**University of Alberta**

# Phase behavior of asphaltenes in organic media

by
Kasra Nikooyeh

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# Dedication

*To Integrity*

*and those who suffer for not giving up on it*

# Abstract

Unwanted phase separation of asphaltenes poses significant challenges in production and processing of heavy oils and bitumen. The analysis and prediction of asphaltene precipitation behaviors and asphaltene-diluent interactions are typically treated either from a solution thermodynamics or a colloid perspective. However, the polydispersity and multi-phase nature of asphaltenes allows for portions of these materials to exhibit both behaviors concurrently at fixed global composition.

Partial specific volume at near infinite dilution and enthalpies of solution are sensitive thermodynamic measures of solute-solvent interactions derived from high precision density and calorimetry measurements for dilute mixtures. Solution calorimetry and density measurements are performed on mixtures of asphaltenes with a variety of diluents ranging from n-alkanes to bicyclic aromatics. The validity of the assumption of solubility of asphaltenes in various diluents is evaluated based on density and calorimetry data. The trends of changes in enthalpies of solution of asphaltenes and their fraction with variations in composition and temperature are used in identifying the interactions of asphaltenes with the diluents and determining the phase state of asphaltenes in organic media.

The results indicate co-existence of a soluble and an insoluble fraction of asphaltenes in each organic diluent and at every fixed temperature and concentration. Endothermic phase transitions and exothermic sorption of diluent are detected in n-alkanes as well as

1-methylnaphthalene, tetrahydrofuran, toluene and quinoline. Asphaltenes are shown to have both intermolecular and interfacial interactions with the studied diluents. The results are in agreement with the hypothesis that only a fraction of asphaltenes undergo a solid-liquid phase change upon mixing with diluents and that fraction is a function of diluent properties, global composition and temperature. These results are inconsistent with the application of dissolution as classically defined to asphaltene + diluent mixtures. Quantitation of the asphaltene fractions potentially present as colloidal particles or as dissolved species in a diluent remains a subject for future study.

# Preface

They asked Loqman, the man of wisdom, "of whom didst thou learn manners?” He replied, "From the unmannerly. Whatever I saw them do which I disapproved of, that I abstained from doing."

“Rose Garden”, Sa’adi - 12th century Iranian Poet

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Life, in its every aspect, is about taking risks and being rewarded for it. It is easy to go all in for the reward when you know there is someone you can turn to at times of desperation. I owe every single achievement of my life to my parents who have always been there for me regardless of the circumstances.

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# Table of Contents

## Chapter 3: Interactions between Athabasca pentane asphaltenes and n-alkanes at low concentration’ .................... 62

## Chapter 4: On enthalpies of solution of Athabasca pentane asphaltenes and asphaltene fractions........ 98

# List of Tables

# List of Figures

# Nomenclature

| | |
|---|---|
| $\alpha$ | Mass fraction undergoing phase change |
| $\beta$ | Mass fraction dissolved |
| $C_p$ | Constant pressure heat capacity |
| $\delta$ | Solubility parameter |
| $\Delta h$ | Enthalpy change per unit mass |
| $\Delta H$ | Enthalpy change per unit mole |
| M | Molar mass |
| n | number of moles |
| R | Universal gas constant (chapter two) |
| R | Mass of sorbed material per mass of asphaltenes (Chapter 3 and 4) |
| $\rho$ | Density |
| T | Absolute temperature |
| $T_m$ | Melting temperature |
| V | Volume |
| v | Specific volume |

| | |
|---|---|
| $\bar{v}$ | Partial specific volume |
| w | Weight fraction |
| x | Mole fraction |

## Acronyms

| | |
|---|---|
| 1-MN | 1-methylnaphthalene |
| DIPPR | Design Institute for Physical Properties Research |
| ppmw | Part per million on a weight basis |
| SAFT | Statistical associating fluid theory |
| SANS | Small angle x-ray scattering |
| SAXS | Small angle neutron scattering |
| SEC | Size exclusion chromatography |
| THF | Tetrahydrofuran |
| VPO | Vapor pressure osmometry |

## Subscripts

| | |
|---|---|
| a | Asphaltenes |
| f | Fusion |
| L | Liquid |

| | |
|---|---|
| m | Chapter two: mixing, Chapters three and four: mixture |
| mix | Mixing |
| p | Constant pressure |
| s | Solvent |
| v | Vaporization |

## Superscripts

| | |
|---|---|
| exp | Experimental |
| l | Liquid |
| s | Solid |
| sol | Solution |

# Chapter 1: Introduction

## 1.1 Asphaltenes, an overview

Asphaltenes are an organic fraction found in “gas oil, diesel fuel, residual fuel oils, lubricating oil, bitumen, and crude petroleum that has been topped to an oil temperature of 260°C”[1]. Unwanted phase separation and precipitation of asphaltenes is a source of major challenges in production, transportation and upgrading of heavy oil and bitumen. In the past four decades a growing body of literature has focused on understanding the structure[2-13], physical and transport properties[14-18], interfacial phenomena[19-23], and phase behavior[17, 24-30] of asphaltenes in the native oil and in organic solvents.

Despite the importance of asphaltene behavior in flow assurance and refining, ambiguities in the mechanism(s) of asphaltene phase separation and interaction of asphaltenes with hydrocarbon diluents remain. The main focus and ultimate goal of all the research conducted in this area is to understand the mechanisms involved in stabilization and destabilization of asphaltene containing mixtures and develop tools for prediction of onset of phase separation that minimize the processing difficulties associated with asphaltenes and maximize the value of products obtained from hydrocarbon resources.

### 1.1.1 *The definition and properties of asphaltenes*

Asphaltenes are defined as the fraction of oil that is insoluble in n-pentane or n-heptane and soluble in toluene[1, 31]. This definition is primarily based on filterability of the asphaltene containing mixture. The solids that are filtered out of a dilute mixture of oil and n-heptane and can be removed from the same filter by washing with warm toluene are defined as asphaltenes. The filters used in these procedures have a pore size of 1.5[1]-2.5[31] μm.

One of the major issues in analysis of the fraction defined as asphaltenes is the poor reproducibility of asphaltene preparation techniques and significant variations in properties of the asphaltenes prepared by the same technique and even the same operator. These problems have been attributed to inconsistencies in the washing procedures[32] and oxidation during the various steps of preparation[33]. In addition, Andersen has shown that the yield of asphaltene separation from the same oil varies significantly with varying the rate of n-alkane[34] addition.

Another major shortcoming of the definition is the misconceptions caused by application of the terms: solubility and insolubility. The material that is precipitated from a mixture with 30-40 volume n-alkanes added to one gram of bitumen may not necessarily be insoluble in that n-alkane. More importantly asphaltenes are in fact a multicomponent mixture[35-40] with a very complex composition[41]. Each of the asphaltene components may have a different saturation concentration in n-alkanes. These concentrations may well be low. However, defining the degree of solubility of a solute in a solvent at which that material can be considered insoluble is arbitrary and relative to the application.

Furthermore, the test for solubility of asphaltenes in toluene does not meet the thermodynamic criteria for solutions. The fact that a mixture of asphaltenes in toluene passes through filters with pore sizes in the micron range is not sufficient for categorizing such mixtures as solutions. Indeed many colloidal suspensions are composed of particles with a mean size far lower than 1.5 microns. In addition, the asphaltene + toluene mixtures are opaque and asphaltenes are shown to be aggregated even at low concentrations in toluene[6, 42-45].

The issue of solubility also arises in determining whether or not a certain hydrocarbon resource fraction falls into the category of asphaltenes. Fractions obtained by partial precipitation of asphaltenes from mixtures of asphaltenes with toluene + heptane have been reported to be insoluble in toluene[42, 46]. According to the definition these materials are not considered asphaltenes although they constitute a portion of what by definition is an asphaltene fraction. These facts collectively raise serious questions about applicability of the concepts of solution thermodynamics to asphaltene + toluene systems.

### 1.1.2 *Size and composition of asphaltene molecules*

The ASTM standard for preparation of asphaltenes asserts: "Asphaltenes are the organic molecules of highest molecular mass and carbon-hydrogen ratio normally occurring in crude petroleum and petroleum products containing residual material."[1] It is not clear whether all the molecules considered operationally as asphaltenes possess the mentioned characteristics. However, the comparison of molar mass and carbon to hydrogen ratio is valid for the asphaltene versus the other fractions.

Asphaltenes are known to have a higher carbon to hydrogen ratio and a higher content of O, N, S and metals compared to other petroleum fractions. The fraction of aromatic carbon is also reported to be high in this fraction. According to Speight[47] and Andersen[41] the hydrogen to carbon ratios of various asphaltenes are in the range of 1.0 to 1.2 which translates to 30% to 50% wt of aromatic carbon . Oxygen contents vary from 0.3% to 4.9%, sulfur contents are in the range of 0.3% to 10.3%, and their nitrogen contents range from 0.6% to 3.3%. The abundance of aromatic rings in the asphaltenes and presence of heteroatoms allows for pi–pi interactions, polar interactions, and hydrogen bonding to be present among such molecules.

For decades the reported molar masses for asphaltenes, determined by vapor pressure osmometry (VPO) and size exclusion chromatography (SEC) were within a wide range from 1000-20000 g/mol. The results of these measurements were later shown to be impacted significantly by the tendency of asphaltenes to aggregate in organic solvents. Evidently, by decreasing the concentration of asphaltenes the measured value of molar mass also decreases significantly. With the employment of fluorescence spectroscopy and non–invasive mass spectroscopy techniques such as laser desorption ionization-time-of-flight (LDI-TOF) mass spectrometry[35, 48] the ranges were narrowed down to “several hundred to 2000-3000 g/mol”. Employment of newer techniques including the Fourier Transform Ion Cyclotron Resonance Mass Spectrometry[37, 49] and extrapolation of vapor pressure osmometry data have lead to a consensus that the molar mass of asphaltenes is 1000 g/mol or lower.

### 1.1.3 *Structure of asphaltene molecules*

There is a large and ongoing debate on the structure of asphaltenes and nature of interactions leading to their aggregation. The structures suggested for asphaltene molecules differ dramatically from one another and are each backed by evidence collected from analysical methods. While these debates, once concluded, may lead to a better understanding of asphaltene aggregation and interactions with the media, constraining the analysis of thermodynamic data by assumptions on asphaltene structure is not constructive. In the current work, these controversial issues have been avoided intentionally. The analysis of interaction of asphaltenes with diluents of different aromaticity, polarity and hydrogen bonding ability presented in this work may be further used in assessment of the suggested asphaltene monomer and aggregate structures. This kind of analysis, however, is beyond the scope of this work.

