitting parameter, together with the equilibrium constant K. This Terminator-Propagator Model has been applied to model VPO measurements of asphaltenes in toluene solutions (Agrawala and Yarranton, 2001) and ITC titrations (See Chapter 4). Herein, asphaltenes are considered to contain only propagators, while the resins and nonylphenol are considered as the terminators. The calculated heat q is:

		C asp cell = 10 g/l								
		LM1 As	p.		KU Asp.		A95 Asp.			
C NP (g/l)	ΔHi	Ki	SS	ΔHi	Ki	SS	ΔHi	Ki	SS	
5	-5.4	2173.5	-9.4	-3.5	3702.9	-0.4	-5.3	1234.7	-0.3	
20	-5.2	304.6	-1.2	-3.7	172.8	-0.9	-5.6	135.0	-0.5	
40	-6.4	101.1	-15.9						-14.2	
100	-5.9	100.8	-42.9							
				C	asp cell = 1	g/l				

$$q = n_{A-N} (mol)^* (\Delta H_i) + n_{A-A} (mol)^* (-\Delta H_A)$$
(12)

		LM1 As	p.		KU Asp.		A95 Asp.			
C NP (g/l)	ΔHi	Ki	SS	ΔHi	Ki	SS	ΔHi	Ki	SS	
5	-2.4	284.4	-0.5	-1.8	234.5	-1.0	-4.8	127.1	-0.3	
20				-1.8	154.2	-0.7	-5.0	75.3	-0.5	

Table 6-2. Results of TERM model with asphaltenes. ΔH in kJ/mol, K in l/mol and SS is in µcal/injection.

TERM model gives values of ΔH_i that are more similar among the tests with different NP concentrations (Table 6-2). Appendix J gathers the rest of the fitted parameters for all the crudes investigated. The goodness of fit is remarkably good for most of the experiments (Figure 6-7). Nevertheless, the equilibrium constants K are still concentration dependent. They tend to decrease as the concentration of nonylphenol increases. This could be interpreted in terms of affinity: at high nonylphenol concentration, it would tend more to self-associate than to interact with asphaltenes. At low concentrations of NP, the proportion of monomeric nonylphenol is higher, allowing a higher interaction with asphaltenes that implies a higher value of the equilibrium constant K. As explained in the previous chapter, activity coefficients may as well be responsible for the variation of K.

Buenrostro-Gonzalez et al. (2002) applied SAFT-VR equation to model the precipitation of Maya asphaltenes from crude with n-alkanes, obtaining an enthalpy of interaction of -3.3 kJ/mol, as a fitted parameter. The agreement between these data and Table 6-2 is very satisfactory. It is observed that there is less heat of interaction NP-ASP per gram of nonylphenol injected as the concentration of NP increases (Figure 6-7b). This supports the above explanation of why K decreases with increasing concentration of NP.



Figure 6-7. (a) Fit of TERM model to the titration of 10 g/l Alaska 95 Asp with 5 and 40 g/l of NP (MW assumed = 1000 g/mol). (b). Fit of TERM model to LM1 10 g/l asphaltenes titrated with several nonylphenol concentrations. (O) 5 g/l NP; (+) 20 g/l NP; () 40 g/l NP; (X) 100 g/l NP and 3 μl per injection.

It must be remembered that this approach is a simplification of the system. The entire asphaltene fraction is represented by only one molecule. The polydispersity in both polarity and aromaticity (Speight, 1999) of the asphaltene fraction is not taken into account. Some of the asphaltene molecules would have more affinity than others to nonylphenol, and some would just not be active in these titrations, as suggested in Chapter 4. Besides, some of the sites that could be used by nonylphenol may be involved in asphaltene-asphaltene bonds. The average molecular weight has been set arbitrarily to 1000 g/mol. Again, the polydispersity in molecular size is not considered in this model. These simplifications are relevant, but, at this stage of the investigation, a simple approach is recommended. Once the picture of asphaltene self-association is better defined, it would be possible to come up with a more detailed model without using too many fitting parameters. Still, the values of ΔH are of the same order of magnitude as hydrogen bonding, showing that the modeling has indeed some merits in understanding the process.

Due to these simplifications, the model is not able to fit the data when process 1 (Figure 6-2) is observed. This is probably due to the complexity of the signal. The calorimeter measures the global heat, while TERM model only considers nonylphenol-asphaltene association. Once this process 1 is over, TERM model can fit very well the data because the only heat measured by the calorimeter is developed by the NP-ASP reaction (Figure 6-8).



Figure 6-8. Fit of TERM model to the titration of 10 g/l Alaska 95 Asp with 20 g/l NP.

6.4. Maximum number of sites available for interaction.

The IR spectrum of nonylphenol in toluene has been obtained in the -OH stretching region (3600-3300 cm⁻¹). The band has been deconvoluted into four peaks located at 3560, 3550, 3462 and 3390 cm⁻¹. Each of these peaks is associated to a state of the -OH group in the solution (free, bonded by the O atom, bonded by the H atom and bonded by both H and O atoms, respectively). The location of the peaks is different from that found in the literature for CCl₄ solutions of phenol (Vinogradov and Linell, 1971). The solvation effect of toluene is very strong and shiftes the peaks to lower wave numbers. IR spectroscopy of nonylphenol show that the band assigned to free -OH (3560 cm-1) decreases with the presence of 10 g/l Alaska 95 asphaltenes (Figure 6-9). The decrease is assigned to the amount of nonylphenol attached to asphaltenes, as reported previously for the interaction with phenol by means of the Phenol Interaction Value (Barbour and Petersen, 1974 and Andersen, 1994). It is considered that the presence of asphaltenes (Chang and Fogler, 1994b).



Figure 6-9. Influence of Alaska 95 asphaltenes on the IR spectra of 20 g/l NP.

The capacity of interaction with nonylphenol of Alaska 95 is estimated to be 3.19 mol NP/kg Asp at that particular concentration. Chang and Fogler (1994b) found that the hydrogen bonding capacity of asphaltenes with dodecylphenol was 1.6-2.0 mol/kg, following the same procedure. This unit has been chosen because the use of molar basis depends on the molecular weight assumed. Besides, an average Mw of 1000 units is often reported as a good estimation, so the molar number of sites per kilogram is also a reliable approximation to the average number of sites per asphaltene molecule. The amount of NP attached to asphaltenes varies significantly with the concentration of both species (Table 6-3). As expected, the amount of NP attached increases with increasing NP concentration, but it decreases as the concentration of asphaltenes rises. Some of the potential sites for NP-ASP interaction are probably occupied in asphaltene-asphaltene bonds at high asphaltene concentration, as suggested in studies of the interaction phenol-asphaltenes (Siddiqui, 2003).

In order to calculate the maximum capacity of interaction with asphaltenes, a high concentration of nonylphenol (300 or 468 mM) was injected into a low concentration of asphaltenes (1 g/l). This dilution assures that asphaltenes have a low aggregation state and most of the sites are available for the interaction with nonylphenol. The exothermic interaction NP-ASP is rapidly compensated by the high heat developed in the break of H bonds among nonylphenol molecules (Figure 6-10).

LM1 ASP	NP=5 g/l	NP=10 g/l	Alaska 95	NP= 1.83 g/l	NP= 18.3 g/l
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C = l g/l	7.1	13.6	C = 1 g/l	1.04	n.d.
C = 10 g/l	0.9	1.1	$C = 10 \ g/l$	0.16	3.19

Time (min) 0 50 100 150 200 250 300 80 60 ucal/sec 40 ASp = 1 q/l20 0 ASp = 0 q0.8 0.6 mcal/injection 0.4 C Asp = 0 g/ C Asp = 1 g/ 0.2 Subtraction 0.0 -0.2 -2 Ò 2 6 8 10 12 14 16 18 20 4 C NP cell (q/l)

Table 6-3. Capacities in mol NP/kg ASP by IR spectroscopy.

Figure 6-10. Titration of 100 g/l of NP into dried toluene and 1 g/l LM1 ASP (Volume per injection = 3 µl).

The subtraction of the reference data (injection of NP into dried toluene) gives the heat developed in the interaction NP-ASP. This heat reaches a value of zero when all sites have been saturated. The concentration of NP (C^*) at which the sites become saturated has been calculated by drawing the trend line in the linear region of the curve (Figure 6-11).

If it is assumed that all nonylphenol molecules in the cell would interact with asphaltenes, C^* gives the number of sites *n* available for interaction. *n* varies from 6 to 8 depending on the asphaltene. In reality, not all nonylphenol molecules are attached to asphaltenes, so these values can be considered an upper limit.



Figure 6-11. Calculation of maximum number of sites per molecule in LM2 asphaltenes.

6.5. Thermodynamic characterization.

TERM model was first used to obtain the thermodynamic parameters of NP-Asphaltene interaction (Table 6-4). Δ H is significantly lower than in the experiments previously shown (see Table 6-2); on the contrary, the equilibrium constants are greater. Δ G is negative, leading to the conclusion that the process is spontaneous.

The fitted values of ΔH_i are one order of magnitude lower than the range assigned to hydrogen bonding (between -10 and -40 kJ/mol, Joesten and Schaad, 1974). As explained in the previous sections, this is believed to be related to the heat contributions that are not explicitly taken into account. The contribution of ΔS to the free energy is greater than the one of ΔH : this may indicate that the process is entropically driven. TERM model has an important drawback due to the fact that the number of sites per asphaltene molecule is fixed to one (see eq. 11). This limits the predictive capacity of the model and creates a greater dependence of K and ΔH with the Mw assumed.

LM1 Lagrave	Ca30	NM1	Yagual	A95	KU	LM2
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n	1	1	1	1	1	1	1	1
ΔH (kJ/mol)	-5.3	-1.5	-0.9	-1.6	-1.2	-1.9	-1.0	-1.8
K	89.1	168.1	225.2	438.2	545.9	254.2	591.3	207.2
ΔG (kJ/mol)	19.8	37.7	42.1	45.3	48.4	39.8	49.8	38.4
ΔS (J/mol)	-11.3	-12.9	-13.6	-15.3	-15.9	-14.0	-16.1	-13.4

 Table 6-4. Results of the fitting of TERM model to experiments with high nonylphenol concentration (300 mM). LM1 was titrated with 468 mM nonylphenol.

One Set of Independent Sites (ONE) model was proposed, as it includes the number of sites as a third fitting parameter. This model has been widely applied in biochemistry (Freire et al., 1990). It considers that asphaltenes contain a number of sites available for the interaction, and they all have the same affinity for nonylphenol. Besides, the binding of one molecule is not affected by the neighboring sites. This means that two sites act as if there were very far from each other, even if they may be in the same molecule. This may be a good approximation to large hydrocarbon structures like asphaltenes. It allows the calculation of the average number of interaction sites at the same time as the enthalpy of association. After the subtraction of the reference data, the resulting heat is assumed to be related only to the binding of nonylphenol with asphaltene.

Inherent in this, it is assumed that the injection of 290.0 μ l in a cell of 1.46 ml does not lead to a substantial heat of dissociation of asphaltene aggregates, as discussed in Chapter 4. The heat developed in each injection is calculated with eq. 16. This model has three fitting parameters that are obtained in the optimization routine: the equilibrium constant K, the enthalpy Δ H and the number of sites n. V is the volume of the cell.

$$q = \Delta H_{A-R} V \Delta [R_B] \tag{13}$$

The heat developed in each injection is calculated by multiplying the enthalpy by the variation in amount of nonylphenol bound to asphaltenes Δ [R_B]. The concentration of bound nonylphenol R_B before and after each injection is calculated by means of eq. 14-15, where [A] is the total concentration of asphaltenes and [R_T] and [R] are the total and free nonylphenol concentrations, respectively (See Appendix J).

$$\left[R_B\right] = \left[A\right] \frac{n K \left[R\right]}{\left[R\right] + 1} \tag{14}$$

$$\begin{bmatrix} R_T \end{bmatrix} = \begin{bmatrix} R \end{bmatrix} + \begin{bmatrix} R_B \end{bmatrix}$$
(15)

It is as well able to fit successfully the experimental data (Figure 6-12).



Figure 6-12. Fit of ONE model to nonylphenol-asphaltene experiments.

Table 6-5 compiles the thermodynamic parameters of the interaction. ΔH is exothermic, as seen with the previous model, but the values are extremely low. They are one order of magnitude lower than the ones obtained with TERM model. This is considered a deficiency of the model. The greater equilibrium constants make ΔG and ΔS be similar to the previously discussed. The number of sites ranges from 2.6 to 5.1 sites per molecule; the agreement between these values and the IR data is as well satisfactory. Elemental analysis (Table 6-6) shows that the number of heteroatoms per molecule of asphaltenes is also in that range.

_	LM1		Lagrav	ve 🛛	Ca30		NM1	
n	2.6 ±	0.9	$4.6 \pm$	0.9	5.1 ±	0.7	5.0 ±	0.6
$\Delta H (kJ/mol)$	-2.0 ±	0.7	-0.07 \pm	0.02	-0.10 ±	0.02	-0.06 \pm	0.01
$\Delta G (kJ/mol)$	-11.1		-17.1		-15.7		-18.8	
ΔS (J/mol)	29.9		56.2		51.4		61.9	
Κ	81 ± 6		900 ± 5	500	500 ± 2	200	2000 ± 1	000
_	Yagual		Alaska	95	KU		LM2	
n	4.1 ±	0.8	4.3 ±	0.4	4.8 ±	0.6	3.2 ±	0.7
$\Delta H (kJ/mol)$	-0.06 \pm	0.02	-0.19 ±	0.02	-0.07 ±	0.01	-0.3 ±	0.1
$\Delta G (kJ/mol)$	-17.4		-16.0		-18.5		-14.4	
ΔS (J/mol)	57.3		52.1		60.8		46.3	

Table 6-5. Results of the fitting of ONE model. n in sites per molecule (Mw = 1000 g/l).

	KU	LM1	NM1	A95	CA30	LM2
mol O/mol ASP	3	1.4	1.4	1.2	1.1	2
mol N/mol ASP	1.2	1.3	1.3	0.9	0.7	1.2
mol S/mol ASP	2.1	1.5	0.9	1	2.4	1.2
TOTAL	6.3	4.2	3.6	3.1	4.2	4.4

Table 6-6. Heteroatom content from elemental analysis. Mw assumed = 1000 g/mol.

This may indicate that the hydroxyl group of nonylphenol is mainly bound to asphaltenes by these heteroatoms. Nevertheless, the capacity of nonylphenol to form bonds with the π -orbitals of the aromatic rings cannot be neglected. For instance, the OH- π intramolecular bond in 2-benzylphenol is reported to have an enthalpy of formation of -1.38 kJ/mol (Bellamy, 1968). This enthalpy is in the same range as the ones reported here, leading to the conclusion that the upper limit of 6-8 sites of interaction found by means of C^{*} is not such a bad estimation, if both heteroatoms and aromatic rings are considered to form bonds with nonylphenol.

Experiments were as well performed with greater nonylphenol concentration (468 mM). These experiments presented a larger scattering of the data (Figure 6-13) due to the

fact that very small volumes were injected $(2\mu l)$. However, the data were useful to check the parameters obtained with 300 mM nonylphenol. Figure 6-12 shows that these parameters are as well able to give a good performance in experiments with a greater NP concentration.



Figure 6-13. LM2 experiments with nonylphenol. (O) Vinjected = 3μ l; C syringe = 300 mM Nonylphenol. (X) Vinjected = 2μ l; C syringe = 468 mM. (-) Fit of ONE model.

The average number of sites (n) obtained is in the same range as those reported or used by other researchers. Leon et al. (1999) found 6.7 molecules of NP per asphaltene molecule asphaltene in adsorption studies on particles in n-heptane. Murgich et al. (1999) used 9 sites available for resins molecular simulations in an asphaltene aggregate, based on the most probable interaction sites in a model molecular structure from Athabasca sand asphaltene. Wu et al. (1998) used 6 sites of interaction per asphaltene molecule in their SAFT calculations. Buenrostro-Gonzalez et al. (2002) used 3-4 sites to successfully fit onset precipitation data with SAFT equation.

However, these numbers are only an estimation of n, as some of the potential sites for NP-Asp interaction are actually occupied in asphaltene-asphaltene bonds.

Both ONE and TERM model are equally able to fit the experimental data. TERM model catches better the complexity of self-association, while ONE model only considers one reaction. However, TERM model is not able to give the number of sites, as this parameter is fixed to one. The Δ H obtained with TERM model are in the range expected, while ONE model gives surprisingly low values of enthalpy. Both are just a first attempt

to model asphaltene-nonylphenol interaction. It is observed that the equilibrium constants vary quite arbitrarily from one experiment to another. The models are unable to catch the complexity of the asphaltene mixture. This is again due to the simplicity of the approach. The assumptions made in both cases are very strong, as they apply a monodispersed approach to a highly polydispersed system. Still, these simple models are able to catch the behavior of nonylphenol and asphaltenes in toluene solutions.

6.6. Toluene-acetone fractions of asphaltenes and nonylphenol.

The titration of KU (Figure 6-14) and LM1 fractions with nonylphenol shows that there is a much lower heat developed when the INS fraction is in the cell, and the heat reaches faster a constant value. The fact that the soluble fraction has a greater heat of interaction with nonylphenol confirms that the SOL fraction is more polar than INS fraction, as discussed in Chapter 4.

Crude	CASP (g/l)	C NP (g/l)	ΔH (kJ/mol)	K (l/mol)	SS
KU SOL	1	5.0	-2.1	141.9	0.4
	1	20.0	-4.1	63.8	0.8
	10	5.0	-3.2	1961.5	0.4
	10	20.0	-3.7	223.6	3.5
KU INS	1	5.0	-2.1	170.1	1.8
	10	5.0	-2.1	5258.6	0.4
	10	20.0	-1.8	718.4	1.4
LM1 SOL	1	5.0	-4.9	143.9	2.0
	10	5.0	-4.9	1081.5	0.1
	10	20.0	-6.4	101.0	0.6
LM1 INS	1	5.0	-3.4	115.7	0.7
	10	5.0	-3.2	1267.2	0.2
	10	20.0	-5.0	95.1	2.9

Table 6-7. Results of the application of TERM model to asphaltene fractions. ΔH in kJ/mol, K in l/mol and SS is in μ cal/injection.

The application of TERM model to the subfractions is as satisfactory as for the entire asphaltenes (Table 6-7). Δ H in kJ/mol of INS is significantly smaller of that of

SOL: if it assumed that the acid-base interaction is the same for all fractions, ΔH should also be the same. This implies there are less bonds formed per mol of asphaltenes; therefore, INS would be less active in the acid-base interaction. The problem is the equilibrium constant of INS fraction, which becomes larger than the one for SOL, which implies there are more moles of PiT formed in INS fraction. This goes against what was expected intuitively: it seems reasonable that SOL has more bonds formed, as the exothermic heat developed is greater. This is considered again a deficiency of the simple fitting model.



Figure 6-14. Titration of 10 g/l of KU fractions with 20 g/l NP and fit of TERM model. The first chart shows the raw data and the second the integrated heats.

6.7. Conclusions.

The results show that the calorimetric experiments open a new way of investigating association in petroleum. Some interesting results have been obtained: first, experimental values of ΔH have been calculated. Second, the specific number of sites of interaction has been obtained, and there is good agreement with the number of heteroatoms in asphaltenes and also with the usual estimations in asphaltene modeling. The simple models used present serious problems related to the complexity of the mixtures they have to handle with. In any case, the maximum number of sites has been obtained directly from the titration curves by means of the calculation of C*.

Besides, it was proved that the fractionation with a mixture of toluene and acetone gives a soluble fraction that is more polar than the insoluble fraction, confirming the highly polydispersed nature of asphaltenes.

However, the analysis is still hindered by the lack of knowledge about asphaltenes. In the light of the very complex mixtures analyzed, the approach taken is very simplistic, as each process is characterized with one set of values of ΔH and K. The numerous assumptions made to calculate the heats of interaction between nonylphenol and asphaltenes suggest that the numerical results should be accepted with caution. A more detailed model would be necessary, but that would greatly increase the number of parameters to be regressed. A better understanding of asphaltene association is needed before developing a more consistent model. In any case, these experimental values could be very useful to reduce the number of fitting parameters in the development of asphaltene models.

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7. Asphaltene Interaction with Resins

Resins have been separated from the de-asphalted oil and characterized by spectroscopy. Calorimetric experiments were carried out in order to obtain the average enthalpy of association and the number of sites available for resin-asphaltene interaction. The points discussed in this section are:

- 7.1. Introduction.
- 7.2. Asphaltene and Resin Yields.
- 7.3. Infrared Spectroscopy.
- 7.4. Fluorescence spectroscopy.
- 7.5. Resin-Asphaltene interaction as studied by ITC.
- 7.6. Modeling Resin-Asphaltene interaction.
- 7.7. Conclusions.

7.1. Introduction.

In this Chapter, asphaltenes and resins are characterized and compared by spectroscopy and their interaction studied by Calorimetry.

The infrared and near-infrared spectra have been collected for a number of crudes of different stability in terms of asphaltene problems. IR radiation only has an impact in the vibrational and stretching states of the molecules (Ewing, 1985). The comparison of spectra allows the determination of the relative importance of the different functional groups in resins and asphaltenes, by means of the IR Index described in Chapter 2.

The near-infrared region (NIR) covers from 780 to 2500 nm (12820 - 4000 cm⁻¹) and many of the bands observed arise from combinations of C-H stretching vibrations. Scattering from particles gives also raise to bands in the region 1300-1600 nm (Aske 2001), allowing the study of the aggregation state of the systems. The more intensity scattered, the larger the concentration or the particle size. The latter case implies more self-association. Nevertheless, other researchers have raised some doubts about this fact, as absorption seems to dominate over scattering (Mullins, 1990). The bands at these wavelengths did not decrease after strong dilution of crude even if the aggregates were believed to dissociate, pointing out that they were caused by absorption, not by dispersion of light.

Fluorescence spectroscopy is applied to study the distribution in aromatic ring size in asphaltenes and resins. A recent study has raised doubts about the convenience of fluorescence studies of such complex mixtures as asphaltenes (Strausz et al., 2002). The spectra obtained are not uniformely representative of the whole asphaltene fraction and the use of a polar solvent such as NMP to fractionate asphaltenes yielded an insoluble fraction that did not emit any fluorescence at all (Ascanius et al. 2003).

Nevertheless, this study focuses on the qualitative comparison of the spectra of asphaltenes and resins. Taking into account the inherent complexity of asphaltenes, it is still possible to gain insight on the characteristics of the population of both fractions by comparing the spectra at different concentrations.

The investigation of mixtures of asphaltenes and resins helps as well in the understanding of the quenching phenomena, in the sense that the presence of large associating molecules like asphaltenes will affect the spectra of resins.

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Isothermal Titration Calorimetry (ITC) has shown its capacity to investigate petroleum fractions in previous chapters, such as the step-wise self-association of asphaltenes and the interaction of nonylphenol with asphaltenes. Once the experimental procedure has been optimized in the study with NP, it is further extended to the interaction with native resins. The final goal is to determine the average number of interaction sites available for resins and the enthalpy of association, in order to provide these values to the models that correlate the behavior of asphaltenes in crude oil.

7.2. Asphaltene and Resin Yields.

The yields of resins and asphaltenes of the four crudes are gathered in Table 7-1. The amount of resins has been found to be greater for crudes with high asphaltene content, as reported by Goual and Firoozabadi (2002). It is observed that the ratio R/A is not a good indication of the stability of asphaltenes. Yagual is an instable crude and has a greater ratio than the stable LM1.

On the other hand, the total amount of resins does correlate with the stability. Oils with large amounts of resins (LM1, LM2 and Alaska95) are stable, while the instable oils (Yagual and Ca30) have small concentration of resins. This fact may be related to the stability of the oil, in the sense that the absence of resins makes the surrounding media less attractive for asphaltenes and thus increasing their tendency to precipitate as a separate phase.

	Resins	Asphaltenes	R/A
Alaska95	16.0	5.3	3.0
LM1	16.6	8.6	1.9
LM2	30.0	9.8	3.1
Yagual	4.3	2.0	2.2
Ca30	4.7	4.6	1.0

Table 7-1. Percent yield and ratio of asphaltenes and resins.

7.3. Infrared spectroscopy.

The interest has been focused on the CH_2 - CH_3 region (3000-2900 cm⁻¹) and also the regions were the polar functionalities appear (3700 to 3200 cm⁻¹ for hydrogen bonding and 1800 to 1100 for other functional groups).

IR spectra of five asphaltenes and resins were recorded. The bands observed in both fractions were very similar in all cases. Only the region around 1100 cm⁻¹ showed a more prominent peak in resins than in asphaltenes (Figure 7-1). This band may be assigned either to sulphoxide or ether functional groups.



Figure 7-1. IR spectra of Ca30 asphaltenes and resins in CCl₄. (C = 10 g/l).

The relative capacity of forming hydrogen bonds was calculated through the index HB (Table 7-2). Yagual fractions have much lower HB than the rest of the crudes. This may be related to the stability of the crude, as it is a problematic crude oil. The incapacity of forming hydrogen bonds between asphaltenes and resins may be the factor why resins are not able to keep asphaltenes in solution, even when the R/A ratio is high.

On the other hand, the second problematic oil (Ca30) presents higher values of HB index. In this case, the instability may be related to other factors. Resin hydrogen bonding seems to be displaced to shorter wavelengths with respect to asphaltenes (Figure 7-2). The hydrogen bonding region is a complex combination of different bands, but this result may indicate that resin hydrogen bonding is –NH based, while asphaltenes have a

	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
A95 Resins	0.47	0.076	1.82	0.021
A95 Asp	0.39	0.054	1.90	0.034
LM1 Resins	0.57	0.111	1.65	0.099
LM1 Asp	0.21	0.059	1.81	0.055
LM2 Resins	0.60	0.099	1.94	0.028
LM2 Asp	0.40	0.061	1.82	0.029
Ca30 Resins	0.68	0.134	1.69	0.096
Ca30 Asp	0.34	0.023	2.20	0.030
Yagual Resins	0.61	0.119	1.85	0.008
Yagual Asp	0.37	0.038	1.95	0.005

greater contribution from –OH groups, as observed by Buenrostro-Gonzalez and coworkers (2001).

Table 7-2. IR indexes of asphaltenes and resins.



Figure 7-2. H bonding region of asphaltenes and resins from Alaska95.

The polar indexes (Carbonyl and Sulphoxide) show that resins have more bands than asphaltenes in the region 1800-1000 cm⁻¹. As explained in the introduction (Figure 1-2), it is possible to have resins that are more polar than asphaltenes. In that case, the majority of asphaltenes would precipitate upon n-heptane addition due to MW issues. The

resin fraction is believed to contain smaller molecules than asphaltenes. A high population of highly-polar small molecules may be responsible for the greater value of this index. Besides, the chromatographic separation of resins has been performed at atmospheric conditions, allowing a greater degree of oxidation. In fact, resins are more easily oxidized than asphaltenes (Lichaa, 1977). The methyl index is expected to be greater for resins than for asphaltenes. It is an indication of the length of alkyl chains, and resins are believed to have more methylene units than asphaltenes. All the crudes except from LM2 show a greater ratio of CH_2 over CH_3 for asphaltenes (Table 7-2). Nevertheless, this index is not fully reliable, as the methylene groups could as well be in bridges and naphtenic rings. The archipielago type of asphaltenes would contain a significant amount of methylene groups. This may explain the observed high values of this index for most of the asphaltenes.



Figure 7-3. Asphaltene and resin spectra in the near-infrared region.

The near-infrared region contains bands that are a result of the inharmonic vibration of polyatomic molecules. In crude oils, the most prominent bands are those related to the overtones of C-H, O-H and N-H groups (Aske, 2002). Scattering from particles causes an elevation of baseline in the region 6250 to 7700 cm⁻¹ (Aske 2001), allowing the study of the aggregation state of the systems. The ratio of scattering to absorption scales with r^3 (radius of particle). The bigger the aggregates or molecules, the

greater intensity is observed at these wavelengths. Figure 7-3 shows the Near-IR spectra of all asphaltenes and resins. It is observed that asphaltenes have a greater elevation of baseline in this region, implying a greater tendency to associate in CCl₄. Nevertheless, other researchers have raised some doubts about the origin of these bands, as absorption seems to dominate over scattering (Mullins, 1990). The band observed in the region 6150 to 5600 cm⁻¹ is assigned to the C-H first overtone absorption (Aske, 2002). Only at 6250 cm⁻¹, the absorption of hydrocarbons is negligible and scattering dominates (Mullins, 1990). The greater bands in that region in asphaltene spectra demonstrate that they have a greater molecular or aggregate size than resins (Figure 7-3).

7.4. Fluorescence spectroscopy.

The fractions were tested in the range 1 - 200 ppm. It has been claimed that the concentration must be less than 6 ppm to avoid concentration effects caused by association (Groenzin and Mullins, 1999). This set of concentrations would allow the study of the influence of concentration in the spectra in the critical region where association begins.

Synchronous spectra were recorded in toluene in the UV-Vis region (250-700 nm). Alaska95, Yagual, LM1 and Ca30 crude oils were under investigation. All crudes follow the same trends. The peak at 290 nm corresponds to the solvent (toluene). It is observed that resins emit at shorter wavelengths than asphaltenes (Figure 7-4).



Figure 7-4. Synchronous fluorescence spectra of LM1 asphaltenes and resins (C=1 ppm).

This implies that the average resin molecule contain conjugated aromatic sheets with less rings than asphaltene molecules. Nevertheless, there is significant overlapping between the two fractions. The maximum intensity in asphaltenes occurs at 470 nm, and that peak is also clearly observed in resins. This fact may indicate that the spectra of asphaltenes are dominated by the most resin-like material. As reported by Strausz et al. (2002), the capability of fluorescence is a function of MW in asphaltenes. The spectra of GC-subfractionated asphaltenes showed that the higher MW of the subfraction, the less it fluoresced. This has been confirmed by fractionation studies that show that a significant fraction of asphaltenes does not emit fluorescence (Ascanius et al., 2003). This suggests that the more resin-like material in asphaltenes is responsible for the emission of fluorescence.



Figure 7-5. Alaska 95. C1 to C7 are 1.3, 2.5, 5, 10 50, 100 and 200 ppm. (a) Resins (b) Asphaltenes.

The evolution of the spectra with concentration was as well investigated (Figure 7-5). It is observed that both fractions suffer from quenching effects at high concentrations. The spectra of resins show a significant decrease in emission at short wavelengths, while the spectra at λ longer than 400 nm is not reduced. This suggests that small aromatic sheets (from 1 to 3) are more prone to quenching than larger structures. This leads to a shift of the spectrum to longer wavelengths (*red shift*) when the concentration is increased. This makes the resin spectrum resemble an asphaltene spectrum at high concentrations. The spectra are dominated by the more asphaltene-like molecules at high concentrations. Asphaltenes do not experience such a big red shift but quenching is more evident and it starts at lower concentrations.



Figure 7-6. Evolution of maximum intensity. (a) Asphaltenes at 470 nm. (b) Resins at 400 nm.

Figure 7-6 displays the comparison of the intensities at the maxima, 400 and 470 nm for resins and asphaltenes, respectively. In theory, the intensity must increase linearly with concentration, as the concentration of active molecules rises. Deviations from the lineal behavior are caused by quenching effects. Asphaltenes start to suffer from quenching at lower concentrations (around 10 ppm). Self-association is one of the possible explanations for quenching. This indicates that asphaltenes tend to associate at lower concentrations than resins. Yokota et al. (1985) reported as well concentration effects in the spectra of asphaltenes at concentrations higher than 5 ppm. Concentration effects are not observed in resin spectra until 50 ppm. It has been claimed that quenching

effects are mainly due to self-association, but size effects cannot be disregarded. Asphaltenes contain bigger molecules than the resin fraction; therefore, the proximity may allow greater re-absorption of the emitted fluorescence.

Mixtures of asphaltenes and resins were as well investigated. Six experiments were carried out with four crudes: Alaska95, LM1, Yagual and Ca30. Spectra were collected of the combination of the following concentrations: 5, 10 and 50 ppm of resins and 5 and 10 ppm of asphaltenes. It is observed that the spectrum of the mixture is quenched with respect to the sum of the individual spectra (Figure 7-7). This phenomenon has been observed in all the mixtures prepared (See Appendix K). As observed in Figure 7-5a, quenching is again more evident at short λ . This confirms that small molecules are more prone to suffer from quenching. The presence of bigger molecules like asphaltenes enhances the quenching effect.



Figure 7-7. Experimental spectra of 5-5 ppm mixture (thick line) and sum of individual spectra (thin line). Ca30 Crude oil.

7.5. Resin-Asphaltene interaction as studied by ITC.

The aim of this study is to determine experimental Δ H and n of asphaltene-resin interaction. The experiments consist of the injection of resin into asphaltenes. Both are dissolved in toluene. All tests are carried out at 30 °C. Syringe concentrations are in the range 5-100 g resins/l, while asphaltenes are tested at 1.0 and 10.0 g/l.

There are several processes ongoing in the cell: The injected toluene causes a decrease in asphaltene concentration that leads to a re-arrangement of the equilibrium between free and associated asphaltenes. The solution of resin in the syringe is also in equilibrium between free and bonded molecules. The dilution into a greater volume causes as well the dissociation of resin-resin bonds. The injection process also leads to some frictional heat. Finally, resins form bonds with asphaltenes.



Figure 7-8. LM2 C RES = 33.9 g/l. C ASP = 30.0 g/l. (a) Raw data. (b) Integrated heats.

ITC experiments with resins were performed to study their tendency to selfassociate. These experiments are used as a baseline for the asphaltene-resin experiments.
Resin solutions with several concentrations ranging from 6 to 100 g/l were injected into dried toluene. The dilution of resins into toluene develops a significant endothermic heat, depicted in Figure 7-8a as positive peaks. The integration of the area below each peak gives the heat developed per injection. The trend of the heat developed is similar to that of asphaltenes so the same step-wise mechanism of self-association is assumed (See the rest of experiments in Appendix G). Resins, as asphaltenes, are believed to form oligomers of low aggregation number in a step-wise manner. The heat developed is assigned to the dissociation of intermolecular bonds between resin molecules. It has been claimed that resins do not self-associate in crude oil (Speight, 1999). The behavior in a favorable solvent like toluene may be different, as suggested by Bardon et al. (1996). The heat developed in the dilution of resins is greater than in the dilution of asphaltenes (Figure 7-8a). The average molecular weight of resins is lower than that of asphaltenes (they have been assumed to be 600 and 1000 g/mol, respectively), so it is expected to see more heat developed in resin tests because there are more molecules per gram. Nevertheless, the heat developed per mol injected is lower for resins than for asphaltenes (Figure 7-8b). The curves have been fitted to Equal K model (See Chapter 4).

		Cs (g/l)	ΔH (kJ/mol)	K (l/mol)
Ca30	RES	31.4	-4.4	24
	ASP	30.0	-3.4	88
A95	RES	35.8	-3.0	15
	ASP	30.0	-5.1	83
YAGUAL	RES	26.1	-4.0	37
	ASP	30.0	-4.5	119
LM2	RES	33.9	-3.4	15
	ASP	30.0	-4.7	64
LM1	RES	47.5	-8.2	31
	ASP	30.0	-5.2	74

Table 7-3. Fitted parameters of EK in the titration of asphaltenes and resins.

In this model, the curves are fitted with two parameters (Table 7-3). It is observed that resins have lower equilibrium constants than asphaltenes. This indicates that asphaltenes have a higher tendency to associate, as expected. Resins are smaller

molecules and it may result easier for them to adapt to the surrounding media. The enthalpies of self-association are in the same range for both fractions. The values are somewhat low, as hydrogen bonding ranges from -8 to -40 kJ/mol, while permanent dipole forces are usually between -4 and -20 kJ/mol. Several processes are involved in the self-association of macromolecules, including tangling of alkyl branches, repulsion forces and solvation effects. These contributions are not taken into account in the simple model proposed, and may be responsible for the underestimation of Δ H.

Resin solutions were then injected into 1 g/l asphaltene solutions. At such a low concentration, asphaltenes are in a low aggregated state, and there are many free interaction sites available for resins. Lower concentrations have not been used due to ITC sensitivity issues.

The resin concentrations in the syringe were calculated from R/A. The intention was to study solutions that have R/A in the range of the actual ratio in the crude oil (Table 7-1). The idea was to get a concentration equal to 0.25, 1 and 4 times R/A in the cell at half of the number of injections in each experiment. By this, it was possible to have experiments with and without saturation of sites. In some cases, an extra concentration at around 90 g/l was used if saturation had not been reached with the previous concentrations. Experiments were as well performed with 10 g/l of asphaltenes in the cell. At that higher concentration, asphaltenes are more associated and there will be fewer sites available for the interaction with resins.

Figure 7-9a shows the raw data of Alaska 95 experiments. The peaks are the result of the combination of exothermic (negative) and endothermic (positive) processes. The injection of resins into pure toluene presents positive peaks because the main process ongoing in the cell is the dissociation of resin-resin bonds. However, the presence of asphaltenes makes the peaks become smaller or "less positive".

This means there is another exothermic contribution that was not present in the dilution of resins, namely the interaction with asphaltenes counteracting the resin heat signal. The heat developed in the dilution of resins is used as a baseline and subtracted from the heat developed in the presence of asphaltenes.

Following the same assumptions as in the study of the interaction with nonylphenol, the remaining heat (Figure 7-9b) is totally assigned to the interaction

between asphaltenes and resins. It is observed that after a certain concentration is reached, the heat becomes zero. This means that all the interaction sites have been saturated and the newly injected resins do not bind to the asphaltenes. At higher asphaltene concentrations (10 g/l), the saturation is not reached, as there are more asphaltene sites in the cell.



Figure 7-9. Alaska 95. 60 g/l Resins into 0, 1 and 10 g/l ASP. (a) Raw data. (b) Integrated heats after subtraction of reference data.

7.6. Modeling Resin-Asphaltene interaction.

In order to obtain the main thermodynamic parameters of the interaction, the Terminator-Propagator (TERM) model was applied. ONE model was used as well. These two models were used successfully in the study of the interaction with nonylphenol.



Figure 7-10. Ca30 C RES= 31.4 g/l (b) Yagual C RES = 65.6 g/l. Fit of TERM model.

TERM model fits successfully all experiments, both at 1 and 10 g/l of asphaltenes (Figures 7-10a and b). The fitted Δ H and K are gathered in Table 7-4. It is observed that the enthalpies are consistently greater in experiments with higher asphaltene concentrations.

Crude	C ASP	C RES	ΔΗ	K	ΔS	ΔG	n
	(g/l)	(g/l)	(kJ/mol)	(l/mol)	(J/mol)	(kJ/mol)	
A95	1	9.0	-2.1	462.9	44.1	-15.5	1
	1	35.8	-2.7	217.8	35.9	-13.6	1
	1	35.9	-2.5	323.6	39.8	-14.6	1
	1	60.0	-2.6	205.1	35.7	-13.4	1
	1	75.3	-3.2	377.0	38.8	-14.9	1
average			-2.6	317.3	38.8	-14.4	1
	10	35.9	-3.1	172.9	32.6	-13.0	1
	10	60.0	-4.3	220.2	30.7	-13.6	1
	10	75.3	-3.7	141.1	28.9	-12.5	1
average			-3.7	178.1	30.7	-13.0	

Table 7-4. Fitted parameters of TERM Model in ASP-RES interaction.

Crude	C ASP	C RES	ΔΗ	K	ΔS	ΔG	n
	(g/l)	(g/l)	(kJ/mol)	(l/mol)	(J/mol)	(kJ/mol)	
LM1	1	18.5	-2.6	1046.1	49.2	-17.5	1
	1	47.5	-2.7	1454.0	51.6	-18.3	1
average			-2.7	1250.1	50.4	-17.9	
	10	18.5	-3.9	2282.6	51.4	-19.5	1
	10	47.5	-3.6	391.7	37.8	-15.0	1
average			-3.8	1337.2	44.6	-17.3	
Ca30	1	7.0	-1.6	996.6	52.1	-17.4	1
	1	12.0	-1.9	1410.3	54.0	-18.3	1
	1	31.4	-1.7	328.2	42.6	-14.6	1
	1	99.0	-1.7	402.5	44.3	-15.1	1
average			-1.7	784.4	48.2	-16.3	
	10	12.0	-2.1	3173.0	60.1	-20.3	1
	10	31.4	-2.3	518.1	44.4	-15.7	1
average			-2.2	1845.6	52.2	-18.0	
Yagual	1	6.0	-2.3	4522.3	62.4	-21.2	1
	1	26.1	-2.4	1336.7	51.9	-18.1	1
	1	65.6	-2.7	1086.7	49.2	-17.6	1
	1	90.0	-2.1	723.6	47.8	-16.6	1
average			-2.4	1917.3	52.8	-18.4	
	10	26.1	-2.9	498.4	42.1	-15.6	1
	10	65.6	-3.0	179.5	33.3	-13.1	1
average			-3.0	339.0	37.7	-14.4	
LM2	1	8.7	-2.2	396.6	42.5	-15.1	1
	1	33.9	-1.9	188.0	37.3	-13.2	1
	1	94.0	-2.0	205.0	37.7	-13.4	1
average			-2.0	263.2	39.1	-13.9	
	10	33.9	-2.8	148.5	32.3	-12.6	1
	10	94.0	-2.9	78.2	26.7	-11.0	1
average			-2.9	113.4	29.5	-11.8	

Table 7-4 (Continuation).

It is possible that, at 10 g/l, resins are to a certain extent able to dissociate asphaltene aggregates. This process develops an endothermic heat that is not taken into account in the model. This leads to an overestimation of the ΔH of the interaction, as it has to compensate for the dispersion of asphaltene aggregates. On the other hand, the variation of ΔH with resin concentration is very small. K presents a greater variation. The many assumptions of this simple model seem to have a greater influence on the equilibrium constant than in ΔH . This fact may be related to the observations of Goual and Firoozabadi (2002b): They reported that the addition of resins retarded the onset point but increased the amount of precipitated material. Some resins become insoluble in n-heptane after the interaction, leading to a change in the equilibrium constant. This reinforces the idea that the limit between resins and asphaltenes is very diffuse. The enthalpies are in the same range as the ones reported for asphaltene interaction with nonylphenol. They are one order of magnitude lower than the typical hydrogen bonding (-10, -40 kJ/mol) and in the lower limit of permanent dipole interactions (-4, -20 kJ/mol). Nevertheless, Buenrostro-Gonzalez et al. (2002) applied SAFT-VR (Variable Range) equation to model the precipitation of Maya asphaltenes, obtaining an enthalpy of interaction of -3.3 kJ/mol, as a fitted parameter. The agreement between this value and Table 7-4 is very satisfactory. This indicates that the ΔH obtained by means of ITC can be used in this type of equation to reduce the number of estimated or fitted parameters.

 ΔG is negative in all cases. This implies the process is spontaneous. The values obtained are inside the interval assigned to hydrogen bonding (between -10 and -40 kJ/mol, Andersen et al., 2001). The contribution of ΔS to the free energy is greater than the one of ΔH : this may indicate that the process is entropically driven. TERM model has an important drawback due to the fact that the number of sites per asphaltene molecule is fixed to one. This limits the predictive capacity of the model and creates a greater dependence of K and ΔH with the MW assumed.

Figure 7-11 displays the concentration profile predicted by TERM model in the titration of Ca30 resins into 10 g/l of asphaltenes. It is observed that the aggregation numbers of asphaltene aggregates decrease as resins are injected. On the other hand, resin-asphaltene aggregates increase their concentration as more resins are added, as

expected. The predicted aggregation numbers are lower than 10 for both ASP-RES and ASP-ASP aggregates.



Figure 7-11. Concentration profiles in Ca30 after the first and last injections, as calculated by TERM model. C RES = 31.4 g/l and C ASP = 10 g/l. (a) Asphaltene oligomers. (b) Asphaltene-resin oligomers.

ONE model was as well applied, as it includes the number of sites as a third fitting parameter. It is as well able to fit successfully the experimental data when high concentrations of resins are injected into 1 g/l (Figures 7-12a and b). If the resin concentration is not enough the reach zero heat developed (saturation of sites), the fitting does not converge. Thus, the model was not able to fit experiments with 10 g/l of asphaltenes, either. This is a drawback compared with TERM model, which has been shown to converge in all cases.



Figure 7-12. Fit of ONE model. (a) A95 CRES=90 g/l. CAsp = 1g/l. (b) LM2. CRES = 94 g/l. CAsp = 1g/l.

Table 7-5 gathers the thermodynamic parameters of resin-asphaltene interaction when ONE model is applied. The average number of sites per asphaltene molecule is in the range 1-2. This is in agreement with the estimation of Buenrostro-Gonzalez et al. (2002), who used 3-4 sites with a MW of 3000 units to successfully fit onset precipitation data with SAFT equation. Other researchers have used larger numbers: Murgich et al. (1999) assumed 9 sites available for resins molecular simulations in an asphaltene aggregate, based on the most probable interaction sites in a model molecular structure from Athabasca sand asphaltene. Wu et al. (1998) used 6 sites of interaction per asphaltene molecule in their SAFT calculations. Gonzalez et al. (2003) estimated the average number to be around 3, based on adsorption experiments.

Crude	C ASP	C RES	n	ΔΗ	K	ΔS	ΔG
A95	1	75.3	0.8 ± 0.8	-3 ± 2	257 ± 42	37.0	-14.2
LM1	1	47.5	1.1 ± 0.9	-0.5 ± 0.1	754 ± 180	53.3	-16.7
Ca30	1	99.0	1.5 ± 0.9	-0.8 ± 0.6	348 ± 91	45.9	-14.7
	1	12.0	1.6 ± 0.1	-0.7 ± 0.1	1595 ± 420	59.2	-18.6
Yagual	1	90.0	1.7 ± 0.6	-0.8 ± 0.3	382 ± 60	46.7	-15.0
	1	65.6	1.8 ± 0.7	-1.1 ± 0.5	359 ± 77	45.4	-14.8
	1	26.1	1.5 ± 0.2	-0.6 ± 0.1	2374 ± 720	62.6	-19.6
LM2	1	94.0	1.6 ± 0.9	-1.1 ± 0.4	359 ± 77	45.4	-14.8

Table 7-5. Fitted parameters of ONE Model in ASP-RES interaction.

The enthalpies are significantly lower than the ones obtained with TERM model. This may be related to the increase in average number of sites, which was assumed to be one in TERM model. The values of ΔH obtained with both models are one order of magnitude lower than the usual binding energies by hydrogen bonding or dipole interactions. It must be taken into account that the energies measured in this work account not only for association but also the energies developed in the conformational changes of the molecules to accommodate for binding. Solvation effects have as well been disregarded. It is not clear, either, that all molecules in both fractions will be equally active in the interaction. It is practically impossible to develop a model that accounts for all these effects in a system of such a complexity as asphaltene and resin fractions. For

the sake of simplicity, the heat developed is assigned to association, but it is necessary to keep in mind that the binding energies may be underestimated. Nevertheless, these experiments can provide data to state-of-art models, which do not consider the polydispersed nature of asphaltenes.

In other to check the reliability of TERM and ONE models, it was attempted to fit the experimental data with one single set of parameters. Five combinations were tried. First, experiments at all concentrations were fitted with the set of parameters (Δ H and K) obtained in the test with the highest resin concentration and 1 g/l of asphaltenes (TERM1). Second, the (Δ H, K) were taken from the experiment with same resin concentration but 10 g/l of asphaltenes (TERM10). It has previously been discussed that the Δ H depend on the asphaltene concentration, so it was expected that the values of TERM1 would not be able to fit experiments with 10 g/l. The third approach was based on the use of the average values for 1 g/l and 10 g/l gathered in Table 7-4 (TERM AV).

Forth, ONE1 uses the parameters obtained with ONE model in the fit of the experiment with highest resin concentration and 1 g/l. The last approach (ONE2) only uses the number of sites n of that experiment, while ΔH and K are used as fitting parameters.



Figure 7-13. Predicting the titration of Alaska95. C RES = 35.8 g/l and C ASP =1 g/l.

	n	∆H (kJ/mol)	K (l/mol)	%AAD
TERM1	1.0	-3.2	377	24
TERM10	1.0	-3.7	141	41
ONE1	0.8	-3.0	257	23
ONE2	0.8	-3.2	174	15

Table 7-6. Sets of parameters used in the prediction depicted in Figure 7-13 and deviation of the fits.

Figure 7-13 shows an experiment in which all models manage to fit successfully the experimental data. Table 7-6 collects the parameters used in the calculations shown in Figure 7-13, together with the average absolute deviation.



Figure 7-14. Predicted fits by TERM model of Alaska 95 experiments with 1 g/l ASP, using the average Δ H and K. (-) Fit of model. C RES = 9 g/l (\Box). 35.8 g/l (*).35.9 g/l (Δ). 60 g/l (+). 75.3 g/l (\Diamond).