### 1.1.4 *Aggregation*

Perhaps the most important property of asphaltenes is their tendency to aggregate in every organic medium studied in the literature. The root cause of the tendency has been attributed to the presence of pi-pi and polar[40, 50] interactions and hydrogen bonding[41, 51] among asphaltenic molecules. Data support the notion that the tendency of asphaltenes to precipitate may be related to aggregation. Resins are the fraction closest to asphaltenes in boiling range and molecular weight and are defined as a crude fraction that does not form aggregates[52]. VPO[53-55] studies on fractionated asphaltenes have revealed that asphaltenes that remain in the liquid phase in mixtures with toluene + n-heptane with a low toluene content are less prone to aggregation.

The aggregation tendency of asphaltenes led researchers to draw parallels with the colloidal behavior of surfactants in water in explaining the state of asphaltenes in organic media. Micelle formation analogies[20, 56, 57] dominated the discourse on the analysis of asphaltene behavior and asphaltenes were believed to exist as monomers up to a critical micelle concentration in the range of 1-10 g/L[20, 40, 57-60] at which they started to aggregate and form the so-called micelles. These micelles were thought to be stabilized by resin molecules on the surface. Merino-Garcia and Andersen[61] showed that the concept of critical micelle concentration was in fact inferred from misinterpretation of surface tension and calorimetric data. Instead they suggested that asphaltenes undergo a stepwise aggregation/association as their concentration is increased in organic diluents. Aggregation of asphaltenes has been studied by fluorescence spectroscopy, near-UV/Vis spectroscopy, high-resolution ultrasonic spectroscopy, nuclear magnetic resonance spectroscopy, ultracentrifugation and nanofiltering, among other techniques. Through application of these techniques it is established that asphaltenes start aggregation in toluene at concentrations as low as 50-100 ppm[6, 15, 43-45, 62].

As the size of these aggregates is in the nanometer range they are referred to as nanoaggregates. Mullins and co-workers have suggested that the size of the aggregates formed at low concentration is in the range of 2-3 nanometers and they contain ~5 asphaltene molecules[42, 62, 63]. These aggregates grow by increase in the concentration and reach a size of 5-10 nm at the concentration range of several grams per liter (several thousand ppms). SAXS and SANS measurements also support a size in the range of 4-10 nm for aggregates formed at medium concentration in organic diluents[64, 65]. These values also agree with the membrane diffusion results by Dechaine and Gray[66]. Temperature has also been shown to have a significant impact on the size of aggregates and the degree of aggregation of asphaltenes in various media. Generally, increasing temperature results in a lower degree of aggregation and smaller aggregates[67-69].

### 1.1.5 *Summary of asphaltene properties*

The properties of asphaltenes discussed in the preceding sections are summarized in Figure 1-1. Boxes marked in red include data that have been refuted. Gray boxes include unresolved issues and the underlined text is for issues that are subject of study in this thesis.

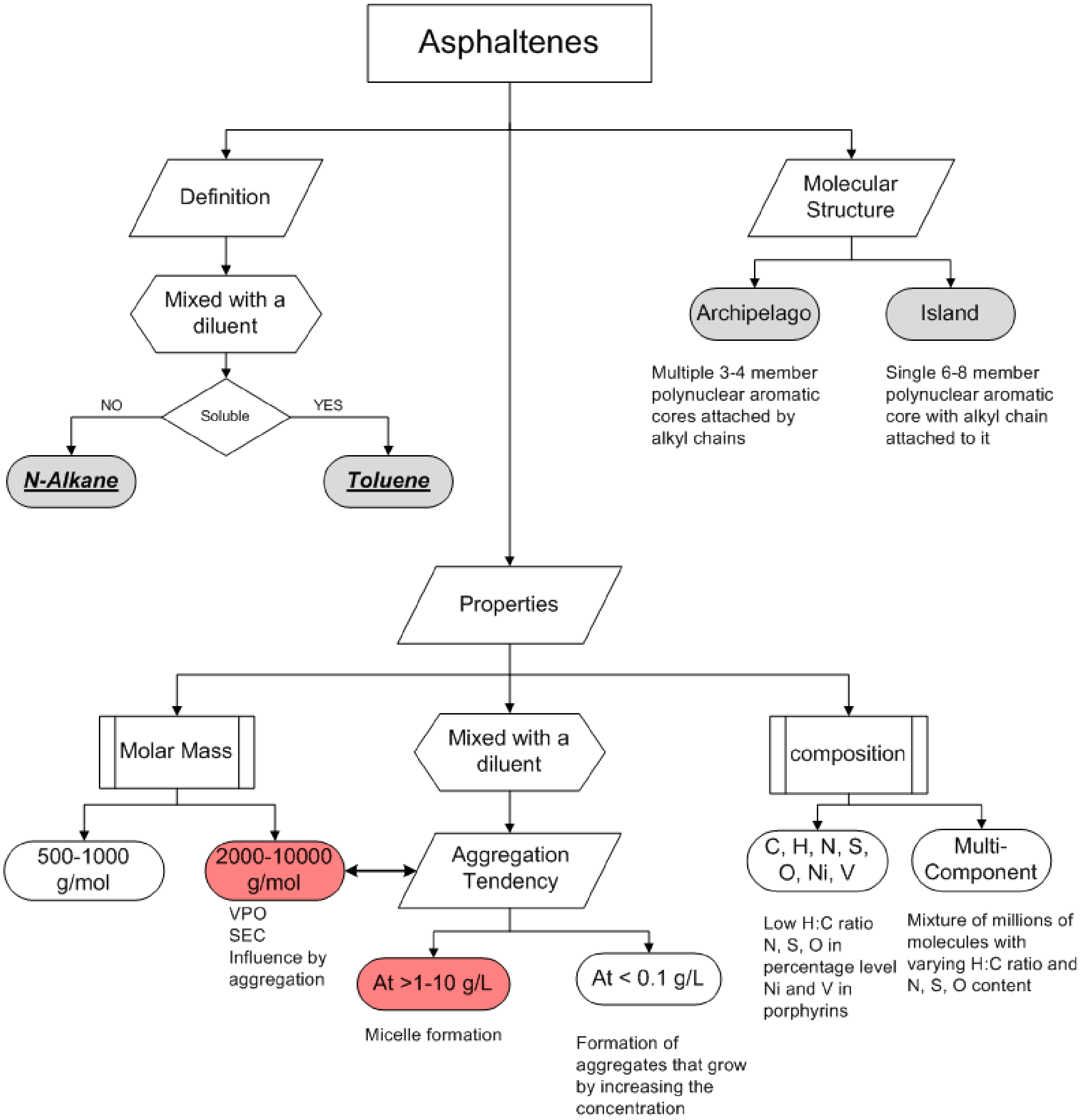

Figure 1-1 Flowchart summarizing asphaltene properties extracted from literature and explained in this chapter

In the current work, applicability of the concept of solubility to asphaltene + diluent systems is investigated from a thermodynamic standpoint. This issue is discussed in detail in the following section.

## 1.2 Phase behavior of asphaltenes in organic media

Understanding the phase behavior of asphaltenes in organic media is key to development of tools required for preventing issues caused by these materials in production, upgrading and refining of heavy oil. Yet, many ambiguities in the mechanism of asphaltene phase separation and interaction of asphaltenes with hydrocarbon diluents have not been addressed.

Recent work has begun to explain the complexity of asphaltene phase behavior on their own, in their native crudes and in organic diluents[10, 17, 18, 24, 70]. Fulem et al. have shown that as-prepared asphaltenes at room temperature consist of at least two solid phases[17]. The first solid phase undergoes a phase transition to liquid crystals and then to isotropic liquid upon heating and the other phase shows a broad endothermic peak indicating melting up to ~ 520K. Bagheri et al. showed that the phase transition to liquid crystals and subsequently to liquid can also be induced by exposure of asphaltenes to toluene vapor[70].

Asphaltenes are defined as insoluble in the n-alkane chosen to precipitate them. However, n-alkanes have been shown to interact with asphaltenes on various levels. Solid asphaltenes are porous[19]. Carbognani et al.[71] have shown that n-alkanes can penetrate into beds of asphaltene particles and cause swelling. Mahmoud et al. observed exothermic behavior of asphaltenes upon mixing with n-alkanes[72]. They hypothesized that asphaltenes impact the orientation of n-alkane molecules on their surface resulting in an exotherm. It is also possible that the diffusion followed by sorption of n-alkane molecules into pores within the solid asphaltene structure may also be a source of the exothermic behavior observed by Mahmoud et al.[72]

Asphaltenes had been largely thought to be soluble in toluene and other diluents defined as solvents for them. However, recent developments have established the particulate nature of asphaltenes at low concentrations in various media. Asphaltenes have been filtered out of their native oil[10] and mixtures with toluene[66]. Centrifugation has also been employed to remove asphaltenes from toluene at low concentrations[62, 73]. The asphaltene content of oil sampled from different depths of a reservoir has also been shown to be larger for samples taken from deeper areas[74].

Asphaltenes are a continuum of molecules differing in size, aromaticity, polarity and heteroatom content. It is not even clear if the whole asphaltene fraction participates in aggregation and whether or not the change in size of these aggregates is accompanied by a change in their composition. However, these molecules all lie within the definition of asphaltenes because they agglomerate upon addition of excess volumes of an n-alkane to their native oil. The possibility of the dissolution of a portion of this material in any solvent cannot be overlooked. With the overwhelming evidence of presence of several nanometer-sized aggregates in asphaltene containing mixtures at low concentrations, coexistence of a dissolved portion as well as a particulate portion is a viable explanation of the behavior of such mixtures and requires investigation. This hypothesis was first suggested by Andersen and Stenby[55] in 1996.