Figure 7-14 shows that the average ΔH and K calculated from the five experiments with 1 g _{ASP}/l are able to fit successfully all experiments of Alaska95 asphaltenes of the same asphaltene concentration. In spite of all the assumptions made, it is possible to model all resin concentrations with one set of parameters. This indicates that the behavior of resins is the same throughout that concentration interval. On the other hand, asphaltenes present a concentration dependent behavior that cannot be caught with one single set of ΔH and K. Resins are smaller molecules with less tendency to associate,

thus, behave more ideally than asphaltenes. The surrounding media seems to be more favorable to resins, while asphaltenes are not so easily accommodated in the solvent and prefer to associate with each other.



Figure 7-15. Number of good fits of the different set of parameters tried (Total = 29).

Figure 7-15 shows the results of the five combinations of parameters in the 29 experiments performed. TERM1 and TERM10 give poor performances. They are only able to fit some of the experiments performed with the same concentration. Parameters obtained with 1 g/l of asphaltenes are not a good estimation for the behavior at 10 g/l. The state of asphaltenes is different and the parameters from other concentrations do not provide a good background for prediction. ONE1 also fails to fit experiments with 10 g/l. It is observed that ONE2 gives a good fit in 21 experiments out of 29. Nevertheless, ONE2 had only the number of sites n fixed, while Δ H and K were allowed to vary. Thus, it cannot be considered a real prediction. However, the use of average parameters in TERM model gives a good response as well in a considerable number of cases. The use of average values seems to be a good approach, as long as the concentration of asphaltenes is not changed. This set of parameters is able to fit resin behavior in a wide range of concentrations. This suggests that resins behave more ideally than asphaltenes, allowing this simple model to catch their behavior in these experiments.

7.7. Conclusions.

IR spectroscopy has shown that nitrogen groups participate more in Hydrogen Bonding in resins, while asphaltenes have a greater contribution from hydroxyl groups. Resins have been found to be more polar than asphaltenes, according to IR indexes.

The near-Infrared region has as well been analyzed. The intensity of asphaltene bands is much greater than that of resins in the scattering region. The question that arises is whether it is only because asphaltene molecules are bigger or because they associate to a larger extent. Both explanations are equally possible, according to the current knowledge about asphaltenes.

At all concentrations, the fluorescence spectra of resins also contain the peaks present in asphaltene spectra, suggesting that asphaltene spectra may be dominated by resin-like molecules. Quenching is more pronounced in asphaltenes and it starts at lower concentrations. This may indicate asphaltenes posses a higher tendency to self-associate.

Experiments with asphaltene-resin mixtures show that quenching is more pronounced in smaller molecules. These evidences prove that asphaltene spectra may be incomplete, as the small aromatic rings are easily hidden by quenching effects, while too large molecules may not emit.

ITC experiments were performed with asphaltenes and resins. It has been observed that the heat developed reaches a value of zero, indicating that saturation of sites is accomplished. Two models were applied to fit the experimental data. Still, some interesting results have been obtained: experimental values of ΔH have been obtained, together with the specific number of sites. To the best knowledge of the author, there is no data available about $\Delta H_{ASP-RES}$ in the open literature.

The predictive capacity seems to be greater for TERM model. Since TERM model is a slightly more complex approach than ONE, it is able to catch better the behavior of asphaltene-resin mixtures. The Δ H are as well more reliable, in the sense that similar values have been used in the past in modeling asphaltene behavior with SAFT equation.

In the light of the very complex mixtures analyzed, both approaches are very simplistic, as each process is characterized with one set of values of ΔH and K. A more

detailed model would be necessary, but that would increase the number of parameters greatly. A better understanding of asphaltene association is needed before developing a more consistent model.

The main drawback of that model is that the number of sites was fixed to one. It is observed that a model that allows the variation of this parameter gives optimal values that are very close to one. This may indicate that the assumption of n=1 may not be too far from reality. The values of n are in good agreement with the usual estimations in asphaltene modeling.

8. Effect of Chemical Alteration on Asphaltene-Resin Interaction

ITC experiments were performed with resins and altered asphaltenes. The aim of the study was to see how the different reactions affected the capacity of asphaltenes to associate with resins. The points discussed are:

8.1. Introduction.
8.2. Methylation.
8.3. Silylation.
8.4. Reduction.
8.5. Reductive Alkylation.
8.6. Discussion of Results.
8.7. Modeling ITC experiments.
8.8. Conclusions.

8.1. Introduction.

Chapter 5 dealt with the study of the self-association of asphaltenes upon certain alterations. For instance, it was observed that the reduction in hydrogen bonding capacity after methylation led to a significant decrease in the heat developed in ITC titrations. In this Chapter, the effect of the alteration on the interaction with resins by calorimetry is studied. Four modifications were performed on asphaltenes. Methylation blocks the acidic oxygen, nitrogen and sulphur functionalities. Silylation only affects oxygen functions. Reduction cleaved oxygen and sulphur bridges and increases the acidity of asphaltenes by subsequent protonation. Reductive alkylation added a butyl chain instead of a hydrogen atom, as occurred in reduction. See Chapter 5 and Appendix I to review with more detail the different chemistries applied in the alterations.



Figure 8-1. Ca30 Crude oil. C_{ASP} =10 g/l and C_{RES} = 31.4 g/l. (a) Raw Data. (b) Integrated heats. See the subtracted heats in Figure 8-2b. REF = Resins into toluene at 30 °C.

Experiments consist of the injection of resins into asphaltene. Both fractions are dissolved in toluene. Results with raw and altered asphaltenes are compared in terms of the variation in the heat developed. Figure 8-1 shows the titration of Ca30 resins into toluene (reference data), raw and methylated asphaltenes. It is observed that experiments in the presence of asphaltenes present smaller peaks. This shows there is an extra

exothermic contribution assigned to asphaltene-resin interaction. The difference between the heat developed in the presence of asphaltenes and the reference data is smaller for MET than for RAW asphaltenes. This means there is less interaction with resins after methylation due to the decrease in hydrogen bonding capacity. The crude oils studied are Alaska95 and LM2, which are stable oils, and Yagual and Ca30, which are two examples of problematic asphaltenes. It was foreseen that the stability of the crude would have an influence on the effect of the alterations, as observed in self-association studies. Experiments have been carried out with two asphaltene concentrations: 1.0 and 10.0 g/l. The lowest concentration was used with the intention of calculating the number of sites by ONE model, as explained in Chapter 7. A high concentration of resins (around 100 g/l) was injected from the syringe. However, the results obtained were not very satisfactory due to a low signal-to-noise. This was caused by the large dilution heats of resin solutions of high concentrations. At such high heats, the subtraction of two values (ref and raw data) very close to each other leads to a greater scattering than at low concentrations (See Appendix G).

Experiments with greater asphaltene concentration (10.00 g/l) were then carried out with a lower resin concentration to assure a better signal-to-noise ratio that would help in the qualitative study of the effect of the reactions.

To quantify the variation in interaction, two different methods were used, depending on the concentration of asphaltenes. At 10.00 g/l, the average of the difference of heat developed between raw and altered asphaltenes is calculated and expressed as percent variation:

$$Variation = \frac{100}{n} \sum_{i=1}^{i=n} \frac{(heat_{RAW} - heat_{ALTERED})}{heat_{RAW}}$$
(1)

At 1.0 g/l, the heat signal becomes zero when the sites become saturated after a certain number of injections. Equation 1 could not be used in that case, as the differences are not in the same range in all injections. Instead, the heat developed in the first point (ΔH_o) is used as follows:

$$Variation = \frac{\left[\Delta H_o(RAW) - \Delta H_o(ALTERED)\right]}{\Delta H_o(RAW)} * 100$$
(2)

8.2. Methylation.

Methylation affects acidic hydrogen and substitutes it by a -CH₃ group. Heteroatoms that respond to methylation are oxygen, nitrogen and sulphur. The substitution of hydrogen by a methyl group reduces greatly the capacity of forming hydrogen bonds between asphaltenes and resins. This leads to a significant reduction in the heat developed in asphaltene-resin experiments, both at low and high asphaltene concentrations (Figure 8-2; see the rest of the experiments in Appendix G).



Figure 8-2. Effect of methylation (a) Alaska95. $\rm C_{ASP}=1$ g/l. $\rm C_{RES}=71.0$ g/l. (b) Ca30. $\rm C_{ASP}=10$ g/l. $\rm C_{RES}=31.4$ g/l.

Table 8-1 gathers the variation of resin-asphaltene interaction in the four crudes studied. All experiments show a significant reduction in heat, based on the heat developed in the first injections. This confirms the expected decrease in hydrogen bonding capacity upon methylation. This implies that hydrogen bonding is an important factor in resin-asphaltene interaction.

Methylated Asphaltene - Resin Interaction											
Alaska95 Ca30					M2	Ya	gual				
1 g/l	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l	1 g/1	10 g/l				
-21%	-21% -26% -39% -46% -24% -16% -17% -41%										

Table 8-1. Variation of RES-ASP interaction after methylation.

It is interesting to notice, however, that instable crudes show a greater decrease than stable oils. Self-association studies showed the opposite trend (See Chapter 5).

8.3. Silylation.

This reaction attacks only the acidic oxygen, while sulphur and nitrogen functional groups remain unaltered. A significant decrease in interaction was expected, due to the block of hydrogen bonding sites. The effect observed in ITC experiments is very small. In some cases, a slight decrease is reported, like in the example shown in Figure 8-3a. The reduction in interaction is smaller than after methylation. Other experiments show a small increase in interaction (Figure 8-b).



Figure 8-3. Effect of silylation. (a) Alaska95 CASP=1 g/l CRES=71 g/l. (b) Yagual CASP=10 g/l CRES=26.1 g/l.

Silylated Asphaltene - Resin Interaction										
Alaska95 Ca30 LM2 Yagual							gual			
1 g/1	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l			
-19%	+4%	-13%	-22%	+16%	+4%	-15%	+2%			

Table 8-2. Variation of RES-ASP interaction after silylation.

It is observed that some asphaltenes behave differently at the two concentrations tested. It has been mentioned already that tests at 1 g/l present a great scattering caused by the subtraction of two large magnitudes that are very close to each other. The scattering is particularly relevant in Yagual experiments (see Appendix G). Thus, experiments at 10 g/l allow probably a better comparison among the reactions performed. At that concentration, it is observed that silylation increases slightly the interaction between resins and asphaltenes. This was also observed in self-association studies. Only CA30 presents the opposite trend. In any case, the effectiveness of silylation is small, as the variation with respect to RAW asphaltenes is small.

8.4. Reduction.

Reduction leads to an increase in the acidic content of asphaltenes. Ethers (-O-) and thioethers (-S-) are transformed into alcohols (-OH) and thiols (-SH), respectively. Reduction increases the acidity of asphaltenes, and a greater interaction with resins is expected, as they are mainly basic (Hammami et al., 1998). Yagual asphaltenes are in agreement with this hypothesis (Figure 8-4b), but Alaska95 present a decrease in interaction after reduction (Figure 8-4a).



Figure 8-4. Effect of reduction (a) Alaska 95 C_{ASP} =1 g/l C_{RES} = 71 g/l. (b) Yagual C_{ASP} =10 g/l. C_{RES} =26.1 g/l.

Reduced Asphaltene - Resin Interaction											
Alaska95 Ca30				L	M2	Ya	gual				
1 g/l	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l	1 g/1	10 g/l				
-21% -18% -5% +6% +69% +123% -7% +18%											

Table 8-3. Variation of RES-ASP interaction after reduction.

At low concentrations, reduced asphaltenes present a general decrease in interaction (Table 8-3). Ca30 and Yagual have a small variation that may be assigned to the scattering of the data. Only LM2 shows a very important increase in interaction. At higher concentrations, a generalized increase in interaction has been obtained. Only Alaska95 does not follow that trend. As pointed out earlier, experiments with high asphaltene concentrations give a more reliable picture of the behavior of altered asphaltenes, based on a better signal-to-noise ratio. Even if some sites may be occupied in asphaltene interactions, the data are of higher quality.

8.5. Reductive Alkylation.

This reaction takes a step forward with respect to the reduction explained in the previous section. The cleavage of C-O and C-S linkages is followed by alkylation resulting in the formation of ethers (O-R) and tioethers (S-R). The chain R added is a butyl group. It was foreseen that the addition of branches would create an additional steric hindrance that would reduce the interaction with resins.



Figure 8-5. Effect of alkylation. (a) Ca30 CASP = 1 g/l. CRES = 94.0 g/l. (b) LM2 CASP = 10 g/l. CRES = 35.0 g/l.

Reduction alkylated Asphaltene - Resin Interaction										
Ala	Alaska95 Ca30				M2	Yagual				
1 g/l	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l	1 g/l	10 g/l			
-40% -18% -34% -16% +18% +10% -22% -8%										

Table 8-4. Variation of RES-ASP interaction after reductive alkylation.

All crudes but LM2 show the expected decrease in interaction (Table 8-4). Figure 8-5a shows that Ca30 presents a significant decrease in heat developed in the first injections. The addition of a butyl chain creates a steric effect that makes it more difficult for resins to reach the interaction sites. LM2 does not follow this trend. The cleavage of bridges may uncover some sites that were unavailable in RAW asphaltenes. In LM2, this effect seems to be more pronounced than in the rest of asphaltenes.

8.6. Discussion of Results.

Methylation is the only reaction with a straight-forward explanation. It reduces the capacity of self-association and interaction with resins in all crudes studied. Instable crudes, like Yagual and Ca30, show a greater decrease upon methylation than stable oils. Self-association studies showed the opposite trend (Figure 8-6a).



Figure 8-6. Comparison of asphaltene alteration effects in self-association and interaction with resins. (a) Methylation. (b) Silylation.

It may be that methylated asphaltenes have their hydrogen bond sites blocked but that may allow other sites, such as π orbitals, to become available. These sites would have been unused in RAW asphaltenes for steric reasons. Resin molecules are believed to be smaller than asphaltenes, thus more able to adapt and reach the hidden sites. This would compensate for the reduction in hydrogen bonding capacity in resin-asphaltene interaction. Bigger asphaltene molecules are not able to reach those sites, and that explains why there is more reduction in self-association experiments. This effect seems to be more important in stable oils, thus allowing a greater resin-asphaltene interaction, even if hydrogen bonds cannot be formed. No further information is available to confirm or reject this hypothesis. Another possibility is related to the fact that asphaltenes are more polar than resins. Asphaltene self-association is attributed to Hydrogen bonding interactions between one H-bonding group and a basic heteroatom, as well as between Hbonding group and π electron charge of aromatic rings. On the contrary, in the case of resins, due to predominantly basic nature of resin molecules, this interaction is perhaps only attributable to H-bonding group of asphaltene with basic heteroatom of resins. The number of such bonds in ASP-ASP may be greater as compared to ASP-RES. Hence reduction in acidity by methylation causes a larger reduction in heat of association for asphaltene as compared to resins.

Silylation affects in a different manner the asphaltenes studied. Some show the expected decrease in interaction due to the blocking of hydrogen bonding sites, but others present an increase, as observed in self-association. Ca30 had an increase in self-association but not in interaction with resins. Variations less than 10% are considered to be inside the experimental error. LM2 had a decrease in self-association but the interaction with resins is slightly increased. This effect cannot be assigned to the blocking of oxygen functionalities. Therefore, other effects, like un-reacted reagent, must be taken into account. It was reported in Chapter 5 that some the reagent may still be present and its amine group may be responsible for this effect. The discussion cannot be taken further due to the lack of knowledge about the yield of the reaction.

Reduction has a different effect than in self-association (Figure 8-7). It was observed, mainly in LM2 and CA30, that the solubility in toluene was considerably reduced after the reaction. It is observed that LM2 resins present a huge increase in interaction with asphaltenes after reduction. Self-association was reduced significantly. The insolubility of a fraction of LM2 may play an important role in this case. The insoluble fraction does not dissociate upon dilution in self-association studies but resins can still adsorb to the surface of the aggregates. Nevertheless, results with Ca30 do not agree with this explanation.



Figure 8-7. Comparison of asphaltene alteration effects in self-association and interaction with resins. (a) Reduction. (b) Reductive alkylation.

Reductive alkylation shows the expected decrease in most of the cases (Figure 8-7b). Butylation creates an additional steric hindrance and makes it more difficult for resins to bind to asphaltenes. Ca30 presented an increase in self-association, while LM2 had an increased resin-asphaltene interaction. Since this increase cannot be assigned to butylation, other processes may become relevant in those cases. Tangling of branches, oxidation, reduction in MW and other effects of difficult quantification may affect the heat developed. The variation is small, and may be due only to the experimental error.

Apart from methylation, the rest of the alterations are a difficult task to explain, because there are several factors that cannot be quantified, such as the yield of the reaction, and the effect of side reactions such as de-sulphurization, oxidation and change in MW. These factors can affect greatly the capacity of self-association and resin-interaction. In terms of crude oil stabilization, reduction would be the best solution because it tends to enhance resin-asphaltene interaction while inhibiting the self-association of asphaltenes. It must be remembered, though, that not all asphaltenes behave like this, and some asphaltenes become insoluble in toluene upon reduction.

8.7. Modeling ITC experiments.

Model ONE has been applied to obtain the thermodynamic characterization of the different altered asphaltenes. Table 8-5 collected the fitted parameters of ONE model with LM2 fractions. ONE model responds very well to this particular crude, as it is able to catch the changes in heat developed observed in ITC titrations (Figure 8-8). All experiments show a good fit, and the parameters follow the starting hypothesis. For instance, methylation presents a decrease in heat developed, and ONE model gives less number of sites and less enthalpy of interaction. Reduction increases the heat of association, and the model gives a greater number of interaction sites. However, LM2 is the only crude that allowed a good correlation between experiments and model.

As explained in Chapter 7, only experiments that reach saturation of sites converge. That is to say, experiments with 1 g $_{ASP}/I$. In the case of altered asphaltenes, however, the high scattering made that some experiments with 1 g/l did not converge. This effect was particularly important in Yagual samples (See the raw data in Appendix G and the fitted parameters in J).



Figure 8-8. Fit of ONE model to LM2: (a) o = MET. $\Delta = SY$. $\Diamond = RAW$. (b) o = R-A. $\Delta = R-H$. $\Diamond = RAW$.

Crude	n	st n	ΔH (kJ/mol)	st H	K	st K	∆S (J/mol)	ΔG (kJ/mol)
RAW	2.7	1.4	-0.9	0.54	117.0	22.0	36.5	-12.0
SY	3.0	1.2	-1.3	0.55	89.5	11.4	33.1	-11.3
MET	1.3	2.0	-1.3	1.98	111.4	27.3	35.0	-11.9
R-H	3.5	0.8	-0.7	0.17	264.6	52.4	44.1	-14.0
R-A	2.2	1.4	-0.9	0.64	139.7	29.2	37.9	-12.4

Table 8-5. Thermodynamic characterization of LM2 asphaltenes by ONE model.

In addition to this, ONE model is very sensitive to the standard deviation. A variation of $\pm 1 \mu$ cal/injection in the integrated heats, which is inside the error of the equipment, gives very different sets of optimal parameters, all with a perfect fit. See the fitting parameters of the rest of experiments in Appendix J (Tables J-13 to J-16). In the rest of crude oils, it was observed that all parameters (K, Δ H and n) varied to obtain the optimal fit. For instance, Yagual experiments only showed a variation in K after silylation, instead of reducing the number of sites, as expected. The possibility of fixing the equilibrium constant was rejected, as it was considered that it would not help significantly in the qualitative study of the system. At this stage, the qualitative study is considered enough due to the important assumptions and unknown facts about the nature of asphaltenes and resins and the yield of the reactions.

TERM model was as well applied. The fitted parameters are only gathered in Table J-7, since it did not provide any helpful information to the discussion presented here.

8.8. Conclusions.

It has been found that alteration modifies significantly the interaction of asphaltenes with resins. The study has focused on the qualitative study more than in the quantitative variation of heat developed, because there are too many factors that are not explicitly taken into account in the discussion. For instance, the actual yield of the reaction is unknown. The remaining reagents may have an influence, as well as the reduction in MW, as discussed in Chapter 5.

As in self-association studies, methylation gives the most consistent results. The capacity of interaction with resins is greatly decreased upon substitution of hydrogen in polar groups by methyl group. This fact stresses the importance of polar functionalities and hydrogen bonding in the stabilization of asphaltenes by resins.

The rest of the reactions showed inconsistent results, in the sense that the response to alteration could not be generalized in both self-association and interaction with resins.

Modeling of the experiments has been carried out, and ONE model catches correctly the behavior of LM2 asphaltenes. The rest of the crudes presented a greater deviation of parameters from what was expected. ONE model had problems to fit some of the experiments due to the large scattering of the data.

9. Conclusions

The main conclusions drawn are listed in this section. They have been divided into two groups, depending on if they are based on experiments or on modeling results.

9.1. Experimental work.

9.2. Modeling of ITC experiments.

9.1. Experimental work.

1. Self-association of asphaltenes:

a) Asphaltenes associate step-wise. ITC results were compared with model compounds and no micellization region has been found even in the ppm range. Other techniques, such as Fluorescence and IR spectroscopy also give evidences of association at low concentrations (in the ppm region), which are in disagreement with the existence of a CMC in the previously reported region (1-5 g/l). These evidences are not in disagreement with the fact that the aggregates may end up having a definite size. This final size is probably not due to a solvent-phobic effect but to the presence of alkyl chains surrounding the aromatic cores.

b) Water may play a role in the association, but it is not the only driving force. No significant differences in self-association were found between dried and saturated samples. It was found that water is tightly bound to asphaltenes in solid state, limiting the capacity of obtaining ultra-pure toluene.

c) The influence of temperature in the degree of self-association has been found to be negligible in the range 30-50 °C. This was unexpected, and a satisfying explanation has not been found yet.

d) It has been observed that the heat developed depends on the solvent used. Solvents with a dipole moment different from zero show a reduction in heat developed, due to a better solvent-asphaltene interaction that leads to a decrease in the degree of self-association.

e) Asphaltenes have been altered in order to study the contribution of several factors to the self-association. Reactions such as methylation block polar functionalities and this led to a decrease in self-association in ITC studies. Silylation results were more controversial, die to the probable presence of reagent. More severe treatments like reduction and reductive alkylation alter the core of the molecules and were foreseen to have a more complex response in the calorimetric titrations. Fluorescence spectroscopy of methylated samples shows the appearance of new bands at short λ that are assigned to previously associated molecules. This discovery has a significant impact in the use of fluorescence spectroscopy to derive asphaltene properties such as MW.

f) In the fractionation with a polar mixture, ITC titrations shows that the soluble fraction develops more dissociation heat when the samples are injected into pure toluene. The picture that comes out of these experiments is an aggregate of asphaltenes formed by the combination of polar and a non-polar (probably stacking) interactions: The strengths of the molecular interactions cover a wide spectrum, from the weak (broken in the calorimetric titrations) to the very strong (present in INS fraction), which are not broken by dilution. The aggregation process would begin at very low concentrations and the size of the aggregates is limited by steric hindrance.

2. Asphaltene-Resin Interaction:

a) IR spectroscopy has shown that nitrogen groups participate more in Hydrogen Bonding, while asphaltenes have a greater contribution from hydroxyl groups. Resins have been found to be more polar than asphaltenes, according to IR indexes.

b) At all concentrations, the fluorescence spectra of resins also contain the peaks present in asphaltene spectra, suggesting that asphaltene spectra may be dominated by resin-like molecules. Effect of quenching more pronounced in asphaltenes and at lower concentrations. Quenching begins at 10 ppm in asphaltenes and around 50 ppm in resins. Experiments with asphaltene-resin mixtures show that quenching is more pronounced in smaller molecules.

c) ITC experiments were performed with asphaltenes and a model resin, nonylphenol. It was found that stable oils had consistently more interaction with this inhibitor than instable crudes. It has been observed that the heat developed reaches a value of zero, indicating that saturation of sites is accomplished. This allowed the estimation of the upper limit of interaction sites. The numbers obtained correlated rather well with the total

number of heteroatoms. An experimental procedure was established and further applied to native resin-asphaltene interaction.

d) In the case of the interaction with native resins, it was found that no correlation existed between the stability of the crude and the magnitude of the heat developed. This may be caused by the fact that resins do not need specific interaction sites to stabilize asphaltenes, as discussed in the next Chapter.

e) In the interaction of resins with altered asphaltenes, methylation gives the most consistent results. The capacity of interaction with resins is greatly decreased upon substitution of hydrogen by methyl group. This fact stresses the importance of polar functionalities in the stabilization of asphaltenes by resins. The rest of the reactions showed inconsistent results, in the sense that the response to alteration could not be generalized in both self-association and interaction with resins.

9.2. Modeling of ITC experiments.

a) The application of polymerization models that are in agreement with the step-wise approach was successfully carried out. The heats of interaction obtained are low, suggesting that a part of the asphaltenes is not active in the titration experiments, or that there are other processes that are not explicitly included in the model. The choice of the model, however, is critical in the final value of ΔH_a . The value used for the average MW is also very important.

b) Several models have been applied to fit experimental data in the interaction of asphaltenes with nonylphenol. The best fits were obtained with the model that considered asphaltenes and resins as propagators and terminators of the growth of the aggregate. The specific number of sites has been obtained with another model taken from biochemistry (One Set of Independent Sites, ONE). The n obtained range from 2 to 5 and are well in agreement with the calculated number of heteroatoms per molecule, based on elemental analysis.

c) ITC experiments were performed with asphaltenes and resins. Two models were successfully applied to fit the experimental data in resin-asphaltene interaction. Since TERM model is a slightly more complex approach than ONE, it is able to catch better the behavior of asphaltene-resin mixtures. The ΔH are as well more reliable, in the sense that similar values have been used in the past in modeling asphaltene behavior. The main drawback of that model is that the number of sites was fixed to one. It is observed that a model that allows the variation of this parameter gives optimal values that are very close to one. This may indicate that the assumption of n=1 may not be too far from reality.

d) These simple models help in the overall understanding of the interaction, but cannot account for the complexity of asphaltene fraction. This leads to significant variations in some of the parameters such as the equilibrium constants when the syringe concentration is changed. Nevertheless, state of the art models for asphaltenes are usually based as well on a single molecule describing the whole asphaltene fraction. The goal is to provide data to these models; hence the data provided in this work are of utility.

10. Future Challenges

The new challenges open for investigation and the ideas that had no time to be tested are listed in this chapter. They have been divided into two sections:

4.1. Experimental

4.2. Modeling

10.1. Experimental work.

1. Acetone fractionation of asphaltenes and interaction with resins: To continue with the work presented in Chapter 4, asphaltenes would be fractionated with several acetone-toluene mixtures. The different fractions would be studied by IR and FS and the interaction with resins would be tested by ITC, to see the evolution of Δ H and number of sites.

2. Toluene-Heptane mixtures: The behavior in a less favorable solvent would be studied. A sequence of heptol mixtures would be used to study the interaction between asphaltenes and resins. At last, experiments in n-heptane would be carried out. It would be interesting to see if an adsorption isotherm can be obtained, as the ones reported by Leon et al. (1999) with model compounds. The experiments could be fit with a model that combines association and adsorption, as presented by Marczewski and Szymula (2002). The presence of solids may cause problems, as the stirring would create a friction with the walls of the cell, thus creating an extra heat contribution that may saturate the signal.

3. Experiments in oil: De-asphalted oil would be injected into asphaltene solutions in both toluene and n-heptane. This would help to see the differences in behavior between organic solutions and a complex system like crude oil.

4. Resin fractionation: Resins are sometimes further fractionated into two groups, one being more polar than the other. The more polar co-precipitates with the asphaltene fraction and is removed in the second washing with heptane. Flocculation onset measurements have given evidence that the polar fraction increases the stability of asphaltenes, while the less polar fraction has very little effect (Hammami et al., 1998). It would be interesting to see if the same phenomenon is observed in ITC titrations.

5. Molecular weight: Since it is a critical property that affects directly the success of the models, a true average value or a reliable distribution of MW should be obtained. As discussed in Chapter 4, current methods are not able to give a conclusive answer to this question.

6. Water-asphaltene interaction: It has not been reported in the thesis, but it was quite interesting to notice that the water content *decreased* when the asphaltenes are added to the water-saturated toluene, and it *increased* when the water content of the toluene is very low. This indicates that there may be some kind of equilibrium in the water-asphaltene

interaction, some kind of equilibrium value, to which the water content tends to when the asphaltenes are added. This phenomenon should be further studied.

7. Influence of water in resin-asphaltene interaction: Experiments have been performed with dried samples. It would be interesting to see if the interaction is increased by the presence of water.

8 Interaction of altered asphaltene with nonylphenol: Since experiments with resins give such a complex response, it has been decided to test nonylphenol again, as explained in Chapter 6. It is expected to give a more straight-through behavior than the complex resin fraction.

9 Altered resins with asphaltenes and altered asphaltenes: Following the study on altered-resin interaction, the effect of alteration of resins should as well be investigated.

10. Interaction of asphaltenes with naphthenic acids: These acids are naturally occurring components of most crude oils. They also cause significant problems due to precipitation in the form of naphthenates. The information that can be obtained by ITC can be of utility in the development of the tools to predict and solve these problems. Naphthenic acids are polar molecules that have been shown to interact with asphaltenes (Östlund et al., 2003). They are usually collected in the resin fraction (Auflem et al., 2002). Therefore, it would be a similar study to that explained in Chapter 7 but focusing on a particular fraction of resins.

11. Acid-Basic fractions of asphaltenes: The same procedure would be applied as in the acetone fractionation. Fractions would be separated following the methods described by Khulbe et al. (1996).

12. Asphaltene separation: It has been claimed that only a fraction os asphaltenes separated in the laboratory from dead oil are actually responsible for deposition problems in live oil. It is therefore necessary to develop a separation procedure that narrows the asphaltenes obtained to obtain a more significant material.

10.2. Modeling.

1. ITC Experiments: Modeling of ITC experiments is still open to improvements. The models reported in this work are able to give good estimations of enthalpies and number of sites, but once the understanding of these complex mixtures is deeper, a more detailed

model should be implemented and tested with the experimental data reported here. This would include a polydispersed description of the system, both in molecular weight and activity in self-association and interaction with resins. A method to include polydispersity in asphaltene modeling was presented by Mannistu et al. (1997).

2. State of ASP-RES in crude oil: It has been especulated that the Pfeiffer and Saal model has created a lot of confusion in the general view of the state of asphaltenes in crude oil. In the light of ITC experiments, it seems like they do not need a specific interaction site to stabilize asphaltenes. It looks more like there is a transition from polar to non-polar species. Therefore, a new whole approach to asphaltene behavior should be formulated, more in connection with the idea that asphaltenes and resins may be part of the same distribution of species. The fact that the addition of a non-solvent like methanol can solubilize some of this material things back into solution when something in asphaltenes is insoluble leads to the believe that resins and asphaltenes are part of the same distribution. Stable oils have a greater amount of resins, that is to say, the smaller and less polar compounds, which allow a better solubilization in the light crudes.





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3. Asphaltene precipitation vs. crystallization: It has been observed that asphaltene precipitation has similarities with crystallization. In both cases, small units are first formed (nucleation or formation of oligomers). Once there are too many of these units, they get together by the action of weak forces like VdW. This idea could be a good starting point to develop a new model.

APPENDIXES
APPENDIX A. ACKNOWLEDGEMENTS

I must apologize if somebody thinks this list is too short, but those who have been helpful, they know it already.

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APPENDIX B. MATERIALS

Toluene (spectroscopic grade, from Rathburn) was double-dried, first with Na and then with molecular sieves, in order to avoid the influence of water in the self-association of asphaltenes. The solutions with different water contents have been prepared by mixing dried and saturated toluene.

Asphaltenes have been obtained from Alaska 95 (USA), NM1, MOT, LM1, LM2 and Yagual (Venezuela), OMV (Austria), KU (Mexico), Lagrave (France) and Ca30 (Qatar).

Altered asphaltenes have been obtained from Alaska 95, LM2, Yagual, Lagrave and Ca30 crude oils.

Resins have been obtained from Alaska 95 (USA), LM1, LM2 and Yagual (Venezuela), and Ca30 crude oils.

Nonylphenol: Obtained from Aldrich. Purity 98%. It was not further purified.

Coronene: Obtained from Fluka. 97% purity. Used as received.

Pyrene: Obtained from Acros. 98% purity. Used as received.

SDS: Obtained from SERVA (>99%). Used as received.

Sodium Cholate: Used as received.

Rhodamine 6G: Used as received.

Reagents for chemical alteration: n-Tetrabutyl Ammonium Hydroxide (40% aqueous solution), Methyl iodide, Sodium Nitrate, THF, Pyridine, TrimethylchloroSilane (TMS), Hexamethyldisilazane (HMDS), Potassium, n-Butyl Iodide and absolute Ethanol. All reagents were of the highest purity grade available, from Sigma Aldrich Co.

Silica Gel. From Aldrich. Grade 62. 60-200. Mesh 150 Å. Used as received.

Pyridine: From Bie&Berntsena-S. 99%.

Carbon tetrachloride: From Flocka. 99.5%.

Carbon disulphide: From Rathburn. Glass distilled grade.

Figure B-1 shows some of the compounds used.



Figure B-1. Schematic drawings of some of the chemicals used.

APPENDIX C. Asphaltene and Resin Separation

Asphaltene Separation.

Asphaltenes are obtained following a modified IP143 procedure: asphaltenes are precipitated with n-heptane (30 ml/g oil) and a constant temperature (25 °C) was used in all separation steps. The composition of asphaltenes depends on the temperature of separation, on the solvent used, on the time of contact and on the ratio of solvent to crude oil. n-Heptane is preferred over pentane due to solvent evaporation issues (Speight, 1999). The mixture of crude oil and n-heptane is treated in an ultrasonic bath for 30 minutes and left overnight to equilibrate. The solid asphaltenes are filtrated with the help of vacuum using MILLIPORE filters and the sequence is repeated several times to remove the resins adsorbed onto the asphaltenes, until the effluent liquid is colourless. The precipitated asphaltenes are recovered with toluene.

This solution is concentrated by distillation of toluene in a rotavapor. Then, the remaining solution is dried under a nitrogen bath. Solid asphaltenes are then repeatedly washed with n-heptane using ultrasonic mixing and separation by centrifugation. This last step removes the remaining resins and lighter species that are still adsorbed on the asphaltenes. This resin material has been reported to decrease the average molecular weight of asphaltenes by around 50%. After this treatment, the samples are dried in an oven under vacuum. The solid samples are stored in a dark place. The sample preparation for ITC experiments is described in Appendix E.

There is an ongoing debate about the best way of obtaining asphaltenes, as different research groups have more or less their own procedure. Issues like best precipitant, temperature and washing procedure have a significant influence in the asphaltene yield and quality. Comparisons between results obtained by different centres may be hindered by this fact. The open discussion can be reached at http://asphaltenes.syncrude-research.karo.com/users/folder.asp.

Resin Separation.

If asphaltenes can be obtained in many different ways, the possibilities with resins are increased twofold. Two main procedures can be applied: precipitation with a solvent, thus defining resins as a solubility class, or separation through a chromatographic column. Goual and Firoozabadi (2002) presented a good review of the different solvents that have been used in the past to separate resins from aromatics and saturates. The separation procedure has a significant impact on the properties of the resulting resins. The amount of resins recovered by adsorption is greater than the one obtained by precipitation with liquid propane (Goual and Firoozabadi, 2002). Resins separated with liquid propane may only contain the most polar fraction of resins, and the resins obtained by adsorption may contain some of the biggest aromatic compounds due to the large retention time.

HPLC was initially used to obtain resins. The equipment is a SHIMADZU CLASS VP (Holm & Holby). Aromatics and saturates are sequentially eluted with n-heptane and toluene, while resins are the only compounds that remain adsorbed on the packing material. Resins are recovered with a back flush of 10% methanol in toluene. Leon et al. (2002) used also back-flush chromatography to recover the resins, but with methanol + acetone + chlorophorm (15:15:70). HPLC separation was discarded, as the amounts of resin recovered were very small (around 0.2 grams per run), compared with the amount of solvent used (around 5 liters of toluene per day) and the time spent in the separation.

Resins were obtained by atmospheric liquid chromatography with silica gel as packing material. The de-asphalted oil was injected into a column with n-heptane as eluent and resins were retained in the packing material while saturates and aromatics could pass through. The solvent is sequentially changed to toluene to avoid the breakage of the column due to the change in solvent polarity. Resins were recovered with a mixture of 10% methanol in toluene. This is a modified scheme based on the proposed procedure by Speight (1999, page 275). In that book, the sequence of solvents is: first pentane, then benzene and finally a methanol-benzene mixture. Since asphaltenes have been defined in terms of solubility in heptane and toluene, they were used instead of benzene and pentane.



Figure C-1. ITC titration of Alaska95 resins obtained by two different processes.

Figure C-1 shows that resins obtained at atmospheric pressure (LC) behave significantly different from those obtained in a High Performance Chromatographer (HPLC). The quality of the resins obtained depends strongly on the method used to obtain them, as suggested by Goual and Firoozabadi (2002). A unified method should be proposed to be able to compare results among different laboratories.

APPENDIX D. VP-2000 ITC Calorimeter Optimization

Preliminary tests.

The equipment was received in September 2000. Several actions were taken to enhance the performance of the device in aqueous experiments:

- The microcalorimeter was electrically isolated, so that no other equipment was connected to the same electric group.
- Increase the initial delay in order to allow the syringe reach the cell temperature before the first injection. This had little effect, as the baseline equilibration time is in the range of 20-30 minutes, which should be enough for the syringe to reach that temperature.
- Instead of degassing the samples in the ThermoVac device supplied with the calorimeter, the vials were placed in an Ultrasonic bath (1510 Branson) for around 20 minutes. A significant improvement in the signal was observed, in terms of stability of the baseline and homogeneity in a reference test (Figure D-1). The noise is very small and the peaks are reproducible.



Figure D-1. Titration of water with distilled deionized water.

Toluene is supposed to give more problems than water, because it is a much more volatile solution and it is prone to higher baseline noise and more imperfections in the

data. The temperature influence was also studied, in order to find out the temperature that could be reached (Figure D-2). The test at 80 °C could not be performed due to a too long calibration time, so 70 °C is taken as the upper limit.



Figure D-2. Temperature influence in toluene tests.

Up to this point, water was always used in the reference cell, despite the advices to use the same liquid in the sample and in the reference cell (Blandamer, 1998). It was believed that water was less volatile and therefore would give a better baseline. To check the convenience of this approach, tests with SDS (See Chapter 3) were performed with both water and toluene in the reference cell. The results show that there is a significant difference in the heat measured, of around 10% (Figure D-3).

The qualitative shape is the same in both cases, but the magnitude of the peaks is also important and the experiment in which the reference cell is filled with a different liquid seems to underestimate the heat developed in the cell. The conclusion is that the same liquid must be used in both the sample and reference tests.



Figure D-3. Injection of 30 g/l of SDS into water. (a) One peak of raw data. (b) Integrated heats.

It is observed that the peaks are broader in the case of using water in the reference cell. It has been claimed that the liquids in both cells need to have more or less the same heat capacity for optimal performance of the ITC. Toluene has a Cp equal to 1.70 J/gK vs. 4.18 J/gK of water (CRC, 2002). The lower Cp of toluene makes the system respond faster to variations, to the expense of giving smaller peaks and underestimating the heat developed in the demicellation.



Figure D-4. Injection of dried toluene into itself. Raw data.

The injection of dried toluene into dried toluene with water and toluene in the reference cell confirmed what was explained above. The heat developed is lower when the reference cell is filled with toluene and the baseline shows less noise (Figure D-4). This experiment allowed the calculation of the heat attributable to the friction losses of the injection process. This was estimated to be around $-2 \,\mu$ cal/injection.

Ultrasound treatment.

The ultrasound (US) treatment is used to degas the samples, and it also enhances the dissolution of asphaltenes. The aim was to check if US had any negative influence in the results. Tests were performed with dried toluene, and the parameters used were the same as the ones set usually in the asphaltene tests ($V_i = 10 \ \mu$ L, spacing = 180 sec). One test was carried out with dried toluene directly taken from the bottle and the second test was done with dried toluene after one hour of US treatment. US increases slightly the temperature of the solution, and therefore there is some stripping of liquid. As the water content is very low, toluene is preferentially stripped off, and the water content increases somewhat. The water content increased from 0.0017% to 0.0038%.



Figure D-5. Influence of US in toluene-toluene titrations (raw data).

The heat evolved without US is not constant (Figure D-5). It decreases with time, and, in principle, this is not what I would expect from the injection of pure toluene into pure toluene. On the other hand, the test with US-toluene has a very similar heat evolved

in all the injections. The noise in the baseline is also slightly lower after US. The conclusion is that the Us-treatment has a positive effect in the titration curves, as the response obtained has a higher quality. This pays off for the small increase in water content.

Reproducibility.

Initial experiments with asphaltenes showed very little reproducibility. It was noticed that the equipment was not to blame for the low reproducibility of the results: when the tests were carried out the same day with samples taken from the same vial, the results obtained where identical. The stirring speed was also investigated and it was shown that it did not have any influence in the results. In any case, the heat signal seems to have slightly less noise when the speed is low (260 and 300 versus 540).

Therefore, the attention was focused on the other two possible reasons, namely the **sample handling** and the **surroundings of the apparatus**. The idea was to keep the working conditions as stable as possible.

The asphaltenes were stored as a solid phase before taking the samples; the solid phase was homogenized by **breaking the grains and forming a powder**, in order to make the sampling more homogeneous. The asphaltenes were then dissolved in toluene and kept **in sealed vials** in a dark place: in previous studies, they were kept in small tubes that did not close hermetically, and the suspicion was that the water content varied with time, as the samples were in contact with the atmosphere. Besides, the samples were **left for at least 24 hours** to let them reach equilibrium, due to the fact that slow kinetics of re-dissolution have been reported (Alboudwarej et al., 2002 and Aske et al., 2002). Strausz et al.(2002) reported that Athabasca asphaltene state of association depends on the age of the solution: 82% of the total fraction dissociated after 14 days: the molecules suffer from a great redistribution of the size of the aggregates. This proofs a dynamic equilibrium between low-MW species and their aggregates. The lifetime of the aggregates depends on the conformation of the molecules: those with the right shape and sites will form associates of longer lifetime

The **ultrasonication** has also been improved, as the sealed vials are placed now in a glass with toluene, to avoid any contact with the water of the bath. Now that the vials are sealed, it is necessary to insert a small needle through the cap of the vial in order to let the bubbles get out of the solution. This decreases the speed of degassing, and the new optimal time has been found to be 50-60 minutes.

In order to assure that the conditions in the surroundings of the calorimeter are as stable as possible, the apparatus was placed inside a **glove box**. With this, the influence of the fluctuations in temperature and draft in the room are minimized. A few dishes with **grains of silica gel** were placed in the interior of the glove box in order to keep the humidity in the inside of the box in a low and constant value.

After these modifications, the reproducibility in consecutive tests was very satisfactory. A sample was prepared with C = 15 g/l and tested in different days (Figure D-6). The heat developed did not vary from day to day.



Figure D-6. Influence of the time elapsed between sample preparation and the experiments.

Strausz et al. (2002) suggests that it is possible that asphaltene molecules present tangling of polymethylene-bridged structures with long chain lengths. These associations

may be difficult to form due to the salvation and the number of sequential conformation steps necessary for it to break. Tanaka (2003) also showed results that may be interpreted through tangling. Thus, when asphaltenes are in solution in may need a long time before the stable aggregates are totally formed.

It is also important to remember that the vials are opened in between tests. The ITC syringe has a stirrer at the end and it cannot suck the solution from the sealed vial. Therefore, some air comes in the vial in the preparation of the test. Asphaltenes are known to oxidize faster in solution than in solid state. The addition of oxygen groups may increase the self-association, which would lead to the observed increase in heat developed. Karlsson (2003) also reported an increase in hydrogen bonding upon aging.

Reproducibility is as well related to the magnitude of the heat developed. Surfactants develop greater heats than asphaltenes and therefore the reproducibility is higher. The solvent used also play a role. A very volatile solvent like toluene may present evaporation problems, both during the storage and the titration, which may lead to a change in concentration that may explain the slight variations among tests. The species tested also have an influence. Asphaltenes may suffer from oxidation and light degradation during the preparation of the samples and tests, which may lead to a greater content of oxygen that can increase the degree of self-association.

Influence of the control mode.

The VP-ITC calorimeter has three options with respect to the control mode. The feedback system can operate with a high gain, with a low gain (both are considered active modes) or without gain (passive mode). The speed of response decreases as the gain decreases. On the other hand, the sensitivity and the stability of the baseline are increased. The parameters of these control modes can be changes through the computer interface but it is not recommended by the manufacturer. The aim of this set of experiments was to determine which control mode was more convenient for asphaltene experiments.

The sequence of tests was the following: first, two tests were performed using the high gain of the control system feedback; one of the tests was carried out with dry toluene samples and the other with 75% water-saturated toluene, so that the influence of the

water content was also checked. After that, another set of tests (one with dried and one with 75%-water saturated toluene) was done, but in this case the feedback was set to have no gain (passive mode). The test with dried toluene was repeated one week after to check the reproducibility of the results.

The first figure shows the differences between the peaks in the tests with active and passive mode. When the gain of the feedback is high, the control system acts very fast and sometimes it overacts, so the response becomes a second order system, with an interval of time where the heat signal is negative, due to the fact that there was too much heat supplied to the cell. Nevertheless, the variation in heat obtained by integrating the peak with and without the second order region was significantly the same. On the other hand, without feedback gain, the response is slower, but there are no exothermic contributions that could mislead to the conclusion that there are several processes ongoing in the cell at the same time, with some of them being exothermic and some endothermic.



Figure D-7. Influence of control mode on: (a) peak shape; (b) baseline.

With respect to the baseline noise, the influence does not seem to be that big, but it is also important to notice that the time the sample spends inside the cell increases a lot (3 vs. 7 hours) and the effect of the evaporation might be more important in passive mode. The noise is 0.008 and 0.010 μ cal/sec for passive and active mode, respectively.



Figure D-8. Comparison of titrations in active and passive mode. (a) Dried toluene into toluene. (b) SDS into water.

Some tests were also performed with pure toluene, injecting dry toluene into dry toluene, with toluene in the reference cell as well. Figure D-8a shows the results and the comparison between the integrated peaks of the tests in active and passive mode.

The test in passive mode shows an increase of the area and height of the peaks after 150 minutes, which might be caused by the evaporation of the toluene. In active mode, all the peaks have more or less the same size, and the only difference between the two solutions is the time they actually spend inside the cell. Tests with aqueous solutions of SDS were carried out in active and passive mode (Figure D-8b). The control mode does not have any influence in the heat developed. Water is not as volatile as toluene, so solvent evaporation is not an issue, and the heats are bigger than in the other cases, so the presence of a small second order peak is negligible.

SDS experiments have shown that the heat developed is the same in both cases, while toluene tests have demonstrated that passive mode may take too long so that evaporation

issues may be of importance. The conclusion is that active mode is more attractive for our experiments.



Influence of the volume per injection.

Figure D-9. LM1 resins into dried toluene with 5 and 10 μl per injection.

Experiments can be performed with several volume injections. 3 μ l has been found to be the limit for operational use: experiments with less volumes show significant variations in heat developed from injection to injection, as if the volume injected was not kept constant. Higher volumes do not show this problem. Besides, it has been observed that the heat developed expressed as heat per gram injected is independent of the volume injected, as expected (Figure D-9).

Signal-to-noise ratio.

In the initial tests the noise was 5-10% of the size of the peaks. After the optimization procedure, the noise has been significantly reduced (Figure D-10). The baseline is automatically created by the computer. Most of the times it gives a good performance, but in some cases the baseline needs to be corrected.



Figure D-10. Comparison of noise levels. (a) November 2000. Cs = 30 g/l Boscan asphaltenes.(b) November 2003. Cs = 30 g/l Alaska 95 asphaltenes.

Comparison between LKB and VP-ITC calorimeters.

Previous studies in this laboratory were performed on asphaltenes with a LKB 2277 bio activity monitor microcalorimeter. CMCs were calculated as the point at which a break in the cumulative heat was observed (Andersen et al., 1991 and 2001). Nevertheless, this break is not observed in the experiments with the VP-ITC calorimeter. Instead, an exponential-decay shape is observed. The comparison of the enthalpograms of the two equipments shows that the curves are not that different (Figure D-11). The combination of a poor signal-to-noise ratio and the belief that THERE WAS a sharp break led to the conclusion that there was a CMC. In any case, it was already reported that the "break" would be more likely due to the transition from a less associated state to a more associated state (Christensen and Andersen, 1999), in agreement with SEC measurements (Andersen, 1994), which indicate there is a graduate change up to a certain concentration.



Figure D-11. Comparison of the performance of the two calorimeters. (a) LKB 2277⁸ (b) VP-ITC 2000.