## 1.3 Fundamentals of asphaltene phase behavior modeling

Models developed for predication of asphaltene phase separation either treat asphaltenes as soluble materials that precipitate upon addition of an anti-solvent, or change of pressure or temperature; or as colloidal particles that are destabilized and thereby settle as a result of the same variations in properties. In order to reduce the complexity of the models the asphaltene fraction is usually represented by only one pseudo-component. The most successful models developed for prediction of asphaltene phase separation are based on regular solution theory. Precipitation of asphaltenes by addition of an n-alkane to an asphaltene containing mixture has been largely assumed to be caused by the subsequent decrease in the solubility parameter of the medium[75-79]. Models using Scatchard-Hidebrand[75, 79-81] and Flory-Huggins[77, 78, 82] equations are primarily based on the Hildebrand solubility parameters. Both equations correlate solubility behavior with the solubility parameter and molar volumes of the solute and the solvent and temperature. The solubility parameter and molar volumes may also depend on temperature, and for crystalline solids a term representing the enthalpy of fusion may also be added. Solubility parameters are readily calculated from enthalpies of vaporization and molar volumes. For asphaltenes, as the enthalpy of vaporization and molar mass are not available, the solubility parameter and molar volume, or molar mass, are often used as fitting parameters. Once the parameters for these models are tuned for the specific systems they are developed for, they show reasonable success in capturing the trend of asphaltene precipitation. These models basically assume asphaltenes are soluble in the original mixture and become insoluble as the solubility parameter of the media changes. The major issue associated with these models is that the parameters estimated for one asphaltene + diluent mixture are not necessarily applicable to a different mixture containing the same asphaltenes. These models are therefore not predictive. Failure in generalization of solubility parameter-based models and prevalence of the evidence suggesting that the behavior of asphaltene mixtures are better explained as colloids[22, 43, 56, 59, 83, 84] rather than solutions has made the case for the search for alternative models. Other models based on the solubility assumption include those based on conventional cubic equations of state[85] or the statistical associating fluid theory (SAFT)[28, 86]. These models appear less successful and include the same shortcomings. SAFT-based models have the capacity to account for associations resulting in aggregation but because of the complex nature of the SAFT equation need significant simplification to be applicable to asphaltene containing mixtures.

Models based on colloidal behavior have been around even before the solubility-based models become popular. In the development of these models asphaltenes are assumed to be particles that remain stable in the hydrocarbon medium surrounding them by association with resins. Some models[87-89] are based on the notion of micellar behavior which has been shown to be inapplicable to asphaltene containing mixtures[61]. They also rely heavily on the assumption of stabilization of asphaltene aggregates by resin molecules and therefore fail to explain the stability of asphaltene + diluent mixtures in which resins are not present.

Aggregation models[89-91] assume that asphaltenes are present as aggregates of varying sizes in solvents at low concentration. These models are successful in explaining the growth of aggregates by increase in asphaltenes concentration. However, they are not meant to be used to determine the onset of phase separation and also fail to explain the mechanism involved in dispersion of asphaltenes in a diluent.

The format and details related to the asphaltene phase behavior prediction models are not the focus of this thesis and discussions on this topic have been intentionally avoided. This work is primarily concerned with testing underlying assumptions used to develop these models and their applicability to asphaltene containing mixtures. Generalizable models for asphaltene precipitation and asphaltene property prediction must capture the underlying mechanisms of mixing and de-mixing of asphaltene + diluent systems.

## 1.4 Experimental measures of phase behavior of asphaltene + diluent mixtures

Once a solid is mixed with a liquid the phase state of each component of the mixture is usually determined by visual observations. These observations can be complemented by filtration or centrifugation of the mixture to check the homogeneity of the mixture and for the presence of solid particles. These techniques are used as the primary test of solubility of asphaltenes in a diluent. If the asphaltenes mixed with the diluent do not settle, pass through filters and survive centrifugation they are assumed to be soluble in that diluent. If the filter pores are small enough or the centrifugal force is strong enough at least a portion of asphaltenes does pass the test of solubility in any diluent. In some cases, a portion of the material considered soluble in a certain diluent becomes insoluble once isolated from the other fractions.

The presence and size of nano-sized aggregates, present in asphaltene-containing mixtures, can be and have been inferred from various spectroscopic measurements including SAXS, SANS, fluorescence spectroscopy, etc. However, one cannot conclude from these results if the whole asphaltene fraction is present in those aggregates and how those aggregates interact with their surrounding medium.

The most direct thermodynamic measures of the mixing behavior of two components are the volume and enthalpy of mixing. Solid to liquid phase changes usually manifest themselves in large volumes of mixing and endothermic enthalpies of solution. Enthalpy and volume of mixing can also be used for tracking the strength of solute-solvent interactions. Details on interpretation of these measurements are included in chapters 2, 3, and 4 of the thesis.

Volumes of mixing and partial specific volume, which represents the contribution of a component to the volume of the mixture can be evaluated through density measurements on pure materials and mixtures with varying compositions. Differences between the partial specific volume of a component at low concentrations in the mixture and its specific volume on its own “ provides significant knowledge of the solute-solvent interaction because of the absence of solute-solute interaction”[92]. Strong interactions result in a value of partial specific volume lower than the specific volume of the solute while a larger partial specific volume is a sign of weak attraction or strong repulsion. The difference between partial specific volume in hydrocarbon mixtures and the specific volume of the solute on its own tend to be small[92]. However, upon a change in the phase state a larger difference between the partial specific volume and the specific volume is expected. Such measurements on asphaltene containing mixtures are rare. Maham et al. [26] performed measurements on Athabasca and Maya crudes in toluene and mixtures of toluene and n-dodecane and concluded that there were no temperature or solvent impacts on measured values within the experimental error. Their work was limited to n-decane + toluene mixtures as diluents and their data were significantly impacted by the large experimental uncertainty. Density measurements on asphaltene + toluene mixtures have largely been used for determination of the density of various asphaltenes. Reporting the apparent density of asphaltenes in toluene as solid asphaltene density inherently implies no impact of phase change on the density and insignificance of interactions between the two components. More precise measurements may permit the parsing of these effects.

Enthalpic measures of mixing generally show a more pronounced variation for different mixtures and are far more informative in reflecting the phenomena occurring upon mixing than the volumetric measures. Enthalpies associated with mixing are determined through dissolution and dilution experiments. Dissolution experiments, performed by solution calorimetry, allow for determination of the enthalpy change involved in the mixing of a small amount of a solute with the solvent. The measurements are particularly important for solid solutes as they reflect the enthalpy change upon phase change of a solid to liquid upon dissolution. Dilution measurements have had a central role in the study of asphaltenes as they reflect the impact of change in concentration on the degree of aggregation of asphaltenes in any diluent. They can also be used to follow the impact of addition of a so-called anti-solvent to asphaltene + diluent mixtures.

There is a wealth of literature available on energy of dissolution and aggregation of asphaltenes in hydrocarbon liquids. Andersen and coworkers [56, 58, 61, 93, 94] studied the interaction energy and aggregation behavior of asphaltenes in pure hydrocarbon liquids and in liquid hydrocarbon mixtures. These pioneers of titration calorimetry evaluated the impact of water[93, 95], asphaltene-resin interactions[96, 97], and degree of aggregation[41, 56, 58, 93, 96] on asphaltene containing mixtures. Rejection of the notion of the micellar behavior of asphaltenes was an important result of the titration calorimetry work of Merino-Gracia and Andersen[61]. Titration calorimetry can also be used to study the enthalpic impact of precipitation of asphaltenes from heavy oil upon addition of n-alkanes. By subtraction of the enthalpies involved in mixing of the alkanes and deasphalted oil from that of alkanes and the oil containing asphaltenes, the enthalpic contribution of asphaltene precipitation can be calculated. The titration calorimetry work of Mahmoud et al.[72] and Stachoviak et al.[98] in this area are particularly informative. Their results were the starting point for the work presented in chapter 3 and are discussed in that chapter.

Titration calorimetry as versatile and informative as it is, does not allow for direct observation on the transition of asphaltenes from solid to bulk liquid phase. Solution calorimetry provides the platform for such analyses. Solution calorimetry work on asphaltene containing mixtures is not as abundant as those in the area of titration. Zhang et al.[99, 100] studied energies associated with dissolution of solid asphaltenes in organic solvents through solution calorimetry. Their analysis of the data included the assumption of complete solubility of asphaltenes in the studied diluents. These data are discussed and analyzed in chapters 2 and 4. Solution calorimetry data are usually collected at room temperature and by addition of a small amount of solid to a large volume of liquid so that complete mixing and dissolution is guaranteed. For simple systems, enthalpies of solution data measured at room temperature and low concentration along with fusion enthalpy of the solute provide useful information on solute-solvent interactions. For asphaltene containing mixtures, with the complexity arising from the multi-component nature of the material and the possibility of partial dissolution, these data on their own may be misleading. Detailed analysis of the trend of enthalpies of solution values with temperature and concentration may help explain the phenomena occurring in asphaltene + diluent mixtures.

## 1.5 Objectives

The common hypothesis in chapters 2-4 is that the behavior of asphaltenes in organic diluents cannot be explained by solubility behavior alone. Asphaltenes are hypothesized to possess a soluble and an insoluble fraction in organic diluents. Observed properties of asphaltene containing mixtures reflect a combination of both solubility and colloidal behavior. The hypothesis tested in chapter 2 is that for a single solute, the volumetric and enthalpic measures of mixing correlate with the solubility parameter of the solvent studied if mixtures follow regular solution theory. Mixtures that do not show this behavior are not regular solutions as defined by Hildebrand's regular solution theory[101]. Chapter 3 is focused on the interactions of asphaltenes with n-alkanes. The goal of this chapter is to challenge the misconception that asphaltenes do not interact with n-alkanes and show how asphaltenes behave once exposed to n-alkanes. In this chapter, the assumption of insolubility of asphaltenes in n-alkanes chosen for their precipitation is challenged. Chapter 4 is dedicated to interactions of asphaltenes with the diluents considered to be able to solubilize asphaltenes. The goal of this chapter is to re-define the concept of solubility as applied to complex systems such as asphaltenes. The analysis of this chapter is intended to challenge the common practice of using either colloidal or solution analogies for understanding of phase behavior of asphaltenes in organic solvents. Co-existence of both soluble and insoluble fractions is tested.

## 1.6 Outline of the thesis

The current chapter provides a general introduction and is followed by three chapters formatted as journal publications. Each chapter includes a literature review which complements the introduction in this chapter. Chapters 2 and 3 have been published in Energy and Fuels while Chapter 4 has been submitted to the same journal for peer-review. Chapter 2 includes a data set of partial specific volumes and enthalpies of solution of two types of asphaltenes in various diluents and at varying conditions. The data is used to evaluate the success of regular solution theory in capturing the volumetric and enthalpic behavior of mixing of asphaltenes.