Final remarks.

The optimization of the calorimeter has allowed us to work at very low concentrations and heats measured ($<5\mu$ cal/injection), yet keeping a good noise level and peak definition (Figure D-12).



Figure D-12. Ranges of heats in the experiments performed.

APPENDIX E. ITC EXPERIMENTAL PROCEDURE

a) Preparation of the samples

Asphaltenes are photosensitive and also very hydroscopic. That is the reason why they are stored in a dark and dry place. The preparation of the solution starts with the weighing of the solid asphaltenes that will be used. From this stage on, all the samples must be sealed, so it is necessary to use the appropriated vials.

The usual volumes of sample needed are 1 ml per test for the sample placed in the syringe and 3 ml per test for the one in the cell. Both values include the 0.5 ml needed to perform two Karl-Fischer titrations to measure the water content in each test. For example, if a sample will be used two times in the syringe and 1 time in the cell, it is necessary to prepare 5 ml of sample. The mass of asphaltenes needed is calculated with the following formula:

Mass asphaltenes (g) = Volume of sample (ml) * Conc. desired (g/l) * 10-3 Once the solid asphaltenes are in the vial, the volume of toluene is injected by means of a pipette. The vial is then sealed and taken to the ultrasound treatment.

b) Ultrasound treatment

The aim of the ultrasound treatment (US) is double: to dissolve faster the asphaltenes and to eliminate the gas dissolved in the toluene. The ITC equipment is very sensitive to the presence of bubbles and the solutions must be gas-free. The ultrasound device is filled with water until the working level, and a small glass is placed over the grid. Sometimes, the glass has been filled with toluene, to assure that there is not much water vapor in the environment that could go inside the vial. However, the effect is very small, and the glass is usually filled with water. The vial is still sealed, but there is some gas that needs to get out of the solution, so it is necessary to put a small needle through the cap, so that the gasses can get out of the vial.

The normal times of US treatment are 50 minutes for asphaltenes samples. After the US treatment, the needle is removed. The sealing cap is changed, as there is a small hole in it due to the needle. It can allow some airflow inside the vial.

c) Storage

The samples are stored in a drawer, below the calorimeter. The vials must be labeled with the following information: Concentration of asphaltenes, Water content, Crude Oil and Date of preparation.

d) Maintenance of the calorimeter

Before performing a test, it is necessary to check the following things:

1. The reference cell must be filled with toluene. There is a small screw in the calorimeter tool kit to open the reference cell. The toluene used does not need to be neither dried nor US-treated. There must not be air bubbles inside the reference cell. Allow 24 hours of stabilization between the change in reference cell and the tests. The liquid in the reference cell should be changed after 10-12 days.

2. Check that the silica gel inside the glove box is not saturated. If so, it is necessary to put it in the oven at ca. 100 °C for 20-30 minutes (until it recovers its initial orange color). It is important not to perform the test right after placing again the silica gel inside the calorimeter after the treatment in the oven because there will be an increase in the temperature inside the glove box, as the silica gel is quite hot. There is a thermometer inside the glove box to check the temperature. Normally, it reads something between 24-27 °C. That small variation in temperature has been proved to have no influence on the results.

e) Preparation of the test

First, the solution that is going to be placed inside the cell is taken with a syringe. It is necessary to take 2 ml with the 2.5 ml-syringe. The bubbles inside the syringe must be removed. Some of the solution will be lost during the removal of the air bubbles. The volume needed is 1.5 ml, so the elimination of the gas bubbles has to be done carefully. Once the syringe is filled, the solution is slowly injected inside the sample cell: *the end of the syringe has to touch gently the bottom of the cell in order to remove the air.* Then, the solution is injected slowly. If the vial still contains solution to perform more tests, it has to be sealed again right after taking the sample with the syringe.

The white stopper is placed on top of the cells, to avoid any contamination of the cell while preparing the syringe solution. This is the most delicate step of the preparation of the test. It is necessary to ask for some help, because the computer has to be used at the same time, and both hands are inside the glove box. The vial that contains the solution that will go in the syringe is unsealed and placed inside the calorimeter. It is as well necessary to have inside the glove box the 2.5ml-syringe and also a small rubber tube. The syringe plug has to be in the OPEN position; that it achieved by pressing the button OPEN FILL PORT in the computer screen.

The rubber tube has to connect the 2.5ml-syringe to the upper connection of the syringe. The holder attached to the calorimeter is not suitable for the type of vials used, so the syringe must be hold with the left hand over the vial, making sure that at least the whole stirrer is dipped inside the solution. The right hand is used to hold the 2.5ml-syringe and this 2.5ml-syringe is used to suck carefully the solution from the vial into the syringe. In order to avoid wasting too much solution, it is a good idea to suck carefully until the level of liquid reaches the upper connection to the rubber tube. Once there, the person in charge of pressing the buttons in the computer has to press CLOSE FILL PORT. Right after that, the person in charge of the syringe has to suck again with the 2.5ml-syringe before the port closes totally, in order to remove the last bubble of air. It is important that there are no bubbles left, because if there are any, the signal will be distorted.

Then, the cell has to be refilled, by pressing the button PURGE-REFILL. This has to be done three times. Once this has been done, the rubber tube has to be disconnected, and the tip of the syringe must be cleaned with toluene because it has been in contact with the asphaltenes (Figure 8). Once the tip is clean, the syringe is carefully placed inside the cell.

f) Cleaning of the cell

The 2.5ml-syringe is used to clean the cell:

- 1. First, remove the solution from the cell.
- 2. Fill the 2.5-ml syringe with toluene and fill and empty the cell three times.

3. Empty and fill again the 2.5ml-syringe with a new solution of toluene and repeat the refill another three times.

4. Do it again. Normally, three times is enough, but if the concentration of asphaltenes was high, maybe it is necessary to repeat it once again.

5. Dry the cell with air, using the THERMOVAC.

g) Cleaning of the syringe

In the first step, a big vial (20 ml) is placed under the holder of the syringe, making sure there is enough toluene to cover the tip of the syringe. Press the button CLOSE FILL PORT (or UP 29 times) to suck the toluene. Press PURGE-REFILL a couple of times. Change the toluene solution and repeat the same procedure.

Then, press the button OPEN FILL PORT and take the syringe out of the glove box. Connect the rubber tube to the upper connection and the rubber tube to the 2.5mlsyringe, just as was done previously in the preparation of the test (Figure 9). Use the 2.5ml-syringe to suck cleaning toluene from a beaker, through the syringe, to finish the cleaning. Repeat this until the toluene that comes out is transparent.

h) Measurement of the water content

The amounts normally used for the KF-Titration are in the range 200-250 μ l/test. Two titrations per test are at least recommended, to be able to calculate the average.

COMMENTS

1. Do not forget to clean the external surface of the syringe. It has been in contact with the solution in the cell during the experiment, and some asphaltenes may have deposit on it.

2. If the white end of the plug of the 2.5 ml-syringe gets swollen due to the effect of toluene, then it is not easy to suck or eject the solution. To solve this problem, it is necessary to dry well the interior of the syringe with compressed air and then to rinse it with water a couple of times. After rinsing with ethanol to remove all the traces of water, dry again with compressed air. It will be ready again to be used.

APPENDIX F. ITC TROUBLESHOOTING

A) Baseline is saturated negatively:

If the signal of the baseline goes down to -40 μ cal/sec as soon as the test is started and stays there, it means that the syringe is bent and that it touches the walls, giving an extra exothermic signal that saturates the baseline. \Rightarrow Try to align the syringe so that it is straight. It must be done carefully, to avoid excessive bending of the syringe that may result in permanent damage of the material.

B) There is a small initial negative peak in all injections:

Sometimes, in the injection of asphaltenes into pure toluene, a small exothermic peak is observed at the beginning of each injection. It is believed that it is caused by the presence of small bubbles of air inside the syringe, as the peak disappears when the experiment is repeated taking special care in filling the syringe properly. \Rightarrow Special care must be taken when filling the syringe in order to remove all the air bubbles.

C) The baseline has a lot of noise:

The sample is probably ill-degassed. \Rightarrow The sample is not well ultrasonicated. Asphaltene samples must be degassed 50 minutes, while toluene has to be degassed at least 20 minutes.

D) The heat signal oscillates after each injection with decreasing amplitude:



This effect, combined with the negative value of the baseline, indicates that the syringe is bent. \Rightarrow Try to align the syringe as in the case A). If the problem persists, change the syringe.

E) The raw data looks like this:



The syringe is bent. \Rightarrow Try to align the syringe as in the case A). If the problem persists, change the syringe.

F) The VP-Viewer program gives an error message saying that the limit temperature has been reached (0.9 °C):

The Calorimeter may be disconnected. \Rightarrow Check the connection to the main electrical source.

<u>G) When opening the Origin file with ITC extension, an error appears that says</u> something like "Cannot read data":

Some words are forbidden in the name of file. IF the letters RAW are written inside the filename, ORIGIN will not be able to open the file \Rightarrow Change the name of the file.

APPENDIX G. ITC TESTS

For space reasons, only resin-asphaltene and resin-altered asphaltene experiments are shown here. The rest of experiments are collected as electronic files in the CD attached.



A) Asphaltenes and resins.

A.1) Alaska95

Figure G-1. Alaska 95. (a) C_{RES} = 60 g/l. (b) C_{RES} = 35.9 g/l.



Figure G-2. Alaska 95. (a) C_{RES} = 75.3 g/l. (b) C_{ASP} = 1 g/l. C_{RES} = 9 g/l.





Figure G-3. Ca30. (a) $C_{ASP} = 1 g/l$. $C_{RES} = 12 g/l$. (b) $C_{ASP} = 10 g/l$. $C_{RES} = 31.4 g/l$.



Figure G-4. Ca30. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 99$ g/l. (b) $C_{ASP} = 1$ g/l. $C_{RES} = 6.96$ g/l.





Figure G-5. LM1. (a) C_{RES} = 47.5 g/l. (b) C_{RES} = 18.5 g/l.





Figure G-6. LM2. (a) C_{RES}= 94 g/l. (b) C_{RES}= 33.9 g/l.



Figure G-7. LM2. C_{ASP}= 1 g/l. (b) C_{RES}= 8.7 g/l.

A.5) Yagual



Figure G-8. Yagual. (a) C_{RES} = 65.5 g/l. (b) C_{RES} = 26.1 g/l.



Figure G-9. Yagual. (a) $C_{ASP} = 1 g/l$. $C_{RES} = 90 g/l$. (b) $C_{ASP} = 1 g/l$. $C_{RES} = 6 g/l$.





Figure G-10. Alaska 95. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 71$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 35.5$ g/l.



Figure G-11. Ca30. (a) $C_{ASP} = 1 g/l$. $C_{RES} = 91.4 g/l$. (b) $C_{ASP} = 10 g/l$. $C_{RES} = 31.4 g/l$.



Figure G-12. LM2. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 94.0$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 35.0$ g/l.



Figure G-13. Yagual. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 90.0$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 26.1$ g/l.





Figure G-14. Alaska 95. (a) $C_{ASP} = 1 g/l$. $C_{RES} = 71 g/l$. (b) $C_{ASP} = 10 g/l$. $C_{RES} = 35.5 g/l$.



Figure G-15. Ca30. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 91.4$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 31.4$ g/l.



Figure G-16. LM2. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 94.0$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 35.0$ g/l.



Figure G-17. Yagual. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 90.0$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 26.1$ g/l.



B.3) Reduction.

Figure G-18. Alaska 95. (a) $C_{ASP} = 1 g/l$. $C_{RES} = 71 g/l$. (b) $C_{ASP} = 10 g/l$. $C_{RES} = 35.5 g/l$..



Figure G-19. Ca30. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 91.4$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 31.4$ g/l.



C RES (g/l)



Figure G-21. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 90.0$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 26.1$ g/l.

B4) Reductive Alkylation.



Figure G-22. Alaska 95. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 71$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 35.5$ g/l..



Figure G-23. Ca30. (a) $C_{ASP} = 1 g/l$. $C_{RES} = 91.4 g/l$. (b) $C_{ASP} = 10 g/l$. $C_{RES} = 31.4 g/l$.



Figure G-24. LM2. (a) $C_{ASP} = 1 \text{ g/l. } C_{RES} = 94.0 \text{ g/l.}$ (b) $C_{ASP} = 10 \text{ g/l. } C_{RES} = 35.0 \text{ g/l.}$



Figure G-25. Yagual. (a) $C_{ASP} = 1$ g/l. $C_{RES} = 90.0$ g/l. (b) $C_{ASP} = 10$ g/l. $C_{RES} = 26.1$ g/l.
APPENDIX H. WATER ROLE IN ASPHALTENE AGGREGATION

Andersen et al. (2001) showed that water played a very important role in the selfassociation of asphaltenes. The use of dried solvent led to the disappearance of the change in trend in the calorimetric curves previously assigned to CMC. On the other hand, experiments performed with the new equipment did not show such a significant difference between saturated and dried samples. The answer may be found in the differences in the protocol followed in the experiments. Table H-1 gathers these differences:

LKB CALORIMETER (1990-1999)	VP-ITC CALORIMETER (2000-2004)
Asphaltene solutions stored in normal vials	Asphaltene solutions stored in sealed vials.
without sealed caps.	
Samples were sometimes injected right after the ultrasound treatment.	Samples were left to equilibrate overnight.
The calorimeter is exposed to room and temperature variations, which are minimized by a bath of water at constant temperature.	The calorimeter is inside a glove box to minimize the external conditions. The control of temperature is electronic.
The signal-to-noise ratio is low.	The signal-to-noise ratio is high.
The baseline is not very stable.	The baseline signal is very stable.
The samples were under ultrasound for 20	The samples were under ultrasound for 50
minutes.	minutes.
The stabilization time of the calorimeter was	The calorimeter is ready for titration in less
around 24 hours.	than 1 hour.

Table H-1. Comparison of experimental set-ups.

The effect of the protocol is more easily visualized with an example. Figure H-1 shows the titrations performed with Alaska 95 asphaltenes in the new VP-ITC equipment. The protocol however had not yet been improved and samples were stored in non-sealed vials. The samples were prepared, treated with ultrasounds and tested in the same day, without allowing the solution to equilibrate. The first test with saturated toluene shows a greater heat developed than the test with dried toluene. Nevertheless, a few hours later, when the second test was prepared the heat measured in the test is much closer to that of

the dried toluene test. This variation in heat developed between Test 1 and 2 is probably due to changes in the solution in the time passed between the experiments.



Figure H-1.VP-ITC results following the old protocol.

After the protocol was optimized, these large variations between tests performed on the same samples were no longer observed.

APPENDIX I. CHEMICAL ALTERATION OF ASPHALTENES

All reactions were done by Dr. Priyanka Juyal at the laboratories of IVC-SEP. Structural elucidation of asphaltenes by chemical derivatization has been performed by several researchers. Moschopedis and Speight (1975a and b, 1978) successfully carried out Halogenation, Nitration, sulphomethylation, condensation with formaldehyde, diazotization and oxidation with several types of reagents on both asphaltenes and resins (also Moschopedis, 1975). The MW of asphaltene was reduced from 6110 to 3547 in a single step reduction with LiAlH₄ (Sawatzky and Montgomery, 1964, and Sawatzky et al., 1967). Cleavage of ether or sulfide bonds was cited as the main cause.

Sternberg et al. (1971 and 1974) employed potassium and naphthalene reduction followed by alkylation for solubilization of coal asphaltenes. Ignasiak et al. (1977a) used the same chemical approach to elucidate and prove the polymeric nature of petroleum asphaltenes. Since then, several modifications have been suggested, especially by Miyake et al. (1980). They precluded the use of naphthalene in these reduction reactions, since it was cited as responsible for contamination by alkylated derivatives of naphthalene. Silylation was first proposed by Friedman et al. (1961) as a tool for quantitative determination of hydroxyl groups in coal and coal-derived products. Ignasiak et al. (1977) successfully applied it to several petroleum asphaltenes. Gould and co-workers (1978 and 1979) also used this chemistry to study molecular weight and viscosities of coal and petroleum asphaltenes. Since then, it has been widely used as a characterization tool.

Selective incorporation of methyl groups in coal and petroleum materials by using quaternary ammonium hydroxide and iodomethane is a well-established characterization tool. Methylation by phase transfer catalysis has been used to selectively block acidic functionalities in petroleum materials for easy identification by spectroscopy (Liotta, 1979, Liotta et al., 1981, and Rose and Francisco, 1987 and 1988).

Phase Transfer Methylation: (Desando and Ripmeester, 2002). Methylation involves selective "blocking" of hydrogen bonding acidic functionalities by mild treatment. The acidic groups in the material (OH, COOH, NH and SH) are converted to corresponding methyl derivatives (i.e. OCH₃, COOCH₃, NCH₃ and SCH₃ respectively) via

deprotonation with an organic base and reaction of the resulting anion with an alkyl halide.

This technique alters the petroleum material without changing the bulk of hydrocarbon structure. The methylated products are useful materials for evaluating the implications of hydrogen bonding interactions on chemical and physical properties of the material. If the substrate has any of these polar functionalities responsible for molecular associations, then there will be a definite reduction in these association forces after Methylation.

Procedure: 1 gram of Asphaltene dissolved in 50 ml of dry toluene was stirred vigorously under Nitrogen at ambient temperature. 2 ml of organic base tetra-n-butylammonium hydroxide (40%, Aldrich) was added dropwise to the stirring solution of asphaltene and the mixture stirred for two hours, followed by the addition of 0.4 ml of Methyl iodide. After 48 hours, reaction mixture was neutralized with just enough HCl acid solution (5ml of 36.5% aqueous HCl in 20 ml of distilled water) to lower the pH to about 7. The contents of the flask were then transferred to a separatory funnel and extracted with 1 litre of 0.5% aqueous sodium nitrate (about 25 extractions) and then with about 5 litres warm distilled water (about 100 extractions). Toluene from organic phase is concentrated on rotavapor and further dried under a stream of nitrogen. The product was then dried in vacuum at ca. 90°C for three days to ensure complete removal of water.

Silylation: (Stanley and Langer, 1958, Schwager and Yen, 1979). Trimethylsilylation is successful for both hydrogen bonded and hindered hydroxyl functionalities in hydrocarbon mixtures. It results in the formation of stable trimethylsilyl derivatives under mild conditions. However, under similar conditions, nitrogen containing functional groups (secondary amines) have been reported not to form silylated derivatives, while thiols either do not react or the reaction is incomplete. The reaction offers a rapid method to study the contribution of hydrogen bonding due to hydroxyl groups on asphaltenes association. Therefore, asphaltenes that have substantial hydroxyl polarity should show a reduction in self-association after silylation.

Procedure: 1 gram of asphaltenes was dissolved in 40 ml of dry tetrahydrofuran and 3 ml of pyridine was added to the solution. Trimethylchlorosilane (0.3ml) and cooled

hexamethyldisilazane (1ml) were transferred in glass pipettes to the reaction mixture which was refluxed at ca. 80 °C in nitrogen for about 1 hour. The solvents and the reagent were removed in a stream of nitrogen gas at ca. 60 °C for several hours. The product was then dried in vacuum overnight.

Reduction and Reductive Alkylation: (Cagniant et al., 2001). Reductive Alkylation and reduction reactions have been used extensively for the solubilization of coal asphaltenes. Pioneering work was reported for the reduction and reductive alkylation for petroleum asphaltenes by Ignasiak (1977a). These are metal-catalyzed destructive reactions, unlike Methylation and Silylation, and result in chemolysis of C-O and C-S linkages. The changes taking place in case of reduction are fragmentation of core structure due to cleavage of C-O and C-S bonds, followed by hydrogenation of aromatic rings and appearance of hydroxy (-OH) and thiol (-SH) groups. Additional attack of metallic potassium to any of the sulphur intermediates can also cause desulphurization and formation of volatile organic matter of low molecular weight due to fragmentation of the core structure. Side reactions due to the reaction of potassium with THF ring have also been reported (Larsen and Urban, 1979). This implies a further possibility of some contamination due to such side products in the product asphaltenes.

In reductive alkylation, chemolysis is accompanied by alkylation, leading to formation of ethers (-OR) and thioethers (-SR). The alkyl chain used in this study is C₄. It has also been reported a decrease in amount of sulphur content attributed to additional attack of potassium on intermediates and subsequent desulphurization (Franz and Skiens, 1978). The –OH, -SH and –COOH groups originally present in the material should also be converted into ethers, thioethers and esters. Volatile organic matter may also be formed. Contamination by ring opening products of THF is also possible. However, the procedure used does not involve the use of naphthalene as an electron transfer reagent and it was supposed that substantial contamination did not occur.

Procedure: The first step for both reduction and reductive alkylation is the same and involves formation of Asphaltene Polyanion. So it can be supposed that destruction of core structure of any given asphaltene occurred to the same degree in both reduction and reductive alkylation.

Asphaltene (1g), potassium (0.2 g, 20% of the weight of asphaltene) and 25 ml of dry THF were taken in a three-necked 100 ml round bottom flask. The reactants were refluxed under constant Argon purging for 24 hours, which ensured complete disappearance of potassium. From this reaction mixture, reduction or reductive alkylation was carried out.

Reduction: The reaction mixture is cooled to room temperature and treated with absolute ethanol (about three times the stechiometry of potassium taken, approx. 1g) and stirred under argon atmosphere for another 24 hours, followed by addition of 25 ml of water and adjustment of pH to 3 with 5-10% HCl solution. The precipitate is filtered under vacuum and washed repeatedly with water and methanol (about 1 litre of each) and dried under vacuum at 50-60°C.

The cleavage of sulphur and oxygen bridges, together with the subsequent creation of acidic groups is expected to increase the self-association of asphaltenes. However, it is also foreseen that some of the molecules created after the derivatization would be volatile and be released during the alteration. Sulphur is especially prone to be released as volatile compounds, and its particular smell was noticed during Ca30 and Yagual derivatization.

Reductive Alkylation: To the reaction mixture, at room temperature, 2.8 g (three times the stechiometry of K taken) of n-Butyl Iodide was added under Argon atmosphere. The reaction continued with stirring for 2 days, then poured into 75 ml of methanol, followed by filtration. The precipitate was washed alternatively with methanol and water, finally with methanol (1 litre of each was used), followed by vacuum drying at 50-60°C.

Cleavage of C-O/C-S bonds and alkylation are expected to cause disruption of intermolecular hydrogen bonds and Van der Waals interactions due to alkylation of already present polar H-bonding functionalities and steric hindrance to molecular association provided by insertion of butyl groups. Intermolecular associations should reduce consequently with increased distance between interacting fragments.

Figure I-1 gathers a schematic review of all reactions. In the processing of all altered asphaltenes, the complete removal of the reagents employed has been attempted. Tetra butyl ammonium iodide is difficult to remove from the asphaltene reaction mixture even after a number of extractions due to its limited solubility in polar and apolar media.

Therefore, an aqueous NaNO₃ solution was used for initial washings to produce an anion exchange reaction with tetra butyl ammonium iodide. Since the tetra butyl ammonium nitrate is more water soluble than the corresponding halide derivative, the nitrate extractions lessen the time required to wash out the by-product. Further we have done conductivity measurement of the washings until it was the same as pure distilled water. In Silylation reactions, drying under nitrogen to remove reagents and further vacuum drying was done and it is expected that excess reagents and solvent are totally removed.

In reduction reactions, substantial washings were as well carried out to remove any reagent left behind and contaminants. It is expected that the influence of these compounds in ITC will be rather small. There are no means to quantify the amount of possible contaminants and it has been assumed as a starting point that the impact is negligible.





Figure I-1. Schematic review of the reactions presented in this work.

APPENDIX J. MODELING CALORIMETRIC TITRATIONS

a) SELF-ASSOCIATION OF ASPHALTENES:

Asphaltenes seem to follow a step-wise mechanism in their aggregation behavior in toluene. Several models have been applied following this approach in order to obtain the enthalpy of self-association ΔH_a . Experimental data are fitted by the model by means of the optimization of the values of the equilibrium constants and the enthalpy. The general equation behind all the models is:

 $A_i + A_1 \leftrightarrow A_{i+1} \qquad \Rightarrow \qquad [A_{i+1}] = K_i [A_1]^{i+1} \qquad i = 1...n \qquad (1)$

Where $[A_1]$, $[A_2]$, ... $[A_n]$ are the concentrations of asphaltene species (monomer A_1 , dimer A_2 and so on up to n-mer A_n). K_i are the equilibrium reactions. The activity coefficients have been assumed to be 1 due to the fact that the solutions are very dilute (30 g/l correspond to 30 ppm assuming a MW of 1000 g/mol).

The subtracted heat is assigned entirely to the association and dissociation of asphaltenes. After each injection, the concentration of the molecular aggregates changes and a new equilibrium has to be reached. The equilibrium constants together with the mass balance allow the calculation of the concentrations of all compounds A_i after each injection. The differences in concentration between the moment after the injection and the equilibrium allows the calculation of the number of association sites broken in the reorganization process and the total heat developed in each injection:

Heat developed = Number of association sites broken (mol) $*(-\Delta H_a)$ (2)

The parameters of the models are optimized by means of a non linear least square fitting of Eq. 2. Four models have been used to fit the experimental data, all of them incorporating the step-wise growth mechanism.

Dimer Model. The first model is based in the dimer formation. It only considers the formation of dimers (A₂), so the experimental data are fitted with one equilibrium constant (K) and the enthalpy of self-association (Δ H_a).

$$A_1 + A_1 \leftrightarrow A_2 \qquad \Rightarrow \qquad [A_2] = K [A_1]^2 \tag{3}$$

The mass balance allows the calculation of the concentration of monomer and dimer in equilibrium.

$$[A_1] + 2[A_2] = C_T / MW$$
(4)

 C_T is the total amount of asphaltenes in g/l. The monomer concentration is calculated as:

$$A_{1} = \frac{-1 + \sqrt{1 + 8K \frac{C_{T}}{MW}}}{4K}$$
(5)

To sum up, it is possible to calculate both dimer and monomer concentrations with this set of equations, just by knowing the equilibrium constant and the total concentration. Thus, to calculate the heat developed in the dissociation it is just necessary to calculate the concentration of both substances before and after the dissociation to see how many bonds have been broken. Right after the injection, the concentration of A_1 and A_2 is equal to the sum of two contributions: the amounts already in the cell after the previous injection plus the amounts injected from the syringe. MW is assumed to be 1000 g/mol.



Figure J-1. Self-association of ASP by Dimer model. (a) Cs= 5 g/l LM1 Crude. (b) Cs= 30 g/l KU Crude.

Then, the equilibrium is reached and the concentration of both monomer and dimer are calculated by means of the equilibrium constant and equation 5. Equation 2 can be re-written to calculate the heat developed in terms of the number of dimmers dissociated:

Heat developed =
$$([A_2]_{after the injection} - [A_2]_{after equilibrium is reached}) * (-\Delta H_a)$$
 (6)

This model is considered to be very simple and is just applied as a first approach. Nevertheless, other studies have been found where asphaltenes were modeled with this same approach (Seidl, 2003). Figure J-1 displays the fit of this model to some asphaltene dissociation experiments.

Equal K model. The second model (EQUAL K or EK) allows the formation of compounds of higher aggregation number. To simplify the approach, it is assumed (Martin, 1996) that the equilibrium constants and the enthalpies are the same for all the reactions: that is to say, dimer formation has the same energy involved as trimer, tetramer, and so on.

$$K = K_2 = K_3 = \dots = K_{n+1}$$
(7)

$$\Delta H_a = \Delta H_{a2} = \Delta H_{a3} = \dots = \Delta H_{an+1}$$
(8)

The equilibrium concentration of the monomer is obtained by means of a mass balance analysis (Martin, 1996):

$$A_{1} = \frac{1 + 2K \frac{C_{T}}{MW} - \sqrt{1 + 4K \frac{C_{T}}{MW}}}{2K^{2} \left(\frac{C_{T}}{MW}\right)^{2}}$$
(9)



Figure J-2. EK model. (a) KU SOL Cs = 5 g/l. (b) NM1 Cs = 30 g/l.

The concentrations of the rest of compounds are easily calculated by combining this expression with equation 1 and sequentially calculate the concentration of the dimer, trimer and so on. In principle, this set of equations would continue to infinity. However, the necessity of calculating all concentrations before and after the equilibrium to state the number of bonds broken and subsequently calculate the heat developed, it becomes necessary to put a limit. The maximum aggregation number has been set to 60. After the calculations, it has been observed that the concentration of decamers (10 units) is already extremely low, therefore 60 units would be a good assumption for "infinite". Figure J-2 displays the fit of this model to some asphaltene dissociation experiments.

Attenuated K model. The third model (ATTENUATED K or AK) (Martin, 1996) considers that the equilibrium constant decreases as the number of components of the aggregates increases, as a result, i.e., of steric effects. The ratio between the values of the K is the following:

$$K = K_2/2 = K_3/3 = \dots K_i/i$$
 (10)

Again, the enthalpy of self-association is assumed to be the same for all reactions. The model requires an iterative procedure for its solution. A MATHCAD sheet has been applied in this case. The mass balance gives again the concentration of monomer:

$$[A_1] \exp\{K[A_1]\} = \frac{C_T}{MW}$$
(11)

Figure J-3 displays the fit of this model to some asphaltene dissociation experiments.



Figure J-3. AK model. (a) LAG Cs = 5 g/l. (b) OMV Cs = 30 g/l.

Terminator model. The previous three models are fitted with only two parameters: ΔH_a (kJ/mol) and K (l/mol). The last model (Terminator model) includes a third parameter: It is assumed there are two species in the asphaltenes, one with multiple interaction sites (*Propagators*, which can continue the growth of the aggregate) and the other one with only one interaction site (*Terminators*, which would stop the growth).

The ratio between terminators and propagators $(T/P)_{o}$ is used as a fitting parameter. It was successfully applied in the modeling of molecular weight distributions of asphaltenes in toluene solutions obtained from VPO experiments (Agrawala et al., 2001).

- Propagation reactions:

$$\mathbf{P}_1 + \mathbf{P}_1 \leftrightarrow \mathbf{P}_2 \qquad \Rightarrow \qquad \left[\mathbf{P}_2\right] = \mathbf{K} \left[\mathbf{P}_1\right]^2 \tag{12}$$

$$\mathbf{P}_2 + \mathbf{P}_1 \leftrightarrow \mathbf{P}_3 \qquad \Rightarrow \qquad [\mathbf{P}_3] = \mathbf{K}^2 \left[\mathbf{P}_1\right]^3 \tag{13}$$

$$P_{n} + P_{1} \leftrightarrow P_{n+1} \qquad \Rightarrow \qquad [P_{n+1}] = K^{n} [P_{1}]^{n+1}$$
(14)

- Termination reactions:

$$P_1 + T \leftrightarrow P_1 T \qquad \Rightarrow \qquad [P_1 T] = K [P_1] [T] \tag{15}$$

$$P_2 + T \leftrightarrow P_2 T \qquad \Rightarrow \qquad [P_2 T] = K^2 [P_1]^2 [T] \tag{16}$$

 $P_{n} + T \leftrightarrow P_{n}T \qquad \Rightarrow \qquad [P_{n}T] = K^{n} [P_{1}]^{n} [T] \qquad (17)$

For simplicity, it is assumed that the association constant is the same for all reactions. This means that the probability of a propagator or terminator monomer to form a link with an aggregate is the same as that of forming a link with another monomer. The main drawbacks I see in this model is that it does not consider aggregate-aggregate interactions, it considers that only one terminator (instead of two) is needed to stop the polymerization and finally, it does not consider the self-association of terminators (T + T \leftrightarrow T₂). It is assumed that propagators and terminators have MW = 1000 g/mol and 600 g/mol, respectively.

The model had two parameters: $(T/P)_o$, which is the ratio of terminators to propagators in the asphaltene fraction, and the equilibrium constant K. In these calorimeter experiments, there is a third parameter, namely the heat of association ΔH_a .

The equations to calculate the equilibrium concentrations of the monomers are:

$$[P_1] = \frac{1 + K (2[P_1]_0 + [T]_0) - \{(1 + K (2[P_1]_0 + [T]_0))^2 - 4K^2 [P_1]_0 ([P_1]_0 + [T]_0)\}^{1/2}}{2 * K^2 ([P_1]_0 + [T]_0)}$$
(18)

$$[T] = [T]_0 (1 - K[P_1])$$
(19)

In the above two equations, $[P_1]_0$ and $[T]_0$ denote the total concentrations of propagators and terminators, respectively. The modelling of calorimetric experiments requires as well the calculation of the concentrations of all the species in the solution, from P_1 to P_n and from P_1T to P_nT . It is necessary to know the concentration of all substances before and after the equilibriums, to be able to determine how many bonds are broken in each injection, so that the total heat developed can be calculated.

As explained above, the maximum aggregation number has been set to 60 for both P_n and P_nT . Figure J-4 displays the fit of this model to some asphaltene dissociation experiments.



Figure J-4. TERM model. (a) KU Cs = 30 g/l. (b) LM1 Cs = 5 g/l.

Tables J-1, J-2, J-3 collect the continuation of the results obtained in the model optimizations with the various asphaltenes studied.

			Yagua	l asphalte	enes					
	C s	syringe = 5	g/l		C syring $e = 30 g/l$					
-	ΔHa	К	(T/P)o	SS	ΔHa	K	(T/P)o	SS		
DIMER	-6.8	1843.4		0.06	-8.6	298.4		0.42		
EK	-3.5	710		1.45	-4.5	118.5		6.70		
AK	-4.5	1100		1.37	-5.8	200		6.10		
TERM	-1.5	598.9	0.16	1.76	2.0	100.7	0.16	8.63		

Ca30 asphaltenes

_	C s	syringe = 5	g/l	$C \ syringe = 30 \ g/l$				
-	ΔHa	К	(T/P)o	SS	ΔHa	К	(T/P)o	SS
DIMER	-4.5	2389.4		1.58	-5.9	210.9		0.1553
EK	-2.1	796		3.88	-3.4	87.55		4.41
AK	-2.7	1100		3.83	-4.4	135		4.18
TERM	-0.9	626	0.16	4.26	-1.5	79.3	0.18	5.34

Table J-1. Continuation Table 4-5.

Lagrave asphaltenes

	C s	yringe = 5	g/l		C sy	ringe = 30) g/l		
	∆Ha	К	(T/P)o	SS	∆Ha	K	(T/P)o	SS	
DIMER	-5.7	1711.5		0.16	-7.3	247.8		0.25	
EK	-3.0	685.7		0.94	-4.0	101.4		5.46	
AK	-3.9	1050		0.89	-5.2	160		5.01	
TERM	-1.3	587.0	0.16	1.16	-1.8	89.2	0.17	6.81	

LM2 asphaltenes

	C s	yringe = 5	g/l	C syring $e = 30 g/l$				
-	∆Ha	К	(T/P)o	SS	∆Ha	К	(T/P)o	SS
DIMER	-4.2	515.9		1.49	-7.3	149.6		0.21
EK	-3.5	164		2.32	-4.7	63.47		3.78
AK	-4.6	260		2.30	-6.1	102		3.71
TERM	-1.5	173	0.23	2.35	-2.0	61.0	0.19	4.43

Table J-2. Continuation Table 4-5.

					Alaska	95 aspl	naltenes	1				
	C syring $e = 5 g/l$			$C \ syringe = 30 \ g/l$				$C \ syringe = 50 \ g/l$				
	∆Ha	K	(T/P)o	SS	∆Ha	K	(T/P)o	SS	∆Ha	K	(T/P)o	SS
DIMER	-6.0	678.4		0.15	-7.3	165.4		0.26	-5.7	91.5		0.68
EK	-4.0	284.0		0.67	-4.3	69.0		6.04	-3.4	39.0		6.20
AK	-5.1	560		0.65	-5.5	126		5.86	-4.3	104		8.91
TERM	-1.2	193.8	0.19	0.75	-1.3	44.1	0.18	7.30	-1.0	25.2	0.18	7.53
	OMV asphaltenes											
	C sy	vringe = .	5 g/l		C sy	ringe = 3	0 g/l		$C \ syringe = 50 \ g/l$			

-	C sy	vringe = 2	5 g/l		C s	$C \ syringe = 30 \ g/l$				$C \ syringe = 50 \ g/l$			
-	∆Ha	Κ	(T/P)o	SS	∆Ha	K	(T/P)o	SS	-	∆Ha	K	(T/P)o	SS
DIMER	-3.6	884.2		0.19	-5.3	156.8		0.06		-5.6	87.2		0.40
EK	-3.9	349.9		1.08	-3.2	66.0		4.78		-3.4	37.4		6.22
AK	-2.8	770		1.09	-4.1	125		4.55		-3.7	109		2.64
TERM	-0.7	228.0	0.19	1.19	-1.0	42.4	0.18	5.69		-1.0	24.4	0.18	7.51

Table J-3. Continuation Table 4-5.

Asphaltene KU	Dried Toluene		75% Water Saturated Toluene		
Conc. (g/l)	ΔH_d [kcal/mol]	K _d [mol/l]	ΔH_d [kcal/mol]	K _d [mol/l]	
5	0.9	8.28x10 ⁻⁴	1.0	6.88x10 ⁻⁴	
30	1.3	3.25x10 ⁻³	1.2	1.80x10 ⁻³	
Asphaltene Alaska 95	Dried Toluene		75% Water Saturated Toluene		
Conc. (g/l)	ΔH_d [kcal/mol]	K _d [mol/l]	ΔH_d [kcal/mol]	K _d [mol/l]	
5	1.7	1.23x10 ⁻⁴	1.4	7.88x10 ⁻⁴	
30	2.1	5.04x10 ⁻³	1.8	3.86x10 ⁻³	
50	1.6	9.11x10 ⁻³	1.4	5.19x10 ⁻³	

Table J-3b. Water content influence.

b) SELF-ASSOCIATION OF ASPHALTENE FRACTIONS:

EK model has been used to fit the ITC data of asphaltene fractions (Figure J-5). The enthalpies and equilibrium constants are in the same range as those of the original asphaltenes.

Crude	CAsp (ad)	Toluene	ΔH	K (l/mol)
	(g/l)		(KJ/MOL)	(1/1101)
KU SOL	5	Dried	-1.9	347.1
	30	Dried	-2.5	86.0
	5	75% sat	-2.5	316.3
	30	75% sat	-1.8	325.8
KU INS	5	Dried	-1.0	2051.2
	30	Dried	-1.4	96.9
	5	75% sat	-2.0	142.9
	30	75% sat	-1.2	2483.3
LM1 SOL	5	Dried	-3.2	272.4
	30	Dried	-5.5	54.9
LM1 INS	5	Dried	-1.9	280.9
	30	Dried	-2.9	59.9

Table J-4. Fitting results of EK model to asphaltene fractions.



Figure J-5. Fit of EK model to asphaltene fractions.

c) INTERACTION WITH MODEL AND NATIVE RESINS

The approach used in the interaction with both model and native resins was the same as in the self-association of asphaltenes (Chemical Theory). After subtraction of the heat due to friction losses, the remaining heat was assigned to the formation and breaking of bonds.

Model 1. The first model applied to the interaction between asphaltenes (ASP) and nonylphenol (NP) was based on the chemical theory and considered three reactions:

- 1. Interaction NP ASP: $A_2 + N \Rightarrow A_2N$ {K, ΔH } (20)
- 2. Breaking of ASP aggregates: $A_2 \implies A + A \quad \{K_A, \Delta H_A\}$ (21)
- 3. Breaking of NP-NP bonds: $N_2 \implies N + N \quad \{K_N, \Delta H_N\}$ (22)

The differences in concentrations between the moment after the injection and the equilibrium allows the calculation of the number of bonds formed and broken in the reorganization process and the total heat developed q in each injection:

 $q = n_{A-N} (mol)^* (\Delta H) + n_{A-A} (mol)^* (-\Delta H_A) + n_{N-N} (mol)^* (-\Delta H_N)$ (23)

 n_{N-A} is the number of ASP-NP bonds formed and n_{A-A} and n_{N-N} are the number of ASP-ASP and NP-NP bonds broken, respectively. The parameters of the models are optimized so that the heat calculated with Eq. 23 is as close as possible to the experimental heat.

MATHCAD has been used to optimize the model by an iterative procedure. The steps are explained below:

1) INTRO KNOWN PARAMETERS

- S Initial concentration of asphaltenes in the cell in g/l
- T Initial concentration of nonylphenol in the syringe in g/l
- MA molecular weight of asphaltenes in g/mol-g
- MN molecular weight of nonylphenol in g/mol-g
- V0 Initial volume of cell in l
- VS Volume injected from syringe in l
- DN Heat of self-association of nonylphenol in kJ/mol
- DA Heat of self-association of asphaltenes in kJ/mol
- KN Equilibrium constant of self-association of nonylphenol in l/mol
- KA Equilibrium constant of self-association of asphaltenes in l/mol
- h vector of 29 elements with the experimental values of heat in μ cal

2) GIVE INITIAL VALUES OF FITTING PARAMETERS

- KI Equilibrium constant of interaction nonylphenol asphaltenes in l/mol
- DI Heat of interaction nonylphenol asphaltenes in kJ/mol

3) CALCULATE INITIAL VALUES OF CONCENTRATIONS IN The CELL

- a1f0 Initial concentration of monomer asphaltenes in the cell in mol/l
- a2f0 Initial concentration of dimer asphaltenes in the cell in mol/l
- b1f0 Initial concentration of monomer nonylphenol in the cell in mol/l
- b2f0 Initial concentration of dimer nonylphenol in the cell in mol/l
- c1f0 Initial concentration of dimer asphaltene-nonylphenol in the cell in mol/l

$$a1f0 = [[KA2 + 16 KA (S/MA)]1/2 - KA] / 4$$

$$a2f0 = S \left[1 - \left[\left[KA^{2} + 16 KA (S/MA) \right]^{1/2} - KA \right] / (8 AS/MA) \right] / MA$$
(25)

(24)

b1f0 = 0

b2f0 = 0

$$c1f0 = 0$$

4) CALCULATE CONCENTRATIONS IN THE SYRINGE

NS Concentration of monomer nonylphenol in the syringe in mol/l

N2S Concentration of dimer nonylphenol in the syringe in mol/l

$$\mathbf{NS} := \left[\left[\mathbf{kN}^2 + 16 \cdot \mathbf{kN} \cdot (\mathbf{T} \div \mathbf{MN}) \right]^{0.5} - \mathbf{kN} \right] \div (4)$$

225

$$\mathbf{N2S} := \mathbf{T} \cdot \left[1 - \left[\left[\mathbf{kN}^2 + 16 \cdot \mathbf{kN} \cdot (\mathbf{T} \div \mathbf{MN}) \right]^{0.5} - \mathbf{kN} \right] \div (8 \cdot \mathbf{T} \div \mathbf{MN}) \right] \div \mathbf{MN}$$
(27)

5) LOOP *i* = 1 ... 29 injections

5.1) CALCULATE CONCENTRATIONS AFTER INJECTION i

- ali Concentration of monomer asphaltenes after injection i in mol/l
- a2i Concentration of dimer asphaltenes after injection i in mol/l
- bli Concentration of monomer nonylphenol after injection i in mol/l
- b2i Concentration of dimer nonylphenol after injection i in mol/l
- c1i Concentration of dimer asphaltene-nonylphenol after injection i in mol/l

$$a2i = a2f(i-1) * (1-VS/(2V0))$$
(28)

$$a1i = a1f(i-1) * (1-VS/(2V0))$$
 (29)

$$b2i = [V0 * b2f(i-1) + VS * N2S] / V0 * (1-VS/(2V0))$$
(30)

$$b1i = [V0 * b1f(i-1) + VS * NS] / V0 * (1-VS/(2V0))$$
(31)

$$c1i = c1f(i-1) * (1-VS/(2V0))$$
 (32)

5.2) RECALCULATE EQUILIBRIA AND GET VALUES FOR Xji

- X1i Degree of advance of asphaltene self-association in injection i
- X2i Degree of advance of nonylphenol self-association in injection i

 $\mathbf{kA} = \frac{(\mathbf{a1i} + 2 \cdot \mathbf{x1i})^2}{(\mathbf{a2i} - \mathbf{x1i} - \mathbf{x3i})}$ X3i Degree of advance of asphaltene-nonylphenol association in injection i

(33-35)

5.3) CALCULATE FINAL EQUILIBRIUM CONCENTRATIONS

$$\mathbf{kN} = \frac{(\mathbf{b1i} + 2 \cdot \mathbf{x2i} - \mathbf{x3i})^2}{(\mathbf{b2i} - \mathbf{x2i})}$$

ЬТ –	(c1i + x3i)
KI –	$(b1i + 2 \cdot x2i - x3i) \cdot (a2i - x1i - x3i)$
a1fi	Concentration of monomer asphaltenes after equilibrium i in mol/l
a2fi	Concentration of dimer asphaltenes after equilibrium i in mol/l
b1fi	Concentration of monomer NP after equilibrium i in mol/l

b2fi	Concentration of dimer NP after equilibrium i in mol/l	
c1f1	Concentration of ASP-NP after equilibrium i in mol/l	
a1fi =	= a1i + 2 * X1i	(36)
a2fi =	= a2i - X1i - X3i	(37)
b1fi =	= b1i + 2 * X2i - X3i	(38)
b2fi =	= b2i – X2i	(39)
c1f1 :	= c1i + X3i	(40)
5.4) (CALCULATE THE HEAT DEVELOPED IN µcal	
hcali	Heat calculated in injection i in µcal	
hcali	$= V(i) * (10^9 / 4.18) * (DA * X1i + DN * X2i + DI * X3i)$	(41)
5.5) (CALCULATE THE RESIDUAL	
r(i)	Residual function of injection i in µcal	
h(i)	Value of vector h in the position i in µcal	
r(i) =	$[h(i) - hcali]^2$	(42)
5.6) (CALCULATE THE SUM OF SQUARES	
SS(i)	Sum of residuals after i injections in µcal	
SS(i)	= SS (i-1) + r(i)	(43)

6) OPTIMIZE LOOP

If final value of SS is minimum, END.

If final value of SS is not minimum, vary KI and DI.

TERM model. The Terminator model is used in the same basis as in the self-association of asphaltenes. P stands for asphaltenes and T stands for resins. Thus, there are again only 2 parameters because the ratio $(T/P)_0$ is directly calculated from the concentrations of each fraction. The subtraction of the reference data leads to a greater scattering in the cases when the heats developed are very high, particularly in experiments with 66 g/l NP and 1 g/l Asphaltenes. In those cases, the model is only fitted to the first injections. The last points are around zero. When they were included in the fitting procedure, the scattering of the data deviated the fit from the experimental data in the region were there

was more heat developed (in the first injections). The model optimized in this way is still able to fit the last points (See Figure J-6).



Figure J-6. Description of fitting procedure. LM2 Asp (Syringe = 66 g/l NP and cell contains 1 g/l Asp). Table J-5 gathers the optimized parameters obtained with all the asphaltenes studied.

Crude	CASP	C NP	ΔH	K	ΔS	ΔG	n
	(g/l)	(g/l)	(kJ/mol)	(l/mol)	(J/mol)	(kJ/mol)	
A95	1	5.0	-4.8	127.1	24.4	-12.2	1
	1	20.0	-5.0	75.3	19.4	-10.9	1
	1	66.0	-1.9	254.2	39.8	-14.0	1
	10	5.0	-5.3	1234.7	41.7	-17.9	1
	10	20.0	-5.6	135.0	22.3	-12.4	1
	10	40.0	-5.8	107.7	19.8	-11.8	1
LM1	1	5.0	-2.4	284.4	39.1	-14.2	1
	1	20.0	-2.6	240.4	37.0	-13.8	1
	1	100.0	-5.3	89.1	19.8	-11.3	1
	10	5.0	-5.4	2173.5	46.1	-19.4	1
	10	20.0	-5.2	304.6	30.4	-14.4	1
	10	40.0	-6.4	101.1	17.3	-11.6	1
	10	100.0	-5.9	100.8	18.9	-11.6	1
KU	1	5.0	-1.8	234.5	39.4	-13.7	1
	1	20.0	-1.8	154.2	35.9	-12.7	1
	1	66.0	-1.0	591.3	49.8	-16.1	1
	10	5.0	-3.5	3702.9	56.8	-20.7	1
	10	20.0	-3.7	172.8	30.6	-13.0	1

Yagual	1	5.0	-2.1	154.6	35.0	-12.7	1
	1	20.0	-1.3	257.4	41.9	-14.0	1
	1	66.0	-1.2	545.9	48.4	-15.9	1
LM2	1	5.0	-4.2	158.9	28.3	-12.8	1
	1	20.0	-2.9	256.0	36.5	-14.0	1
	1	66.0	-1.8	207.2	38.4	-13.4	1
NM1	1	5.0	-2.5	146.0	33.2	-12.6	1
	1	20.0	-1.9	254.0	39.8	-14.0	1
	1	66.0	-1.6	438.2	45.3	-15.3	1
Ca30	1	5.0	-0.9	549.0	49.5	-15.9	1
	1	20.0	-1.3	359.7	44.6	-14.8	1
	1	66.0	-0.9	225.2	42.1	-13.6	1
Lagrave	1	5.0	-2.1	171.0	35.8	-13.0	1
	1	20.0	-2.1	224.6	38.1	-13.6	1
	1	66.0	-1.5	168.1	37.7	-12.9	1

Table J-5. Thermodynamic characterization of NP-ASP interaction (TERM model).