Chapter 3 includes density and solution calorimetry measurements on asphaltene + n-alkane systems at low concentrations and room temperature. Chapter 4 includes a variety of enthalpy of solution measurements at various concentrations and temperatures on asphaltenes and their fractions.  Chapter 5, a short chapter, provides a new perspective on the mixing behavior of asphaltenes and discusses the impact of this perspective on experimental and modeling studies of asphaltene containing mixtures.

Conclusions and contributions of this research project are summarized in chapter 6 along with suggestions for those who may choose to further the lines of inquiry initiated with this work.

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# Chapter 2: On the applicability of regular solution theory to asphaltene + diluent mixtures[a]

## 2.1 Introduction

Regular solution theory, as postulated by Hildebrand, is a modified version of van Laar's model for solutions. The theory assumes that the free energy change upon mixing is correlated with the internal energy per unit volume of the species in the mixture and thereby makes predictions about the solubility behavior of materials. To apply regular solution theory, a mixture must meet the following criteria[1]:

1- components of the mixture should be subject to the same types of forces within the mixture as in pure liquids,

2- mutual energy (interactions) of two molecules should not depend on their relative orientation or on the presence of other molecules,

3- the distribution of molecules should be random, i.e.: excess entropy of mixing is negligible,

4- equilibrium relationships should be applicable to constituents collectively.

Even though asphaltenes are defined as soluble in toluene, it is not clear whether asphaltene + diluent mixtures meet the above criteria because the operating definition for solubility of asphaltenes in toluene, for example, is based on macroscopic filtration measurements[2]. This definition is inconsistent with the thermodynamic definition of

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solubility of solids in liquids, which includes a phase change, from solid to liquid, for the solute followed by molecular level dispersion in the solvent. Further, asphaltenes aggregate in organic media even at low concentrations[3-8]. There is a growing body of literature that asserts that asphaltenes can be separated from toluene by centrifugation and filtration [9, 10], and asphaltenes have been shown to undergo stepwise transitions at low concentrations through titration calorimetry and surface tension measurements[11-15]. These transitions are generally referred to as changes in the degree of aggregation. Thus there is some doubt concerning the applicability of simple concepts of solubility to asphaltene + diluent mixtures.

Regular solution theory and the Hildebrand solubility parameter [1], have been used extensively to model rejection of asphaltenes from native oil or toluene upon addition of a non-solvent [16-23] and the properties of asphaltene + solvent mixtures[24, 25]. In many cases, the models were successfully fit to the behavior of the mixtures. Solubility parameters have proven to be advantageous in averaging the properties of a solvent + an anti-solvent, e.g., heptane-toluene mixtures, once one or more additional fitting parameters are introduced. However, these models and the related parameters have not been successfully applied in a predictive as opposed to a correlative mode. For example, Dechaine et al.[26] showed that solubility parameter based models fail to predict the solubility of asphaltenes and model compounds accurately.

Application of multidimensional solubility parameters and Flory-Huggins parameters are common modifications to the Hildebrand approach. The Hansen[8, 27]-solubility-parameter is used to account for interactions other than van der Waals forces. The Flory-Huggins[18] correction accounts for the entropy change resulting from large differences between the size of diluent and solute molecules. Hansen solubility parameter based models have also been applied to asphaltene + diluent mixtures and reservoir fluids[23, 28] but their use is infrequent because a minimum of three parameters must be obtained to describe asphaltene properties from experimental data.

The focus of the current chapter is to take a step back and investigate whether the basic assumptions in solubility parameter based models are applicable to asphaltene + diluent mixtures. In order to investigate the validity of the underlying assumptions, the first step is to determine whether the models capture trends in thermodynamic properties even qualitatively. Experimental measures related to the change in volume and enthalpy upon mixing for pyrene (a model solute) and asphaltenes, derived from Maya crude and Athabasca bitumen, are used to evaluate aspects of these models and limits to their application to asphaltene + diluent mixtures.

## 2.2 Theory

Energy and volume change measurements possess model independent definitions from which working equations can be derived to probe properties of interest. For example solute-solvent interactions are best probed at infinite dilution, where solute-solute interaction is minimized[29] [30, 31] [32]. Partial molar volume of a solute in solution is defined as:

$$\bar{v}_{1,L} = \left( \frac{\partial V}{\partial n_1} \right) \qquad \text{(2-1a)}$$

where $\overline{v}_{1,L}$ is the partial molar volume of solute, $V$ is the volume of the mixture and $n_1$ is the number of moles of solute. The above equation as well those that follow are valid "at constant temperature and pressure", however, the notation in the form of subscript T, P is dropped as they are inherent. The difference between the molar volume of a constituent in the liquid state, $v_{1,L}$, and the partial molar volume in solution is a broadly used measure of solute-solvent interaction. In general, $\overline{v}_{1,L}$ is obtained from mixture density measurements as:

$$\overline{v_{1,L}} = M_1\left[\frac{1}{\rho} - \frac{1}{\rho^2}\frac{\partial \rho}{\partial w_1}\right] \qquad \text{(2-1b)}$$

where $\rho$ is the density of the mixture and $w$ is the mass fraction and $M$ is the molar mass. At infinite dilution:

$$\overline{v_{1,L}} = M_1\left[\lim_{x_1 \to 0}\left(\frac{1}{\rho} - \frac{1}{\rho^2}\frac{\partial \rho}{\partial w_1}\right)\right] \qquad \text{(2-1c)}$$

$$\lim_{x_1 \to 0}\left(\frac{1}{\rho}\right) = \frac{1}{\rho_2} \qquad \text{(2-1d)}$$

$$\overline{v_{1,L}} = M_1\left[\frac{1}{\rho_2} - \frac{1}{\rho_2^2}\frac{\partial \rho}{\partial w_1}\right] \qquad \text{(2-1e)}$$

where subscript 2 refers to the solvent. If the liquid molar volume and partial molar volume are equal, the mixture is an ideal solution or the components are immiscible. Differences between partial molar volume and molar volume for liquid organic solutes tend to be small (<1%)[29, 32, 33]. For solid solutes, the reference state is sub-cooled liquid, not solid, otherwise large apparent differences arise[34].

Enthalpy changes measured in the laboratory, $\Delta H^{exp}$, enthalpy of solution, $\Delta H^{sol}$, and enthalpy of mixing, $\Delta H_m$, must be discriminated with care. $\Delta H^{exp}$ includes all transitions linked to combining constituents and is composition and temperature specific. It is normally defined on a mole of mixture basis. $\Delta H_m$ only concerns the energy associated with combining two liquids. If the solute is a liquid, $\Delta H_m = \Delta H^{exp}$. If the solute undergoes a phase transition, such as from a crystalline solid to a liquid, during dissolution, the enthalpy of fusion, $\Delta H_f$, must be subtracted:

$$\Delta H_m = \Delta H^{\exp} - x_1 \left[ \Delta H_f^{T_m} + \int_T^{T_m} \left( C_p^s - C_p^l \right) dT \right] \tag{2-2}$$

$T_m$ is the melting temperature, $C_p^s$ and $C_p^l$ are the solid and liquid heat capacity respectively. The temperature correction term, though readily calculated on the basis of solid and liquid heat capacity data and correlations, is small relative to the enthalpy of fusion of crystalline solids[35, 36]. Enthalpy of mixing, $\Delta H_m$, is composition and temperature dependent and is also normally expressed on a per mole of mixture basis. Enthalpy of solution, $\Delta H^{sol}$, includes all effects but is referenced to the solute, and is normally expressed on a per mole of solute basis:

$$\Delta H^{sol} = \frac{\Delta H^{\exp}}{x_1} \tag{2-3}$$

where $x_1$ is the mole fraction of solute in the mixture.

### 2.2.1 *Thermodynamic measures in terms of the Hildebrand solubility parameter*

Regular solution theory asserts that the enthalpy of mixing is correlated with the internal energy per unit volume of species in solution. Hildebrand suggested use of the "Hildebrand solubility parameter[1]", $\delta_i$, to represent this property. This parameter is defined as:

$$\delta_i = \left( \frac{\Delta H_{v,i} - RT}{v_{i,L}} \right)^{0.5} \qquad (2\text{-}4)$$

where: $\Delta H_{v,i}$ is the molar enthalpy of vaporization of component *i* at temperature T, and R is the ideal gas constant. According to this theory, there is a direct correlation between the difference in the solubility parameter values of the solute and the solvent and the main thermodynamic measures of dissolution - the partial molar volume of solutes in solution and the enthalpy of mixing. The difference between the partial molar volume of a species in solution, $\overline{v_{1,L}}$, and the molar volume of a species as a pure liquid, $v_{1,L}$, is:

$$\frac{\overline{v_{1,L}} - v_{1,L}}{v_{1,L}} = \frac{(\delta_1 - \delta_2)^2}{\left( \partial E / \partial v \right)_T} \qquad (2\text{-}5a)$$

where E is the internal energy per unit mol of the mixture.

By substituting for the energy term in the denominator using van der Waals equation of state at infinite dilution equation 2-5a becomes[37]:

$$\frac{\overline{v_{1,L}} - v_{1,L}}{v_{1,L}} = \frac{(\delta_1 - \delta_2)^2}{(\delta_2)^2} \qquad (2\text{-}5b)$$

The enthalpy of mixing is correlated with the solubility parameter as [1]:

$$\Delta H_m = \left(x_1 v_{1,L} + x_2 v_{2,L}\right)\left(\delta_1 - \delta_2\right)^2 \left[\frac{\left(x_1 \frac{M_1}{\rho_1}\right)\left(x_2 \frac{M_2}{\rho_2}\right)}{\left[x_1 \frac{M_1}{\rho_1} + x_2 \frac{M_2}{\rho_2}\right]^2}\right] \tag{2-6a}$$

which at infinite dilution becomes:

$$\Delta H_m = \left(v_{2,L}\right)\left(\delta_1 - \delta_2\right)^2 x_1 \left[\frac{\frac{M_1}{\rho_1}}{\frac{M_2}{\rho_2}}\right] \tag{2-6b}$$

where $M_1$ and $M_2$ are the molar masses of solute and solvent and $\rho_1$ and $\rho_2$ are the densities of the solute and solvent respectively. If composition is expressed in terms of mass fraction equation 2-6b becomes:

$$\Delta H_m = v_{1,L}\left(\delta_1 - \delta_2\right)^2 w_1 \left[\frac{M_2}{M_1}\right] \tag{2-6c}$$

and on rearrangement, a relationship between solubility parameter and mass-based measured mixture properties at infinite dilution is anticipated:

$$\frac{\left[\frac{\Delta H_m}{M_2}\right]}{w_1\left[\frac{v_{1,L}}{M_1}\right]} = \left(\delta_1 - \delta_2\right)^2 \tag{2-6d}$$

The enthalpy of solution can also be linked to solubility parameter at infinite dilution. For liquid solutes:

$$\Delta H^{sol} = \frac{\Delta H_m}{x_1} \tag{2-7a}$$

At infinite dilution

$$x_1 = \left[\frac{M_2}{M_1}\right](w_1) \tag{2-7b}$$

So

$$\Delta H^{sol} = v_{1,L}\left(\delta_1 - \delta_2\right)^2 \tag{2-7c}$$

and on rearrangement, a relationship between solubility parameters and measured mixture properties for liquid solutes is anticipated by Regular Solution Theory:

$$\frac{\Delta H^{sol}}{v_{1,L}} = \left(\delta_1 - \delta_2\right)^2 \tag{2-7d}$$

For crystalline solid solutes:

$$\Delta H^{sol} = \frac{\left[\Delta H_m + x_1\left[\Delta H_f^{T_m} + \int_T^{T_m}\left(C_p^s - C_p^l\right)dT\right]\right]}{x_1} \tag{2-8a}$$

At infinite dilution equation 2-8a becomes:

$$\Delta H^{sol} = v_{1,L}\left(\delta_1 - \delta_2\right)^2 + \Delta H_f^{T_m} + \int_T^{T_m}\left(C_p^s - C_p^l\right)dT \tag{2-8b}$$

and enthalpy of solution is expected to be a positive-valued linear-function of the square of the solubility parameter difference. Thus, according to regular solution theory, ( $\overline{v_1} \geq v_1$ ), ( $\Delta H_m \geq 0$ ), ( $\Delta H^{\exp} \geq 0$ ) and ( $\Delta H^{sol} \geq 0$ ). Hildebrand and coworkers[1] did comment though that if the boiling point of the solute is significantly higher than the boiling point of the solvent, $\overline{v_1}$ could be less than $v_1$ but that a qualitative relationship would continue to exist between the volume difference ($\overline{v_1} - v_1$) and $(\delta_1 - \delta_2)^2$.

### 2.2.2 *Thermodynamic measures in terms of the Hansen solubility parameter*

Hansen[38] introduced a three-dimensional solubility parameter to account separately for the energies arising from London dispersion forces, polar forces and hydrogen bonding separately. The solubility parameter suggested by Hildebrand (δ) is replaced by three separate parameters, $\delta_d$, $\delta_p$, and $\delta_h$ for dispersion, polar and hydrogen bonding contributions respectively. The term $(\delta_1 - \delta_2)^2$ appearing in the equations based on the Hildebrand solubility parameter is replaced by: $(\delta_{d,1} - \delta_{d,2})^2 + \frac{1}{4}\left((\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2\right)$. The sign restrictions noted above also apply as the Hansen solubility parameter term is the sum of squares. For this study, solubility parameter values for the Hansen model for asphaltenes were obtained from Redelius et al.[39].

### 2.2.3 *Thermodynamic measurements for asphaltene + diluent mixtures*

Thermodynamic measurements for asphaltene + diluent mixtures present a number of challenges with respect to interpretation. The phase state(s) of asphaltenes are poorly defined[40, 41]. At room temperature asphaltenes comprise a minimum of two phases: an amorphous solid or a glass and a phase that undergoes a transition to liquid crystals and then to liquid at higher temperatures or on exposure to diluents such as toluene at room temperature[42]. While the molar volume, molar enthalpy and density of subcooled liquid pyrene can be computed from the literature,[43] these properties for asphaltenes as a subcooled liquid are not accessible experimentally and cannot be computed from extrapolation of high temperature data. Thus, solubility parameter values for asphaltenes are not accessible experimentally. Asphaltene mean molar mass is also poorly defined and it is not clear whether asphaltenes undergo partial or full phase change on mixing with typical diluents, irrespective of concentration. Thus the definitions of partial specific volume and enthalpy of solution are not fully met and care must be taken not to over interpret experimental results. While not imposed in this report, these measures should be labeled "apparent" enthalpy of solution, and "apparent" partial specific volume because the mass fraction and nature of constituents present in asphaltenes, however defined, interacting with specific diluents is unknown.

### 2.2.4 *Specific volume and partial specific volume of asphaltenes*

Specific volume and partial specific volume are proportional to molar volume and partial molar volume respectively. One merely divides these latter measures by specie molar mass. Specific volumes for liquid asphaltenes $\left[\frac{v_{1,L}}{M_1}\right]$ are not accessible, while specific volumes for solid $\left[\frac{v_{1,S}}{M_1}\right]$ and partial specific volume in the liquid phase $\left[\frac{\overline{v_{1,L}}}{M_1}\right]$ are accessible for asphaltenes. The structure of the relationship with solubility parameter difference, according to Regular Solution Theory is unaffected by this division. The possible existence of a relationship between $\left[\frac{\overline{v_{1,L}}}{M_1}\right]$ and $\delta_2$ as implied by equation 2-5b can be probed, assuming $\delta_1$ and $v_{1,L}$ are unknown constants. A cusp is expected to arise in the relationship, if diluents with a broad enough range of solubility parameters are investigated.

### 2.2.5 *Enthalpy of mixing and enthalpy of solution for asphaltenes*

As the molar mass of asphaltenes is approximately one order of magnitude greater than the molar mass of the diluents, the enthalpy change values measured in the laboratory are readily expressed on a mole of mixture basis, particularly at low concentrations, because the number of moles of asphaltenes can be neglected in the calculations. While this formalism is followed, the working equations linking $\Delta H^{exp}$ and the enthalpy of solution, by combining equations 2-3 and 2-7b:

$$\Delta H^{sol} = \frac{\Delta H^{\exp}}{\left[\frac{M_2}{M_1}\right](w_1)} \tag{2-9a}$$

are readily expressed on a mass basis at near infinite dilution:

$$\left[\frac{\Delta H^{sol}}{M_1}\right] = \frac{1}{w_1}\left[\frac{\Delta H^{\exp}}{M_2}\right] \tag{2-9b}$$

Connecting $\Delta H^{sol}$ to $\Delta H_m$ for asphaltenes is complex because the phase state(s) of asphaltenes are poorly defined, and because the asphaltene constituents and the mass fraction undergoing dissolution or other processes may vary with the global mass fraction of asphaltenes in a diluent, and the composition of the diluent. Equation 2-2 becomes:

$$\Delta H_m = \Delta H^{\exp} - w_1\left[\frac{M_2}{M_1}\right]F \tag{2-10a}$$

where F is an unknown function of composition and temperature. By substituting in equations 2-6c and 2-9b and rearranging, one obtains:

$$(\delta_1 - \delta_2)^2 = \frac{\frac{\Delta H^{sol}}{M_1}}{\frac{v_{1,L}}{M_1}} - \frac{F}{v_{1,L}} \qquad \text{(2-10b)}$$

where both the enthalpy of solution per unit mass of asphaltenes and the partial specific volume of asphaltenes in the diluents are measured. Only if F << $\Delta H^{sol}$ or is invariant, is a relationship expected between $\Delta H^{sol}$ and $\Delta H_m$ and hence $\delta_2$, even if Regular Solution Theory is appropriate for this application. Again, a cusp is expected to arise in the relationship, if diluents with a broad enough range of solubility parameters are investigated.

## 2.3 Experimental

### 2.3.1 *Materials*

Maya crude oil is a commercial heavy oil blend from Mexico and was supplied by the Mexican Petroleum Institute. Athabasca bitumen was supplied by Syncrude Canada Ltd. Pyrene (98 wt% purity) was supplied by Sigma-Aldrich. Other chemicals were supplied by Fisher, Sigma-Alrich and Acros. The purity of 1-methylnaphthalene was 97 wt %. The purity of the other compounds was 99 wt % or higher. The Hildebrand solubility parameters for these compounds at 25 °C are listed in Table 2-1. N-pentane, n-heptane, and n-dodecane precipitated asphaltenes were obtained from Athabasca Bitumen and Maya oil. For asphaltene preparation, the alkane of choice was added at a ratio of 40 ml per gram of feedstock. The mixtures were mixed for 24 hours and then filtered using filter paper Q2, with a pore size 1-5 μm, washed and dried. Maya asphaltenes do not contain mineral solids while these solids account for ~6% of Athabasca bitumen asphaltenes.

Table 2-1. Hildebrand solubility parameter values at 25 °C[44]

| Diluent | $MPa^{0.5}$ |
|---|---|
| dodecane | 15.9 |
| toluene | 18.3 |
| tetrahydrofuran (THF) | 19.1 |
| 2,6 - lutidine | 19.3 |
| anisole | 20.1 |
| 1-methylnaphthalene (1-MN) | 20.2 |
| pyridine | 21.8 |
| quinoline | 21.9 |
| methylene chloride | 20.4 |

To prepare solids-free (S/F) Athabasca asphaltenes, the asphaltenes were combined with toluene (1 wt %) and mixed for 1 hour. Solids were then separated by centrifugation for 5 min at 3500 rpm (1000 RCF) at 20 ˚C. As the measured properties of the asphaltenes varied somewhat from batch to batch, even when the same procedure was followed, comparisons based on density and enthalpy measurements are reported for asphaltenes from the same batch only. Batch to batch variations for $\bar{v}_1 / M_1$ as high as 0.01 g/cm$^3$ were observed, while $\Delta H^{sol} / M_1$ values varied as much as 3 J/g. These deviations are greatly in excess of the property measurement repeatabilities for sub samples within batches as noted below.