Figure J-7. Example of TERM fit in NP-ASP experiments. Ca30 (C_{NP} = 20 g/l; C_{ASP} = 1 g/l).

Table J-6 collects the results of the optimization of TERM model in resinasphaltene experiments, together with the averages used in the prediction of ITC enthalpograms in Chapter 7.

Crude	CASP	C RES	ΔH	K	ΔS	ΔG	n
	(g/l)	(g/l)	(kJ/mol)	(l/mol)	(J/mol)	(kJ/mol)	
A95	1	9.0	-2.1	462.9	44.1	-15.5	1
	1	35.8	-2.7	217.8	35.9	-13.6	1
	1	35.9	-2.5	323.6	39.8	-14.6	1
	1	60.0	-2.6	205.1	35.7	-13.4	1
	1	75.3	-3.2	377.0	38.8	-14.9	1
average			-2.6	317.3	38.8	-14.4	1
	10	35.9	-3.1	172.9	32.6	-13.0	1
	10	60.0	-4.3	220.2	30.7	-13.6	1
	10	75.3	-3.7	141.1	28.9	-12.5	1
average			-3.7	178.1	30.7	-13.0	
LM1	1	18.5	-2.6	1046.1	49.2	-17.5	1
	1	47.5	-2.7	1454.0	51.6	-18.3	1
average			-2.7	1250.1	50.4	-17.9	
	10	18.5	-3.9	2282.6	51.4	-19.5	1
	10	47.5	-3.6	391.7	37.8	-15.0	1
average			-3.8	1337.2	44.6	-17.3	
Ca30	1	7.0	-1.6	996.6	52.1	-17.4	1
	1	12.0	-1.9	1410.3	54.0	-18.3	1
	1	31.4	-1.7	328.2	42.6	-14.6	1
	1	99.0	-1.7	402.5	44.3	-15.1	1
average			-1.7	784.4	48.2	-16.3	
	10	12.0	-2.1	3173.0	60.1	-20.3	1
	10	31.4	-2.3	518.1	44.4	-15.7	1
average			-2.2	1845.6	52.2	-18.0	

Table J-6. Thermodynamic characterization of RES -ASP interaction (TERM model).

Crude	C ASP (g/l)	C RES (g/l)	∆H (kJ/mol)	K (l/mol)	$\Delta S (J/mol)$	$\frac{\Delta G}{(kJ/mol)}$	n
Yagual	1	6.0	-2.3	4522.3	62.4	-21.2	1
	1	26.1	-2.4	1336.7	51.9	-18.1	1
	1	65.6	-2.7	1086.7	49.2	-17.6	1
	1	90.0	-2.1	723.6	47.8	-16.6	1
average			-2.4	1917.3	52.8	-18.4	
	10	26.1	-2.9	498.4	42.1	-15.6	1
	10	65.6	-3.0	179.5	33.3	-13.1	1
average			-3.0	339.0	37.7	-14.4	
LM2	1	8.7	-2.2	396.6	42.5	-15.1	1
	1	33.9	-1.9	188.0	37.3	-13.2	1
	1	94.0	-2.0	205.0	37.7	-13.4	1
average			-2.0	263.2	39.1	-13.9	
	10	33.9	-2.8	148.5	32.3	-12.6	1
	10	94.0	-2.9	78.2	26.7	-11.0	1
average			-2.9	113.4	29.5	-11.8	

Table J-6 (Continuation).



Figure J-8. Example of TERM fit in RES-ASP experiments (a) LM1 C_{RES} =47.5 g/l. (b) A95. C_{RES} =35.9 g/l.

Crude	Type	CASP	C RES	ΔH	K	ΔS	⊿G	n
A95	RAW	1.0	35.5	-2.0	81.4	30.0	-11.1	1
	MET	1.0	35.5	-1.2	102.1	34.5	-11.7	1
	SY	1.0	35.5	-2.5	67.7	26.8	-10.6	1
	R-H	1.0	35.5	-2.0	100.0	31.7	-11.6	1
	R-A	1.0	35.5	-1.9	117.4	33.4	-12.0	1
	RAW	10.0	71.0	-1.6	372.6	43.9	-14.9	1
	MET	10.0	71.0	-1.1	727.9	51.2	-16.6	1
	SY	10.0	71.0	-1.7	356.5	43.2	-14.8	1
	R-H	10.0	71.0	-1.5	404.6	45.0	-15.1	1
	R-A	10.0	71.0	-1.5	778.9	50.4	-16.8	1
Ca30	RAW	1.0	91.4	-2.2	963.4	49.9	-17.3	1
	MET	1.0	91.4	-1.2	208.6	40.4	-13.5	1
	SY	1.0	91.4	-1.8	589.3	47.1	-16.1	1
	R-H	1.0	91.4	-1.7	424.6	44.7	-15.2	1
	R-A	1.0	91.4	-1.4	319.9	43.3	-14.5	1
	RAW	1.0	31.4	-1.7	325.2	42.5	-14.6	1
	MET	1.0	31.4	-1.1	1070.9	54.4	-17.6	1
	SY	1.0	31.4	-2.7	208.6	35.5	-13.5	1
	R-H	1.0	31.4	-1.7	547.5	46.8	-15.9	1
	R-A	1.0	31.4	-1.7	448.3	45.2	-15.4	1
	RAW	10.0	31.4	-2.4	455.3	43.0	-15.4	1
	MET	10.0	31.4	-1.5	568.5	47.8	-16.0	1
	SY	10.0	31.4	-2.2	499.0	44.4	-15.7	1
	R-H	10.0	31.4	-2.0	2477.5	58.4	-19.7	1
	R-A	10.0	31.4	-2.2	570.8	45.5	-16.0	1

The optimization of TERM model in resin-altered asphaltene experiments is collected in Table J-7.

 $Table J-7. Thermodynamic characterization of RES - Altered ASP interaction (TERM model). \\ Concentrations in g/l. \Delta H and \Delta G in kJ/mol. \Delta S in J/mol. K in l/mol.$

LM2	RAW	1.0	94.0	-2.7	130.7	31.6	-12.3	1
	MET	1.0	94.0	-1.6	190.4	38.4	-13.2	1
	SY	1.0	94.0	-3.4	102.2	27.2	-11.7	1
	R-H	1.0	94.0	-2.7	407.6	41.1	-15.1	1
	R-A	1.0	94.0	-2.4	171.4	34.8	-13.0	1
	RAW	10.0	35.0	-2.7	168.3	33.7	-12.9	1
	MET	10.0	35.0	-1.5	363.7	44.1	-14.9	1
	SY	10.0	35.0	-2.5	200.8	35.8	-13.4	1
	R-H	10.0	35.0	-3.5	358.9	37.4	-14.8	1
	R-A	10.0	35.0	-2.5	277.9	38.5	-14.2	1
Yagual	RAW	1.0	90.0	-2.2	897.6	49.3	-17.1	1
	MET	1.0	90.0	-1.7	955.3	51.4	-17.3	1
	SY	1.0	90.0	-2.1	1314.0	52.8	-18.1	1
	R-H	1.0	90.0	-1.5	355.7	43.9	-14.8	1
	R-A	1.0	90.0	-1.4	458.8	46.3	-15.4	1
	RAW	10.0	26.1	-3.1	454.8	40.7	-15.4	1
	MET	10.0	26.1	-2.2	659.5	46.7	-16.4	1
	SY	10.0	26.1	-3.1	426.8	40.1	-15.3	1
	R-H	10.0	26.1	-3.2	2624.4	54.9	-19.8	1
	R-A	10.0	26.1	-2.7	2816.2	57.1	-20.0	1

Table J-7 (Continuation).



Figure J-9. Example of TERM fit in RES-Altered ASP experiments. (a) Yagual R-A C_{RES} =26.1 g/l. C_{ASP} =10 g/l. (b) LM2 MET C_{RES} =35.5 g/l. C_{ASP} =10 g/l.

ONE model. One set of independent sites considers that there is a number of sites n available for resin-asphaltene interaction in an asphaltene molecule. Resins can attach to them, and the affinity for resins molecules is the same for all these sites (see a detailed explanation of the derivation of the equations by Van Holde, 1971). Besides, the formation of one bond is not influence by the presence of other resin molecules attached to the same asphaltene. The mass balance for resins is:

$$\begin{bmatrix} R_T \end{bmatrix} = \begin{bmatrix} R \end{bmatrix} + \begin{bmatrix} R_B \end{bmatrix}$$
(44)

Where R_T is the total amount of resins, R_B is the concentration of bonded resins and R the concentration of free resins.

The fraction of sites occupied is defined as:

$$\theta = [\mathbf{R}_{\mathrm{B}}] / \{\mathbf{n}[\mathbf{A}]\} \tag{45}$$

[A] is the total concentration of asphaltenes and n is the number of sites per asphaltene molecule.

The binding process is described by the following equilibrium:

$$\theta = K [A]/\{1 + K[A]\}$$
(46)

It is possible, then, to calculate the concentration of bound resin, by means of the equilibrium constant:

$$[R_B] = [A] \frac{n K [R]}{K[R] + 1}$$

$$\tag{47}$$

The heat developed in each injection is calculated as⁵:

$$q = \Delta H_{A-R} \, V \, \Delta[R_B] \tag{48}$$

$$q = \frac{\left(1 + [A] n K + K[R_T]\right) - \left[\left(1 + [A] n K + K[R_T]^2 - 4[A] n K^2[R_T]\right)\right]^{1/2}}{\frac{2K}{V \Delta H}}$$
(49)

ORIGIN 5.0[©] has implemented a protocol to fit this model to ITC experiments. Initial values of K, n and Δ H have to be provided and the iteration process leads to the optimal values of these parameters. The iteration stops when the deviation expressed as CHI^2 is not reduced any further.



Figure J-9. Examples of ONE fit in NP-ASP experiments. C_{ASP} = 1 g/l.

Nonylphenol experiments are collected in Tables J-8 and J-9. Table J-8 shows the optimal parameters of the experiments that converge with ONE model. Table J-9 gathers the optimal parameters when the number of sites was kept constant.

Crude	ASP (g/l)	NP (g/l)	n	st n	ΔH	st H	K	st K	ΔS	ΔG
LM1	1	5	-	-	-	-	-	-	-	-
	1	20	3.1	0.5	-0.5	0.09	233.4	27.9	43.5	-13.7
	1	100	2.6	0.9	-2.0	0.72	81.0	6.0	29.9	-11.1
Lagrave	1	5	-	-	-	-	-	-	-	-
	1	20	2.9	0.7	-0.6	0.15	198.7	30.6	42.1	-13.3
	1	66	4.6	0.9	-0.1	0.02	889.0	514.6	56.2	-17.1
Ca30	1	5	-	-	-	-	-	-	-	-
	1	20	2.0	0.6	-0.4	0.13	243.7	34.8	44.3	-13.8
	1	66	5.1	0.7	-0.1	0.02	504.7	150.1	51.4	-15.7
NM1	1	5	4.6	0.3	-0.1	0.01	493.0	276.3	51.3	-15.6
	1	20	3.3	0.6	-0.3	0.05	356.4	71.4	47.9	-14.8
	1	66	5.0	0.6	-0.1	0.01	1754.0	1024.0	61.9	-18.8
Yagual	1	5	-	-	-	-	-	-	-	-
	1	20	1.5	0.7	-0.5	0.25	214.0	32.3	43.0	-13.5
	1	66	4.1	0.8	-0.1	0.02	1022.0	635.0	57.3	-17.4
Alaska95	1	5	-	-	-	-	-	-	-	-
	1	20	-	-	-	-	-	-	-	-
	1	66	4.3	0.4	-0.2	0.02	570.6	120.5	52.1	-16.0
LM2	1	5	-	-	-	-	-	-	-	-
	1	20	3.5	0.5	-0.5	0.09	350.0	60.0	46.9	-14.8
	1	66	3.2	0.7	-0.3	0.08	300.9	58.0	46.3	-14.4
KU	1	5	-	-	-	-	-	-	-	-
	1	20	-	-	-	-	-	-	-	-
	1	66	4.8	0.6	-0.07	0.01	1600.0	900.0	60.8	-18.5

Table J-8. Thermodynamic characterization of NP-ASP interaction (ONE model). Concentrations in g/l. Δ H and Δ G in kJ/mol. Δ S in J/mol. K in l/mol. St denotes the standard deviation of the optimal parameters.

Crude	$ASP\left(g/l\right)$	NP (g/l)	n	St n	ΔH	st H	K	st K	ΔS	⊿G
LM1	1	5	2.6	0.9	-0.49	0.05	100	10	36.3	-11.5
	1	20	2.6	0.9	-0.7	0.01	210	9	42.2	-13.5
	1	100	2.6	0.9	-2.0	0.7	81	6	29.9	-11.1
Lagrave	1	5	4.6	0.9	-0.1	0.03	300	200	46.6	-14.2
	1	20	4.6	0.9	-0.3	0.01	280	20	45.9	-14.2
	1	66	4.6	0.9	-0.1	0.02	900	500	56.2	-17.1
Ca30	1	5	-	-	-	-	-	-	-	-
	1	20	5.1	0.7	-0.15	0.01	510	70	51.3	-15.7
	1	66	5.1	0.7	-0.10	0.02	500	200	51.4	-15.7
NM1	1	5	5.0	0.6	-0.1	0.01	500	300	51.2	-15.6
	1	20	5.0	0.6	-0.2	0.01	570	80	52.2	-16.0
	1	66	5.0	0.6	-0.06	0.01	2000	1000	61.9	-18.8
Yagual	1	5	4.1	0.8	-0.09	0.02	200	100	45.2	-13.8
	1	20	4.1	0.8	-0.15	0.005	390	40	49.2	-15.0
	1	66	4.1	0.8	-0.06	0.02	1000	600	57.3	-17.4
Alaska 95	1	5	4.3	0.4	-0.21	0.01	190	20	43.0	-13.2
	1	20	4.3	0.4	-1.01	0.02	84	4	33.5	-11.2
	1	66	4.3	0.4	-0.19	0.02	600	100	52.1	-16.0
LM2	1	5	3.2	0.7	-0.28	0.02	180	20	42.5	-13.1
	1	20	3.2	0.7	-0.60	0.01	320	20	46.0	-14.5
	1	66	3.2	0.7	-0.33	0.08	300	60	46.3	-14.4
KU	1	5	4.8	0.6	-0.07	0.02	400	400	49.4	-15.0
	1	20	4.8	0.6	-0.27	0.01	230	20	44.3	-13.7
	1	66	4.8	0.6	-0.07	0.01	1600	900	60.8	-18.5

Table J-9. Thermodynamic characterization of NP-ASP interaction (ONE model). Concentrations in g/l. ΔH and ΔG in kJ/mol. ΔS in J/mol. K in l/mol. St denotes the standard deviation of the optimal parameters. The optimization was carried out by keeping the number of sites constant and varying ΔH and K.

Table J-10 gathers the thermodynamic variables of RES-ASP interaction by ONE model. Table J-11 gathers the results of ONE model when the number of sites n is fixed by the experiment of highest resin concentration.

Crude	CASP	C RES	n	st n	ΔΗ	st H	K	st K	ΔS	∆G
A95	1	75.3	0.8	0.8	-3.0	2	257	42	37.0	-14.2
LM1	1	47.5	1.1	0.9	-0.5	0.1	754	180	53.3	-16.7
Ca30	1	99.0	1.5	0.9	-0.8	0.6	348	91	45.9	-14.7
	1	12.0	1.6	0.1	-0.7	0.1	1595	417	59.2	-18.6
Yagual	1	90.0	1.7	0.6	-0.8	0.3	382	60	46.7	-15.0
	1	65.6	1.8	0.7	-1.1	0.5	359	77	45.4	-14.8
	1	26.1	1.5	0.2	-0.6	0.1	2374	720	62.6	-19.6
LM2	1	94.0	1.6	0.9	-1.1	0.4	359	77	45.4	-14.8

Table J-10. Thermodynamic charac	terization of RES-ASP interaction	(ONE model). Concentrations in g/l.
Δ H and Δ G in kJ/mol. Δ S in J/mol.	K in l/mol. St denotes the standard	deviation of the optimal parameters.

Crude	CASP	C RES	n	ΔΗ	st ΔH	K	st K	ΔS	ΔG	%AAD
A95	1	9.0	0.8	-1.6	0.1	326	36	42.7	-14.6	9
	1	35.8	0.8	-3.2	0.2	174	17	32.2	-13.0	15
	1	35.9	0.8	-2.1	0.04	242	9	38.6	-13.8	6
	1	60.0	0.8	-4.1	0.13	229	13	31.5	-13.7	22
	1	75.3	0.8	-3.0	2.0	257	42	36.2	-14.0	20
	10	35.9	0.8	-1.5	0.1	136	23	35.9	-12.4	5
	10	60.0	0.8	-2.8	0.1	130	14	31.3	-12.3	11
	10	75.3	0.8	-2.8	0.1	91	9	28.4	-11.4	10
LM1	1	18.5	1.1	-1.2	0.1	632	180	49.8	-16.2	51
	1	47.5	1.1	-0.5	0.10	754	180	53.4	-16.7	175
	10	18.5	1.1	-2.0	0.2	76	1125	29.5	-10.9	48
	10	47.5	1.1	-0.6	0.14	239	187	43.6	-13.8	25

Table J-11. Fitting of all experiments keeping the value of n of the tests with highest resin concentration. %AAD indicates the deviation and the numbers in bold denote tests with a good predicting fit of ONE model. Concentrations in g/l. Δ H and Δ G in kJ/mol. Δ S in J/mol. K in l/mol. St denotes the standard deviation of the optimal parameters.

Table J-12 contains the %AAD of the fit of all experiments with the parameters (Δ H, K and n) obtained with the highest resin concentration into 1 g/l.

Ca30	1	7.0	1.5	-0.6	0.1	1107	544	56.4	-17.7	16
	1	12.0	1.5	-0.7	0.03	1437	212	58.3	-18.3	10
	1	31.4	1.5	-0.8	0.04	333	34	45.6	-14.6	13
	1	99.0	1.5	-0.8	0.6	348	91	45.9	-14.7	334
	10	12.0	1.5	-4.7	52.7	13	1760	5.7	-6.4	1096
	10	31.4	1.5	-1.3	2.4	76	295	31.6	-10.9	20
Yagual	1	6.0	1.7	-0.4	0.19	2558	5027	63.9	-19.8	133
	1	26.1	1.7	-0.5	0.02	2955	645	64.8	-20.1	73
	1	65.6	1.7	-1.2	0.03	346	28	44.8	-14.7	49
	1	90.0	1.7	-0.8	0.3	382	60	46.7	-15.0	96
	10	26.1	1.7	-1.9	10.3	44	426	25.3	-9.5	21
	10	65.6	1.7	-1.0	0.26	145	121	38.1	-12.5	17
LM2	1	8.7	1.6	-0.7	0.03	413	35	47.6	-15.2	5
	1	33.9	1.6	-0.8	0.02	181	11	40.6	-13.1	8
	1	94.0	1.6	-1.1	0.4	359	77	45.4	-14.8	92
	10	33.9	1.6	-0.9	1.09	75	200	33.0	-10.9	14
	10	94.0	1.6	-0.6	0.05	101	24	36.3	-11.6	11

Table J-11 (Continuation).



Figure J-10. Fit of ONE model in RES-ASP experiments. (a) Ca30 1 g/l ASP and 99 g/l RES. (b) LM1 47.5 g/l RES and 1 g/l ASP.

Crude	C ASP	C RES	%AAD	Crude	C ASP	C RES	%AAD
	(g/l)	(g/l)			(g/l)	(g/l)	
A95	1	9.0	78	Yagual	1	6.0	163
	1	35.8	23		1	26.1	253
	1	35.9	30		1	65.6	38
	1	60.0	27		1	90.0	96
	1	75.3	20		10	26.1	25
	10	35.9	130		10	65.6	21
	10	60.0	27	LM2	1	8.7	12
	10	75.3	45		1	33.9	18
LM1	1	18.5	56		1	94.0	92
	1	47.5	175		10	33.9	51
	10	18.5	12982		10	94.0	79
	10	47.5	31				
Ca30	1	7.0	16				
	1	12.0	33				
	1	31.4	14				
	1	99.0	334				
	10	12.0	1858				
	10	31.4	25				

Table J-12. Deviation of set of parameters ONE1 in RES-ASP interaction.

Tables J-13 to J-16 collect the parameters of the fitting of ONE model to the interaction of altered asphaltenes with resins.

Crude	n	st n	$\Delta H (kJ/mol)$	st H	K	st K	$\Delta S (J/mol)$	$\Delta G (kJ/mol)$
RAW	2.4	0.6	-0.3	0.09	275.7	41.0	45.6	-14.1
SY	1.5	0.9	-0.5	0.31	230.0	45.5	43.6	-13.7
MET	1.8	0.9	-0.3	0.18	247.7	50.6	44.6	-13.9
R-H	1.9	0.7	-0.3	0.12	296.5	51.2	46.2	-14.3
R-A	2.2	0.7	-0.1	0.06	713.4	239.9	54.1	-16.5

Table J-13. Alaska95 Altered and resins by ONE model.

Crude	n	st n	$\Delta H (kJ/mol)$	st H	K	st K	$\Delta S (J/mol)$	$\Delta G (kJ/mol)$
RAW	1.7	0.9	-0.7	0.42	296.8	59.4	44.9	-14.3
SY	2.2	0.7	-0.4	0.14	444.6	92.6	49.3	-15.3
MET	1.3	2.0	-0.8	1.23	142.6	39.4	38.6	-12.5
R-H	1.7	0.9	-0.8	0.46	238.2	41.2	42.7	-13.8
R-A	1.2	1.4	-0.8	1.01	188.7	44.3	40.8	-13.2

Table J-14. Ca30 Altered and resins by ONE model.

Crude	n	st n	$\Delta H (kJ/mol)$	st H	K	st K	$\Delta S (J/mol)$	$\Delta G (kJ/mol)$
RAW	2.7	1.4	-0.9	0.54	117.0	22.0	36.5	-12.0
SY	6.2	0.6	-0.4	0.05	235.2	32.4	44.1	-13.7
MET	1.3	2.0	-1.3	1.98	111.4	27.3	35.0	-11.9
R-H	3.5	0.8	-0.7	0.17	264.6	52.4	44.1	-14.0
R-A	2.2	1.4	-0.9	0.64	139.7	29.2	37.9	-12.4

Table J-15. LM2 Altered and resins by ONE model.

Crude	n	st n	$\Delta H (kJ/mol)$	st H	K	st K	∆S (J/mol)	$\Delta G (kJ/mol)$
RAW	1.1	0.7	-0.6	0.50	1347.0	813.0	57.7	-18.1
SY	1.1	0.9	-0.6	0.48	885.5	476.8	54.5	-17.1
MET	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0
R-H	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0
R-A	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0

Table J-16. Yagual Altered and resins by ONE model.



Figure J-11. Fit of ONE model in Resin-Altered LM2 experiments. (a) SY. (b) R-H.
APPENDIX K. FLUORESCENCE TESTS

a) Asphaltenes



Figure K-1. KU asphaltenes. (a) 75% Saturated (b) Dried Toluene.



Figure K-2. MOT asphaltenes in saturated toluene.



Figure K-3. LM1 asphaltenes.



Figure K-5. Ca30 asphaltenes. $C_1 = 1.3$ ppm. $C_2 = 2.5$ ppm. $C_3 = 5$ ppm. $C_4 = 10$ ppm. $C_5 = 50$ ppm. $C_6 = 100$ ppm. $C_7 = 200$ ppm.

excitation λ (nm)



Figure K-6. Yagual asphaltenes. $C_1 = 1.3$ ppm. $C_2 = 2.5$ ppm. $C_3 = 5$ ppm. $C_4 = 10$ ppm. $C_5 = 50$ ppm. $C_6 = 100$ ppm. $C_7 = 200$ ppm.



Figure K-7. LM1 asphaltenes. $C_1 = 1.3$ ppm. $C_2 = 2.5$ ppm. $C_3 = 5$ ppm. $C_4 = 10$ ppm. $C_5 = 50$ ppm. $C_6 = 100$ ppm. $C_7 = 200$ ppm.

b) Asphaltene fractions



Figure K-7. Soluble fraction of LM1 asphaltenes in 4060 acetone-toluene mixture.