### 2.3.2 *Density measurements*

Density measurements were performed for pyrene and asphaltene containing mixtures. Asphaltene + diluent mixtures were prepared by addition of diluent to asphaltenes followed by sonication. Samples were left for one hour and were checked for deposition of solids. If deposits were visible the samples were re-sonicated and left for an additional hour. This procedure was repeated until no deposit appeared at the bottom of the sample holder. All samples were prepared at least 24 hours before experiments and were kept sealed. For asphaltene containing mixtures, measurements were performed on samples at low (200 - 1000 ppm), medium (2500 – 8000 ppm) and high (1-10 wt %) asphaltene concentrations. Densities were measured from 10 to 80 ˚C using an Anton Paar DMA5000 oscillating u-tube density meter. The instrument controls the temperature to ±0.01 ˚C and records the temperature with an accuracy of ±0.001 ˚C. Measured values for density were reproducible to within ±0.000 002 g/cm$^3$. Pyrene + diluent mixtures, comprising between 0.5-5 wt % pyrene were all well below the solubility limit of pyrene and did not require special preparation procedures. Most measurements for Pyrene and asphaltenes were performed in the range of 0.25-0.8 wt%. The partial specific volumes of pyrene and asphaltenes were calculated using equations 2-1b and 2-1c, where the density derivatives were obtained by fitting inverse density versus wt fraction of asphaltenes. Each derivative was obtained using at least 6 data points as illustrated

Figure 2-1. With the propagation of errors, the specific partial volumes have absolute deviations <0.005 cm$^3$/g at less than 1000 ppm asphaltenes. The absolute deviation decreases to <0.002 cm$^3$/g at higher concentrations. The density of solid asphaltenes was measured using a pycnometer where the free volume was filled with heptane. These measurements were repeatable to within ±0.005 g/cm$^3$. The density of solid pyrene was available from the literature.

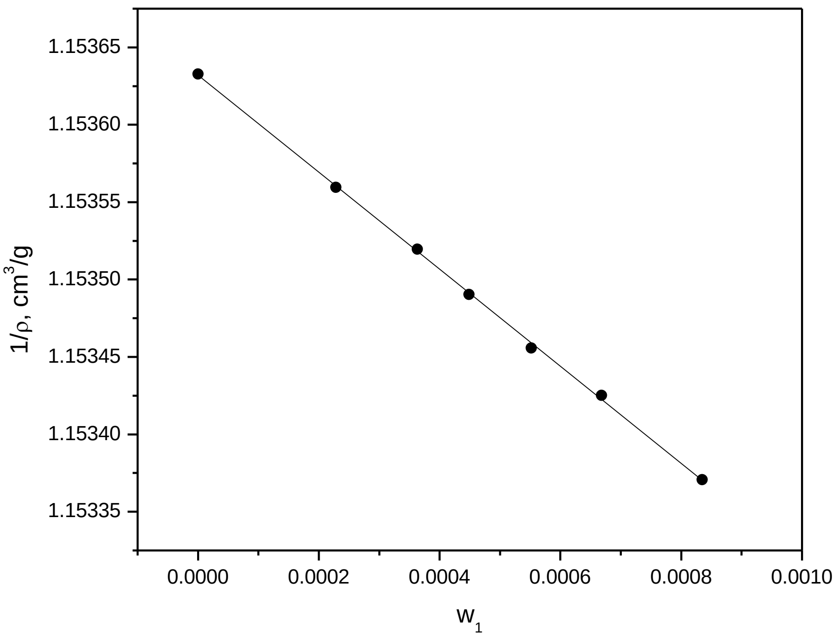

Figure 2-1- Example inverse density vs weight fraction graph for Athabasca heptane-asphaltenes (1) in toluene mixtures at 20 °C.

### 2.3.3 *Experimental enthalpy measurements*

Experimental enthalpy changes and enthalpies of solution, on either a unit mass or mole basis, were calculated[45], based on temperature signals obtained using a TA Instruments precision solution calorimetry module, SolCal, in combination with a TAM III thermostat. The equipment measures the difference between the temperature of the cell and the set temperature of the thermostat- called temperature offset. All measurements were performed within a temperature offset range of -100 mK to 100mK. SolCal is a semi adiabatic system with a short-term noise of <10 μK/5 min. The module comprises a 25 ml cell filled with diluent and a 1 ml glass ampoule containing 25-30 mg of pyrene or asphaltenes placed within in the cell. The module was inserted in the thermostat at a set temperature and allowed to reach steady state, which was defined as a standard deviation of an exponential fit to the temperature signal of less than 10 μK over 5 min. A mixing rate of 500 rpm was used for all experiments. Heat calibrations using a heat signal of 2.5-5 J were performed before and after the ampoules were broken to determine equipment related parameters. After the first calibration a 7 minute baseline was collected. At the end of this period the glass ampoule was broken. For most experiments a 5-minute period was allowed for release/sorption of the energy followed by another 7 minute baseline. A second calibration was then performed.

## 2.4 Results and discussion

### 2.4.1 *Pyrene + diluent mixtures*

The principles of the thermodynamic measurements and the application of regular solution theory are illustrated using pyrene + solvents mixtures. Pyrene is a crystalline polycyclic aromatic solid that dissolves readily in the diluents and at the concentrations employed in this work. Experimental values for the partial specific volumes in solution and computed specific volume values for sub-cooled liquid pyrene are reported in Table A-1. Fractional differences between the partial specific volume of pyrene in diluents and the specific volume of pyrene are reported in Figure 2-2 using subcooled pyrene liquid (Figure 2-2a) and solid pyrene (Figure 2-2b) as references states. Figure 2-2 is intended to illustrate two principles:

1. $\frac{\overline{v_{1,L}} - v_{1,L}}{v_{1,L}}$ may be positive or negative, even for simple mixtures of polynuclear aromatic compounds and organic solvents,

2. for a solid solute, the use of the solid molar volume or specific molar volume in calculations distorts the interpretation of results, i.e.: all $\frac{\overline{v_{1,L}} - v_{1,s}}{v_{1,s}}$ values for pyrene are positive, yielding apparent agreement with regular solution theory by this measure.

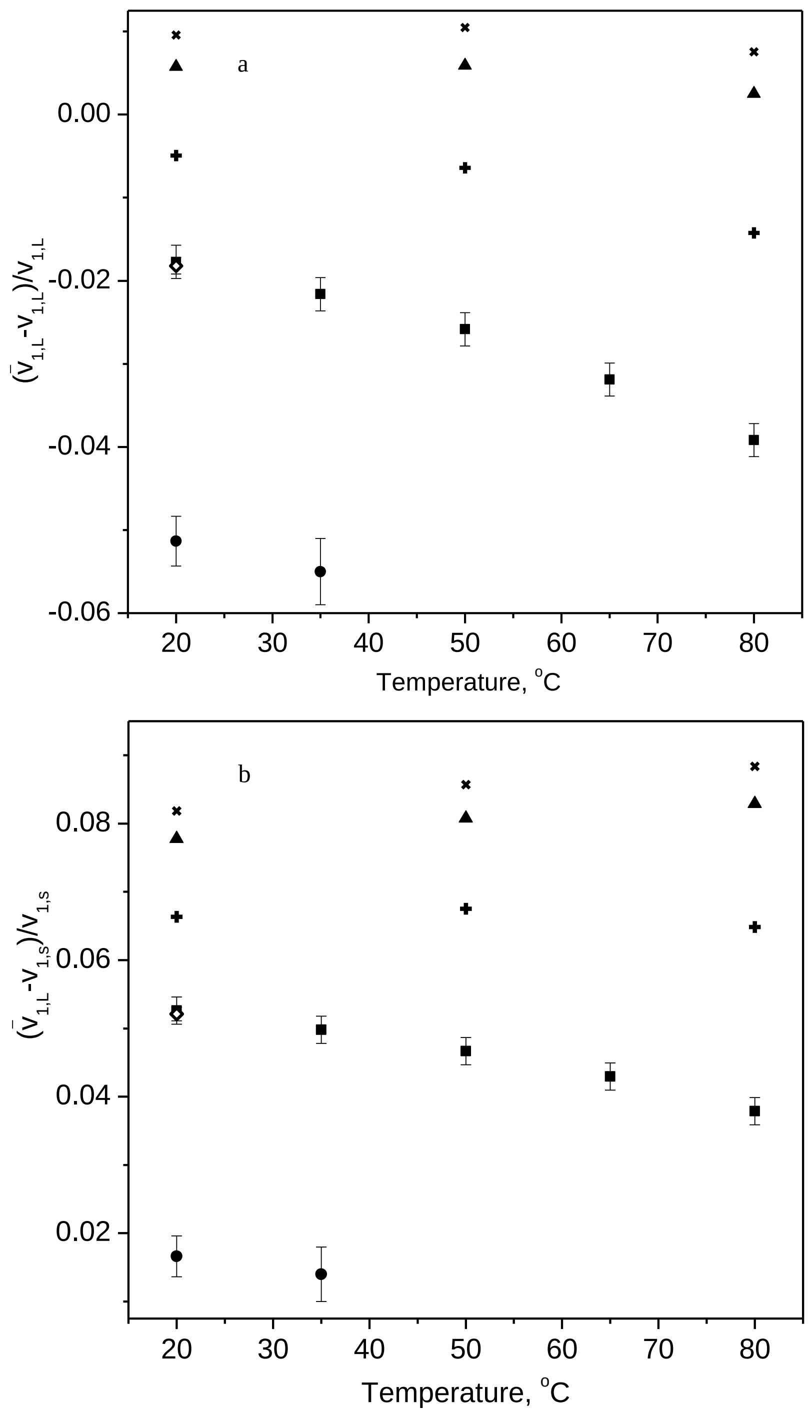

Figure 2-2- Relative deviation of the partial specific volume of pyrene from a) the sub cooled liquid specific volume b) the solid molar volume. Symbols: THF (●), toluene (■), 1-MN (▲), quinoline (×), anisole (+), methylene chloride (◇).

The Hildebrand solubility parameter for pyrene at 25 °C, 21.4 MPa$^{0.5}$, is readily calculated and it is possible to probe for a functional relationship between $\frac{(\delta_1 - \delta_2)^2}{(\delta_2)^2}$ and $\frac{\overline{v_{1,L}} - v_{1,L}}{v_{1,L}}$ directly, as anticipated by equation 2-5b. These ratios are cross-plotted in Figure 2-3. From regular solution theory, a linear relationship with a positive slope and positive values is expected. For most cases, the relative volume difference is negative.