Figure K-8. Insoluble fraction of LM1 asphaltenes in 4060 acetone-toluene.



Figure K-9. Soluble fraction of KU asphaltene in an acetone-toluene mixture.



Figure K-10. Insoluble fraction of KU asphaltene in an acetone-toluene mixture.

c) Altered asphaltenes



Figure K-11. Altered Ca30 asphaltenes. C = 2 ppm.



Figure K-12. Altered LM2 asphaltenes. C = 2 ppm.



Figure K-13. Altered Yagual asphaltenes. C = 2 ppm.



Figure K-14. Alaska 95 altered asphaltenes. C = 2 ppm.





Figure K-15. LM1 Resins. $C_1 = 1.3$ ppm. $C_2 = 2.5$ ppm. $C_3 = 5$ ppm. $C_4 = 10$ ppm. $C_5 = 50$ ppm. $C_6 = 100$ ppm. $C_7 = 200$ ppm.



Figure K-16. Yagual Resins. $C_1 = 1.3$ ppm. $C_2 = 2.5$ ppm. $C_3 = 5$ ppm. $C_4 = 10$ ppm. $C_5 = 50$ ppm. $C_6 = 100$ ppm. $C_7 = 200$ ppm.



Figure K-17. Ca30 Resins. $C_1 = 1.3$ ppm. $C_2 = 2.5$ ppm. $C_3 = 5$ ppm. $C_4 = 10$ ppm. $C_5 = 50$ ppm. $C_6 = 100$ ppm. $C_7 = 200$ ppm.



Figure K-18. Alaska 95 Resins. $C_1 = 1.3$ ppm. $C_2 = 2.5$ ppm. $C_3 = 5$ ppm. $C_4 = 10$ ppm. $C_5 = 50$ ppm. $C_6 = 100$ ppm. $C_7 = 200$ ppm.

e) Resin-asphaltene mixtures

- Alaska95 Mixtures



Figure K-19. Alaska 95 (a) 5 ppm Resins and 5 ppm ASP. (b) 10 ppm Resins and 5 ppm ASP.



Figure K-20. Alaska 95 (a) 50 ppm Resins and 5 ppm ASP. (b) 5 ppm Resins and 10 ppm ASP.



Figure K-21. Alaska 95 10 ppm Resins and 10 ppm ASP.

- LM1 Mixtures





Figure K-23. LM1 (a) 50 ppm Resins and 5 ppm ASP. (b) 5 ppm Resins and 10 ppm ASP.



Figure K-24. LM1 (a) 10 ppm Resins and 10 ppm ASP. (b) 50 ppm Resins and 10 ppm ASP.

- Ca30 Mixtures





Figure K-26. Ca30 (a) 50 ppm Resins and 5 ppm ASP. (b) 5 ppm Resins and 10 ppm ASP.



Figure K-27. Ca30 (a) 10 ppm Resins and 10 ppm ASP. (b) 50 ppm Resins and 10 ppm ASP.

- Yagual Mixtures



Figure K-28. Yagual (a) 5 ppm Resins and 5 ppm ASP. (b) 10 ppm Resins and 5 ppm ASP.



(a) (b) Figure K-29. Yagual (a) 50 ppm Resins and 5 ppm ASP. (b) 5 ppm Resins and 10 ppm ASP.



Figure K-30. Yagual (a) 10 ppm Resins and 10 ppm ASP. (b) 50 ppm Resins and 10 ppm ASP.

APPENDIX L. INFRARED TESTS

a) Asphaltenes and Resins



Figure L-1. IR spectra of Alaska95 fractions in CCl₄.



Figure L-2. IR spectra of Yagual fractions in CCl₄.



Figure L-3. IR spectra of LM1 fractions in CCl₄.



Figure L-4. IR spectra of LM2 fractions in CCl₄.



Figure L-5. IR spectra of Ca30 fractions in CCl₄.

b) Altered asphaltenes

* Alaska95 Asphaltenes



Figure L-6. IR spectra of Alaska95 RAW asphaltenes in CS2.



Figure L-7. IR spectra of Alaska95 MET asphaltenes in CS2.



Figure L-8. IR spectra of Alaska95 SY asphaltenes in CS₂.



Figure L-9. IR spectra of Alaska95 R-H asphaltenes in CS2.



Figure L-10. IR spectra of Alaska95 R-A asphaltenes in CS₂.

* Ca30 Asphaltenes



Figure L-11. IR spectra of Ca30 RAW asphaltenes in CS2.



Figure L-12. IR spectra of Ca30 MET asphaltenes in CS_2 .



Figure L-13. IR spectra of Ca30 SY asphaltenes in CS₂.



Figure L-14. IR spectra of Ca30 R-H asphaltenes in CS_2 .



Figure L-15. IR spectra of Ca30 R-A asphaltenes in CS₂.

* Lagrave Asphaltenes



Figure L-16. IR spectra of Lagrave RAW asphaltenes in CS2.



Figure L-17. IR spectra of Lagrave MET asphaltenes in CS₂.



Figure L-18. IR spectra of Lagrave SY asphaltenes in CS₂.



Figure L-19. IR spectra of Lagrave R-H asphaltenes in CS₂.



Figure L-20. IR spectra of Lagrave R-A asphaltenes in CS₂.



Figure L-21. IR spectra of LM2 RAW asphaltenes in CS2.



Figure L-22. IR spectra of LM2 MET asphaltenes in CS₂.



Figure L-23. IR spectra of LM2 SY asphaltenes in CS₂.



Figure L-24. IR spectra of LM2 R-H asphaltenes in CS₂.



Figure L-25. IR spectra of LM2 R-A asphaltenes in CS2.

* Yagual Asphaltenes



Figure L-26. IR spectra of Yagual RAW asphaltenes in CS2.



Figure L-27. IR spectra of Yagual MET asphaltenes in CS₂.



Figure L-28. IR spectra of Yagual SY asphaltenes in CS₂.



Figure L-29. IR spectra of Yagual R-H asphaltenes in CS₂.



Figure L-30. IR spectra of Yagual R-A asphaltenes in CS₂.

Alaska 95	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
RAW	0.60	0.030	1.79	0.050
SY	0.47	0.029	1.71	0.084
MET	0.42	0.080	1.79	0.013
R-A	0.67	0.071	1.79	0.023
R-H	0.75	0.071	1.84	0.050
Yagual	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
RAW	0.46	0.022	2.14	0.018
SY	0.48	0.031	1.99	0.046
MET	0.50	0.024	1.88	0.017
R-A	0.51	0.020	1.93	0.020
R-H	0.57	0.024	2.02	0.044
Ca30	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
RAW	0.50	0.017	2.32	0.031
SY	0.41	0.027	1.87	0.139
MET	0.49	0.026	1.97	0.017
R-A	0.43	0.024	1.99	0.018
R-H	0.71	0.030	2.54	0.023
LM2	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
RAW	0.67	0.032	1.73	0.066
SY	0.52	0.034	1.65	0.059
MET	0.57	0.040	1.72	0.016
R-A	0.41	0.034	1.59	0.024
R-H	0.80	-0.389	-0.55	0.119
Lagrave	I (C=O)	I (S=O)	I (CH2/CH3)	I (HB)
RAW	0.31	0.024	1.87	0.028
SY	0.25	0.026	1.84	0.062
MET	0.34	0.029	1.90	0.011
R-A	0.31	0.031	1.91	0.025
R-H	0.37	0.036	1.87	0.044

Table L-1. Altered asphaltene IR indexes.

APPENDIX M. UNRESOLVED ISSUES

1. SOLVATION EFFECT: In Chapter 4, it has been reported that the heat developed in the titration of asphaltenes varies with the solvent used. ITC titrations of asphaltenes into pure solvent involve a re-arrangement of solvent molecules around the monomers and oligomers. In the modeling, it has been assumed that the solvation energy is small compared to the heat developed in the dissociation of asphaltene molecules. The nature of the solvent has as well an effect on the association degree. It is not possible to quantify separately these two effects.

2. WATER TESTS DO NOT MATCH PREVIOUS STUDIES: As explained in Appendix H, the expected influence of water is not really observed in the new equipment. This reduces the relevance of water as the main driving force of self-association, but it does not exclude the possibility of having water acting as a bridge between asphaltene molecules, as proposed by Murgich et al. (2002, included in the CD as a pdf file). Besides, the water content has been found to be significant even in dried solvents. Once water is efficiently removed, more conclusive work can be performed. This involves a further study on asphaltene-water interaction, as water has been shown to be inside the asphaltene structure. It has not been reported in the thesis, but it was quite interesting to notice that the water content *decreased* when the asphaltenes are added to the water-saturated toluene, and it *increased* when the water content tends to when the asphaltene interaction, some kind of equilibrium value, to which the water content tends to when the asphaltenes are added. This has been left for future studies.

3. TRY TO OBTAIN EXPERIMENTAL VALUES THROUGH A MODEL THAT HAS VERY CRITICAL ASSUMPTIONS: ITC titrations are valuable by themselves in order to get a qualitative picture both in self-association and interaction with resins. Nevertheless, if some quantification is required, it is necessary to apply a model to obtain the parameters such as enthalpies and number of sites. Current knowledge about asphaltenes implies that numerous assumptions and simplifications have to be taken, limiting the applicability of the values obtained. If one of the goals is to provide experimental data to reduce the number of fitting parameters in modeling, this fact can

affect greatly the quality of the estimations. In any case, this is the first time this technique has been applied on these systems. The data are believed to be of high quality, and the modeling can be further improved, following the advances of asphaltene research. **4. SOLUTIONS OF ASPHALTENES HAVE BEEN CONSIDERED IDEAL:** Asphaltenes are very complex molecules capable of self-associating even at high dilutions. It is very probable that activity coefficients are different from one, but for the sake of simplicity, this has not been included in the modeling (Yarranton et al., 2002). Equilibrium constants are apparent magnitudes, and this makes them vary significantly when the concentration is changed.

5. DISPERSIVE EFFECT OF RESINS: It has been observed that NP titrations into asphaltenes present an endothermic peak that is not fully understood. It has been assigned to dispersive effects, but no further information is available to support this hypothesis. Dispersive effects, in the sense of having a resin molecule displacing an asphaltene molecule from an interaction site may have an influence in the final value of the heat developed. This effect has not been taken into account in the simple models presented here, leading to a probable underestimation of the enthalpies of interaction.

6. COMPARISON OF ITC EXPERIMENTS OF ASPHALTENE FRACTIONS: There is always the recurrent doubt about the reason why in one fraction the heat developed is greater. Is it because there are more bonds or because the bonds are stronger? Spectroscopic techniques have not been very helpful in discerning between these two possibilities.

7. YIELD OF ALTERATION REACTIONS: Due to the complexity of asphaltene fraction, it is not possible to quantify how much reagent is still in the solution, in order to estimate the yield of the reaction. Therefore, if one asphaltene has no effect after alteration, it is not possible to know if it is due to the low yield of the reaction or because the functional group attacked had no influence in self-association.

8. ELEMENTAL ANALYSIS: The discussion is hindered by the fact that the sum of weight percent of the elements is most of the times above one. No significant variations have been found, either upon alteration or in fractionation studies.

9. EFFECT OF TEMPERATURE: It has not been possible to explain why the increase in temperature did not lead to a decrease in self-association, as expected for weak forces as the ones believed to govern in these systems. It was suggested that the temperature gradient inside the syringe may have an influence. Even if the system is stabilized over one hour, the syringe may still be colder than the cell. The top of the syringe is in contact with the atmosphere, thus creating a temperature gradient. Nevertheless, the temperature in the tip of the syringe should be close enough to the one inside the cell, as it is made of metal and it allows a good heat transfer during the equilibration time.

10. MODELING WITH ONE: One Set of Sites Model is sometimes problematic. In some cases, it cannot fit the data because it does not converge successfully.

11. PYRENE EXPERIMENTS: As shown in Chapter 3, experiments with pyrene indicate that stacking may comprise both endothermic and exothermic processes. In asphaltene self-association modeling, it is assumed that dissociation is always endothermic. This indicates that the enthalpy of self-association may be underestimated. At the present stage of the investigations, it is considered as a reasonable approach to neglect the underestimation of heat developed. The heat developed in ITC titrations is either due to formation or dissociation of bonds. For the sake of simplicity, it is assumed that each type of process always develops heat in the same direction (for instance, dissociation of bonds is always endothermic). Nevertheless, there are other processes such as tangling of alkyl chains, repulsion, solvation and others that may be relevant but are not taken directly into account.

APPENDIX N. DESCRIPTION OF CD ATTACHED

The folders included are:

- THESIS = An electronic version of the thesis is available in this folder.
- POSTERS = All the posters presented throughout the 3 years are included as well.
 See Appendix O for the list of posters and the places where they were presented.
- PRESENTATIONS = The presentations listed in Appendix O are collected here in Powerpoint format.
- PUBLICATIONS = pdf files of all published material are gathered here.
- ITC DATA = These Excel files contain all the data obtained with the VP-ITC Calorimeter. When more than one test has been carried out with the same sample, the data presented are the average and standard deviation.
- FS DATA = The fluorescence spectra shown in Appendix K are gathered here.
- IR DATA = The infrared and near-infrared data are collected in these files.
- MODELING = The fits of the several models are collected in this folder.

APPENDIX O. PUBLICATIONS, CONFERENCES AND COURSES

a) Publications

- "Molecular Modeling And Microcalorimetric Investigations Of The Effects Of Molecular Water On The Aggregation Of Asphaltenes In Toluene Solutions" 2002. Murgich J., Lira-Galeana C., Merino-Garcia D., Andersen S.I. and del Rio-Garcia J.M. Langmuir. 18: 9080-9086.
- "Isothermal Titration Calorimetry and Fluorescence Spectroscopy Study Of Asphaltene Self-Association In Toluene And Interaction With A Model Resin" 2002. Daniel Merino-Garcia and Simon I. Andersen. Petroleum Science and Technology. 21(3&4): 507-525.
- "Asphaltene Self-Association: Modeling and Effect of Fractionation With A Polar Solvent" 2003. Merino-Garcia D. Murgich J. Andersen S.I. Accepted in Petroleum Science and Technology.
- "Interaction of Asphaltenes With Nonylphenol by Microcalorimetry". D. Merino-Garcia, S. I. Andersen. 2004. Langmuir. 20: 1473-1480.
- "Analysis of Asphaltenes Sub-fractionated by N-methyl-2-pyrrolydinone" B.E. Ascanius, D. Merino-Garcia, S.I. Andersen. Submitted to Energy&Fuels.
- 6. "Thermodynamic Characterization Of Asphaltene-Resin Interaction By Microcalorimetry". D. Merino-Garcia, S. I. Andersen. Accepted in Langmuir.
- "Effect on Molecular Interactions of Chemical Alteration of Petroleum Asphaltenes (1)". P. Juyal, D. Merino-Garcia, S. I. Andersen. IN PROCESS.
- "Effect on Molecular Interactions of Chemical Alteration of Petroleum Asphaltenes (II)". P. Juyal, D. Merino-Garcia, S. I. Andersen. IN PROCESS.
- "Infrared and Fluorescence Spectroscopy Study of Petroleum Asphaltenes and Resins" D. Merino-Garcia, S. I. Andersen. Submitted to Petroleum Science and Technology.
- 10. "Effect of chemical alteration on the interaction of asphaltenes with resins". D. Merino-Garcia, P. Juyal, S. I. Andersen. IN PROCESS.
- 11. "Calorimetric Evidences about The Application Of The Concept Of CMC To Asphaltene Self-Association" 2003. Merino-Garcia D. Andersen S.I. Submitted to Journal of Dispersion Science and Technology.
b) Proceedings:

- "Study On The Self-Association Of Asphaltenes And Their Interaction With Resins By Calorimetry" 2002. Daniel Merino-Garcia and Simon I. Andersen. Proceedings of 3rd International Conference on Petroleum Phase Behavior and Fouling. I.A. Wiehe (Editor). AIChE, New York, p. 269.
- "Effects of Trace Water on the State of Petroleum Asphaltenes in Solution" 2002. Andersen S.I., Kvostitchenko D.S., Merino-Garcia D. Proceedings ECTP 16th European Conference on Thermophysical Properties
- "Asphaltene Self-Association: Modelling And Effect Of Fractionation With A Polar Solvent" 2002. Daniel Merino-Garcia and Simon I. Andersen. Proceedings 2002 Heavy Organic Deposition International Conference, Puerto Vallarta, Mexico. Editor Carlos Lira-Galeana.
- "Interaction Of Asphaltenes With Nonylphenol In Toluene Solutions" 2002. Daniel Merino-Garcia and Simon I. Andersen. Proceedings 2002 Heavy Organic Deposition International Conference, Puerto Vallarta, Mexico. Editor Carlos Lira-Galeana.
- "Interaction of asphaltenes with resins in toluene solutions" 2003. Proceedings 4th International Conference on Heavy Oil Deposition and Fouling. Trondheim, Norway. Editor Johan Sjöblom.

c) Presentations:

- Petroleum Day at DTU, Denmark (3rd May 2001): "Study of the interactions of resins and asphaltenes by isothermal titration microcalorimetry"
- AIChe Spring National Meeting 2002, New Orleans: "Study On The Self-Association Of Asphaltenes And Their Interaction With Resins By Calorimetry".
- Petroleum Day at DTU, Danmark (3rd May 2002): "Self-Association of Asphaltenes and Interaction with Resins by Calorimetry"
- External Discussion Meeting IVC-SEP, Helsingør, Denmark (29th -31st May 2002): "Self-Association of Asphaltenes and Interaction with Resins by Calorimetry"
- 2002 Heavy Organics Deposition Conference (HOD 2002, 17th -21st November 2002): "Asphaltene Self-Association: Modelling And Effect Of Fractionation With A Polar Solvent.
- Petroleum Day at DTU, Danmark (15th May 2003): "Interaction of asphaltenes with model and native resins in toluene solutions"
- External Discussion Meeting IVC-SEP, Gentofte, Denmark (2nd 4th June 2003): "Interaction of asphaltenes with model and native resins in toluene"
- 4th International Conference on Heavy Oil Deposition and Fouling. Trondheim, Norway. 22nd-26th June 2003: "Interaction of asphaltenes with model and native resins in toluene solutions"

d) Posters:

- Danish SPE Meeting (23rd October 2001): "Self-association of asphaltenes by fluorescence spectroscopy" and "State of asphaltenes in toluene solutions by isothermal titration calorimetry".
- Petroleum Day at DTU, Danmark (15th May 2003): poster about asphaltene selfassociation. "Self-association of asphaltenes in toluene solutions".
- 2002 Heavy Organics Deposition Conference (HOD 2002, 17th -21st November 2002): "Interaction Of Asphaltenes With Nonylphenol In Toluene Solutions".
- External Discussion Meeting IVC-SEP, Gentofte, Denmark (2nd 4th June 2003): *"Self-association of asphaltenes in toluene solutions"*.
- 4th International Conference on Heavy Oil Deposition and Fouling. Trondheim, Norway. 22nd-26th June 2003: "Effect of chemical alteration of petroleum asphaltenes on molecular interactions". Juyal P. Merino-Garcia D. Andersen S.I. "Analysis of Asphaltenes Sub-fractionated by N-methyl-1-pyrrolydinone" Elkjær-Ascanius B. Merino-Garcia D. Andersen S.I. "Self-association of asphaltenes in toluene solutions" Merino-Garcia D. Andersen S.I.
- Danish SPE Meeting (16th December 2003): "Interaction of asphaltenes and resins by Isothermal Tiitration Calorimetry" Merino-Garcia D. Andersen S.I.

e) Courses followed:

- Continuing Education Course on Petroleum Fluids Nov. November 2000 af IVC-SEP (DTU)	1 point
- Phase Equilibria in non-ideal solutions. 2nd Semester 2001 at IVC-SEP (DTU)	5 points
- Phase Equilibria, Reservoir Fluids and Process Simulation	
Summer 2001 at IVC-SEP (DTU)	5 points
 Management of R&D international projects July 2001-January 2002 (Nordiske Universitet) 	7 points
- Instrumental analysis. Spring 2002 (Kemisk Institut ,DTU)	5 points
- Instrumental analysis (Laboratory course). June 2002 (Kemisk Institut, DTU)	5 points
- Pedagogisk Course. September 2003 (Institut for Teknologi og Samfund, DTU)	2 points

APPENDIX P. ABBREVIATIONS

%AAD	Absolute average deviation
31SD	75% water-saturated toluene
А	Asphaltene
A95	Alaska 95 Crude oil
AFM	Atomic Force Microscopy
AK	Attenuated K model
AOT	Aerosol Sodium bis(2-ethylhexyl) sulfosuccinate
ASP	Asphaltenes
a.u.	Arbitrary Units
C*	Concentration of RES or NP at which saturation is reached
Ca30	Oatar Crude Oil
Ccall	Concentration of a certain compound in the ITC cell
CMC	Critical Micellar Concentration
C _n	Length of alkyl chain
Cn	Heat Capacity in J/g K
D	Debves
DBSA	Dodecyl-benzensulphonic acid
EK	Equalt K model of asphaltene self-association
FoS	Equation of State
ESR	Electron Spin Resonance
FS	Election Spin Resonance
GPC	Gel Permeation Chromatography
HB	Hydrogen Bonding
H/C	Ratio in weight percent of hydrogen and carbon atoms
HPLC	High Performance Liquid Chromatography
HRTEM	High Resolution Transmission Electron Microscony
INS	Insoluble fraction in fractionation studies
IR	Infrared Spectroscopy
	Isothermal Titration Calorimetry
K	Fauilibrium Constant
K	Asphaltene self association equilibrium constant
K _a KE	Kart Fisher titration
K	Asphaltene self association equilibrium constant
K _n	Maya Crude Oil (Mexico)
LAG	Lagrave Crude Oil (France)
	Atmospheric Liquid Chromatography
LC I M1	Venezuelan Crude Oil
LM1 LM2	Venezuelan Crude Oil
MET	Methylation reaction
MOT	Venezuelan Crude Oil
MPa	MegaPascals
MW	Molecular Weight
1v1 vv	number of sites in asphaltene molecule
N	Nonvinhenol
	Near infrared Spectroscopy
NM1	Vanazualan Cruda Oil
ND	Venezuerali Ciude Oli Nonvinhanal
NP OF	Nonyiphenoi
UF	Unset Flocculation

OMV	Asphaltene deposit from Austria
ONE	One set of sites model
ppm	parts per million (mg/L)
r	Radius of particle
R	Resin
[R]	Free resin or nonylphenol concentration in ONE model
[R _T]	Total resin or nonylphenol concentration in ONE model
$[R_B]$	Bound resin or nonylphenol concentration in ONE model
RA	Reductive alkylation of asphaltenes
R/A	Ratio in weight per cent of resins over asphaltenes
RAW	Unaltered asphaltenes
RES	Resins
RH	Reduction of asphaltenes
RICO	Ruthenium Ion Catalyzed Oxidation
SAFT	Statistical Associating Fluid Theory
SANS	Small Angle Neutron Scattering
SARA	Saturates, Aromatics, Resins and Asphaltenes
SAXS	Small Angle X-ray Scattering
SDS	Sodium Dodecyl Sulphate
SEC	Size Exclusion Chromatography
SF	Synchroneous Fluorescence
SOL	Soluble fraction in fractionation studies
STM	S Tunneling Microscopy
SY	Trimethylsilalation or silylation reaction
TERM	Terminator-Propagator model
$(T/P)_0$	Ratio of Terminators to Propagators
US	Ultrasound treatment
VdW	Van der Waals interaction
VPO	Vapor Pressure Osmometry
wt%	Weight percent
XANES	X-Ray Absorption Near-Edge Structure
YAG	Yagual Crude Oil (Venezuela)
φ _v	Apparent Volume
λ	wavelength
μ	Viscosity
ρ	Density
δ	Solubility Parameter
ΔH	Enthalpy of interaction NP-ASP and RES-ASP
ΔH_i	Enthalpy of interaction RES-ASP
ΔH_{mic}	Enthalpy of surfactant micellization
ΔH_o	Heat developed in the first injection of ITC experiments
ΔH_A	Asphaltene self-association enthalpy
ΔH_N	Enthalpy of self-association of nonylphenol
ΔH_{S-S}	Average heat of injection of pure solvent into pure solvent
ΔG	Free energy of interaction NP-ASP and RES-ASP
ΔS	Entropy of interaction NP-ASP and RES-ASP

APPENDIX Q. REFERENCES

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