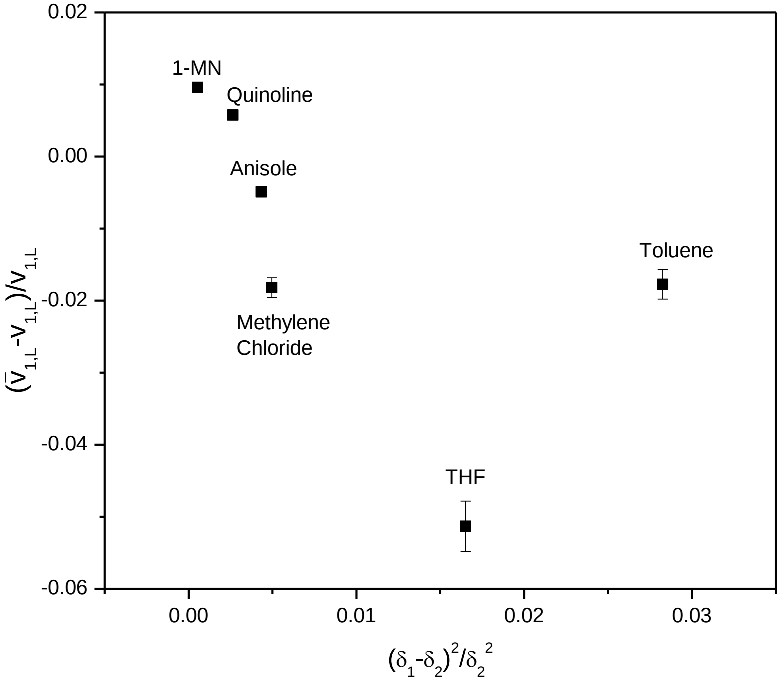

Figure 2-3 – Cross-plot for the relative deviations of partial specific volumes vs the Hildebrand solubility parameter differences for pyrene + various solvents at 20 °C.

This can be attributed to the relative boiling points of the solvents and pyrene. The boiling point of pyrene (394 °C) is significantly larger than that of the solvents except for 1-methylnaphthalene (245 °C) and quinoline (237 °C) where a positive volume difference arises. The observations are at variance with the theory, and only a weak correlation appears to exist between the two ratios.

The enthalpy of fusion for pyrene at 25 °C, 75J/g, was calculated using enthalpy and heat capacity values from the DIPPR database[43] as indicated in equation 2-2. It is possible to probe for a functional relationship between $\frac{\Delta H_m}{M_2 w_1\left[\frac{v_{1,L}}{M_1}\right]}$ and the solubility parameter difference $(\delta_1 - \delta_2)^2$ according to equation 2-6d. The trend, shown in Figure 2-4, is opposite to the one anticipated from Regular Solution Theory.

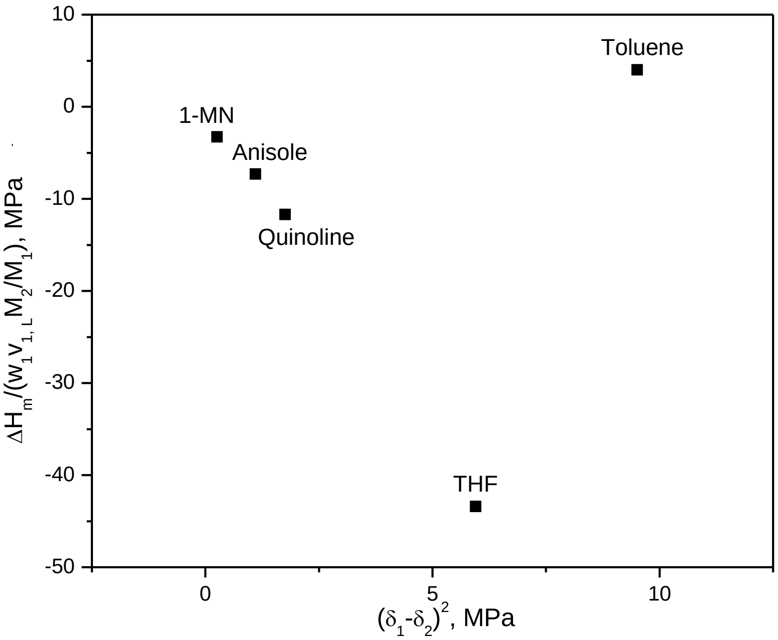

Figure 2-4- Cross-plot for the enthalpy of mixing group, defined by equation 2-6d, and Hildebrand solubility parameter difference for pyrene + various solvents at 25 °C.

Toluene is an apparent outlier. This result is especially significant as the theory is based on estimating the enthalpy of mixing. Pyrene clearly does not follow the pattern of behavior anticipated by Regular Solution Theory. Dechaine et al.[10] concur. They found that regular solution theory does not predict the solubility behavior of pyrene in organic solvents. However, they were able to correlate experimental solubility data with the solubility parameter of pyrene. With the exception of toluene, it would also be possible to establish correlations for volume and enthalpy of mixing for pyrene based on its solubility parameter, even though key elements of the theory are violated. We attribute the apparently anomalous behavior of pyrene in toluene to dimer formation,[46] as this affects the enthalpy and volume of mixing and would impact the apparent value of the solubility parameter vis-à-vis the other diluents where dimerization may not occur.

### 2.4.2 *Asphaltene + diluent mixtures*

Partial specific volume values for Maya and Athabasca heptane asphaltenes at 20 °C are presented in Figure 2-5. Variations among diluents are significant. However, the values are independent of the wt fraction of asphaltene within experimental error. Experiments at temperatures other than 20 °C were carried out at $0.0025 < w_1 < 0.0075$. The specific volume of Athabasca heptane asphaltenes, 0.852 +/- 0.004 $cm^3/g$, evaluated at 20 °C, is greater than or equal to the partial specific volumes in all five diluents at 20 °C.

The partial specific volume values for Athabasca bitumen heptane asphaltenes in quinoline, 1-methylnaphthalene and pyridine equal one another over the whole temperature range, as shown in Figure 2-6. The values in toluene and THF are consistently lower throughout this temperature range.

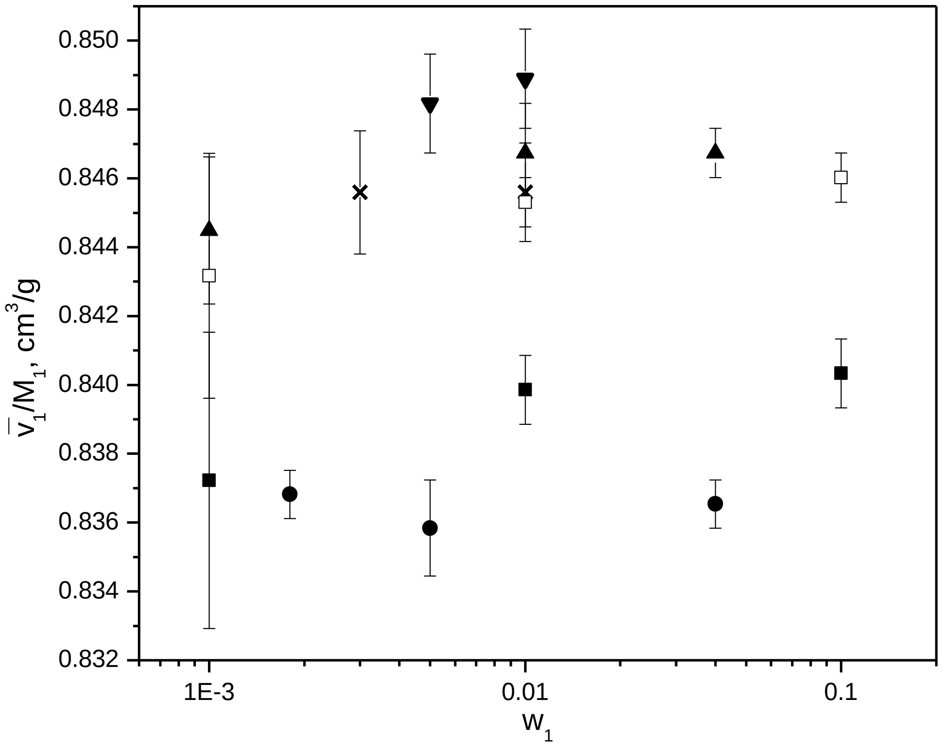

Figure 2-5- Partial specific volume of Athabasca heptane asphaltenes at 20 °C in THF (●), toluene (■), 1-MN (▲), quinoline (×), pyridine (▼), and Maya heptane asphaltenes in toluene (□)

As 1-methylnaphthalene, pyridine, and quinoline are substantially different in structure, polarity and hydrogen bonding, significant differences had been anticipated for the partial specific volume of Athabasca n-heptane asphaltenes in these diluents. That the partial specific volumes in the diluents are less than or equal to the specific volume of the solid asphaltenes is less surprising because asphaltenes are amorphous solids or glasses. The difference between the specific volume of solid and liquid is expected to be negligible. As shown in Figure 2-6 b the behavior of Maya asphaltenes in toluene, THF and 1-MN is also identical to that of Athabasca asphaltenes, i.e., $v_{THF} < v_{toluene} < v_{1\text{-}MN}$ throughout the temperature range.

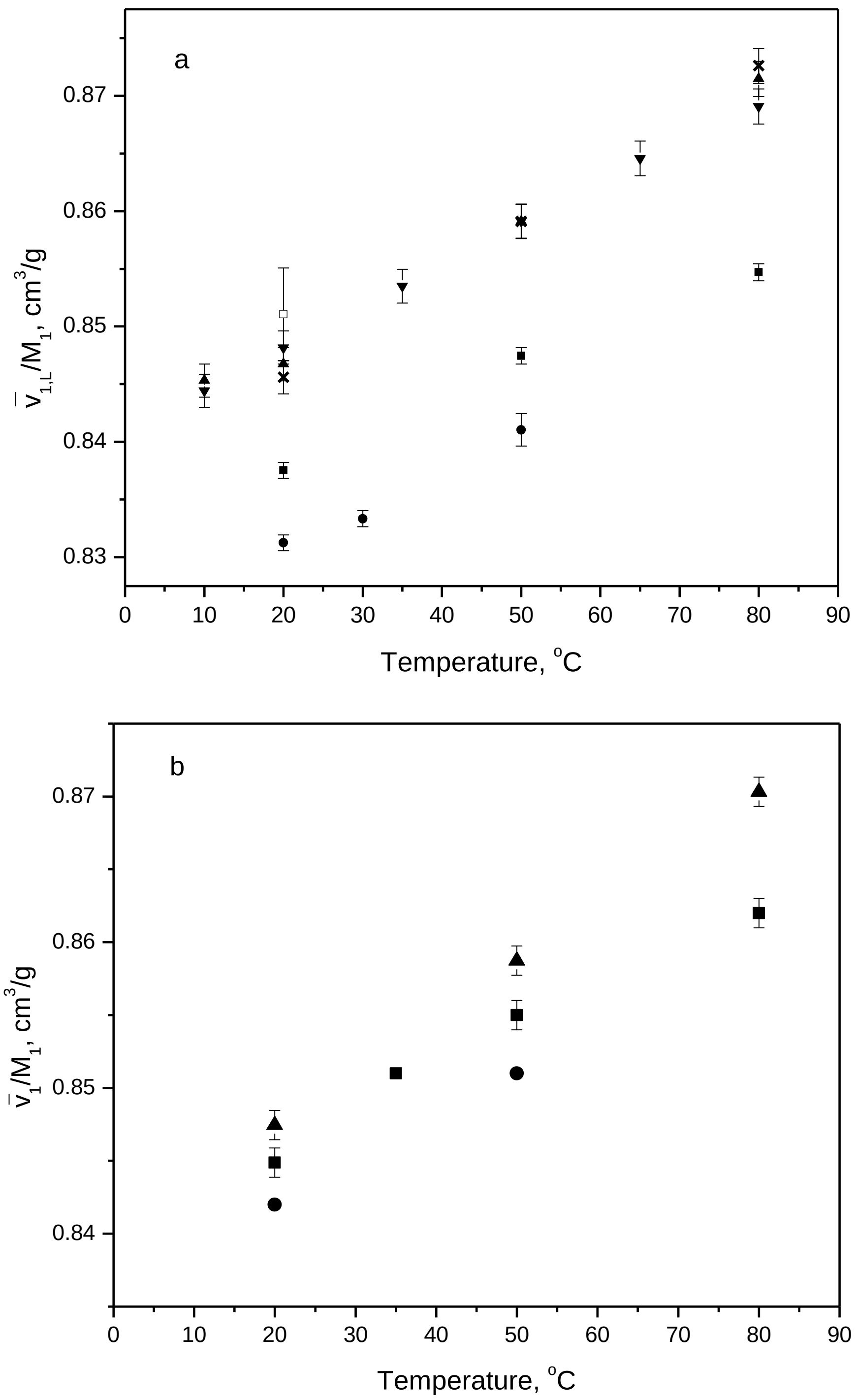

Figure 2-6- Partial specific volume of a) Athabasca heptane asphaltenes in: THF (●), toluene (■), 1-MN (▲), quinoline (×), pyridine (▼), solid asphaltenes (□) b) Maya heptane asphaltenes in THF (●),1-MN (▲), and toluene (■).

As neither the liquid density nor the solubility parameter for liquid asphaltenes are accessible, the possible existence of a relationship between diluent solubility parameter,

$\delta_2$ and $\frac{\overline{v_{1,L}}}{M_1}$ anticipated from Regular Solution Theory is probed at 20 °C (Figure 2-7), and at 50 °**C** and 80 °C (Figure 2-8). Partial specific volume for Athabasca and Maya asphaltenes, based on various definitions are presented in these Figures and are clearly uncorrelated with diluent solubility parameter value. In Figure 2-7 a and b values for pentane and heptane Athabasca asphaltenes, and heptane Maya asphaltenes in pyridine, quinoline, anisole, 1-methylnaphthalene, and a mixture of decane and toluene are shown to possess similar partial specific volumes even though the solubility parameter values of the diluents and their properties vary widely. No value for the Hildebrand solubility parameter of the asphaltenes can account for the absence of a trend in these data. Moreover, significant differences between pairs of diluents with similar solubility parameter values also arise. A similar behavior is apparent at 50 °C and 80 °C (Figure 2-8) where the partial specific volume of Athabasca heptane asphaltenes in 1-methylnaphthalene, pyridine and quinoline agree to within the measurement error despite significant differences in their solubility parameter values. More limited data sets for solids free Athabasca asphaltenes and pentane Maya asphaltenes, at 20 °C presented in Figure 2-9, are also consistent with this finding.

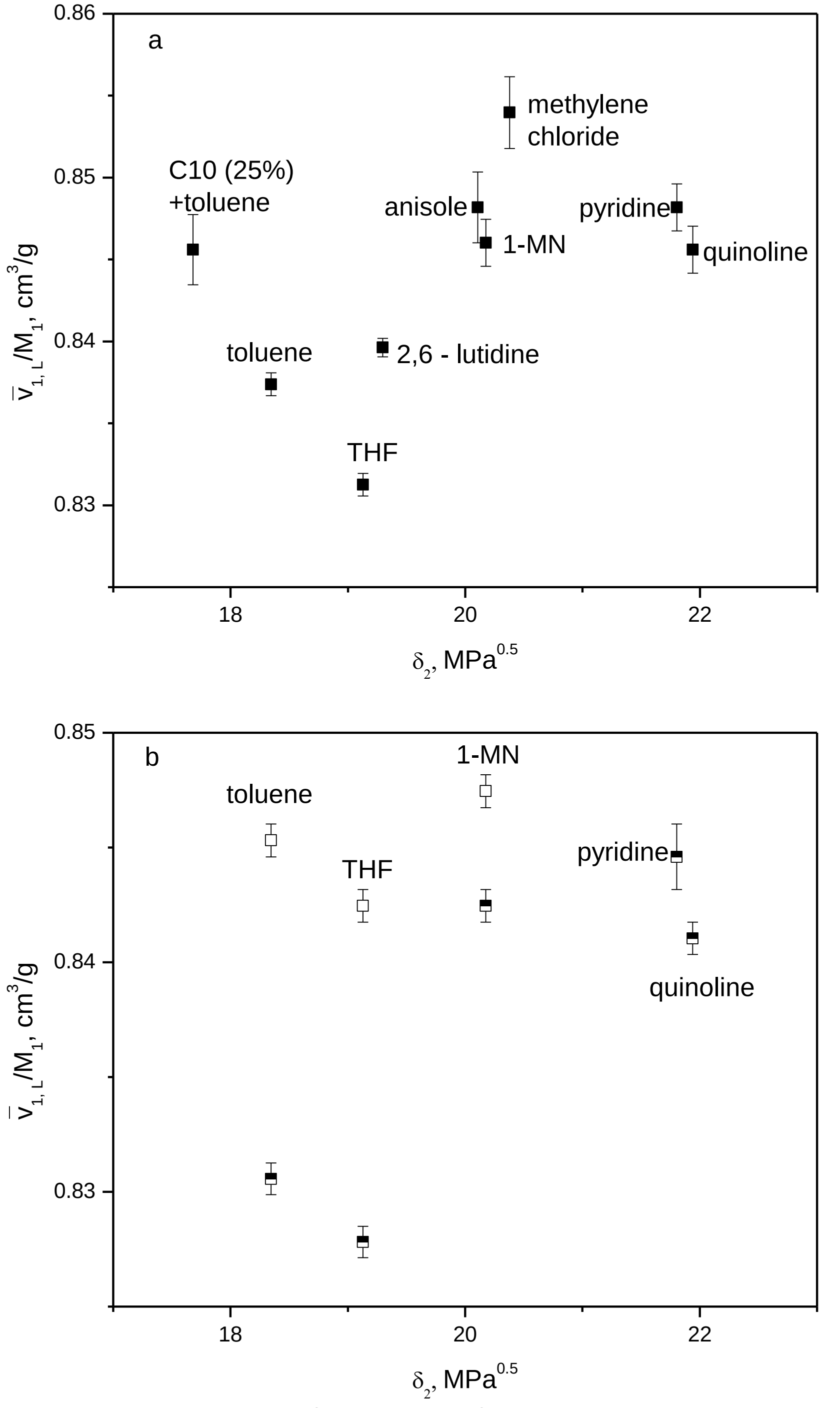

Figure 2-7- Partial specific volume of asphaltenes in various diluents at 20 ˚C versus the Hildebrand solubility parameter of the diluent: a) Athabasca heptane solids-free asphaltenes (■), b) Athabasca pentane asphaltenes (⬓), Maya heptane asphaltenes (□).

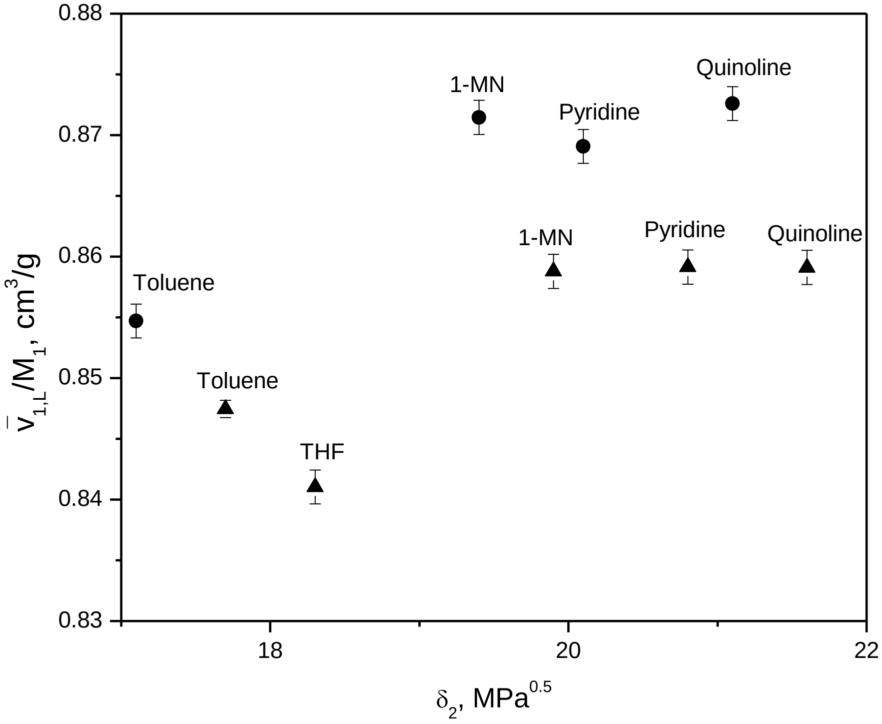

Figure 2-8- Partial specific volume of Athabasca heptane asphaltenes in various diluents versus diluent Hildebrand solubility parameter at 50 °C (▲) and 80 °C (●)

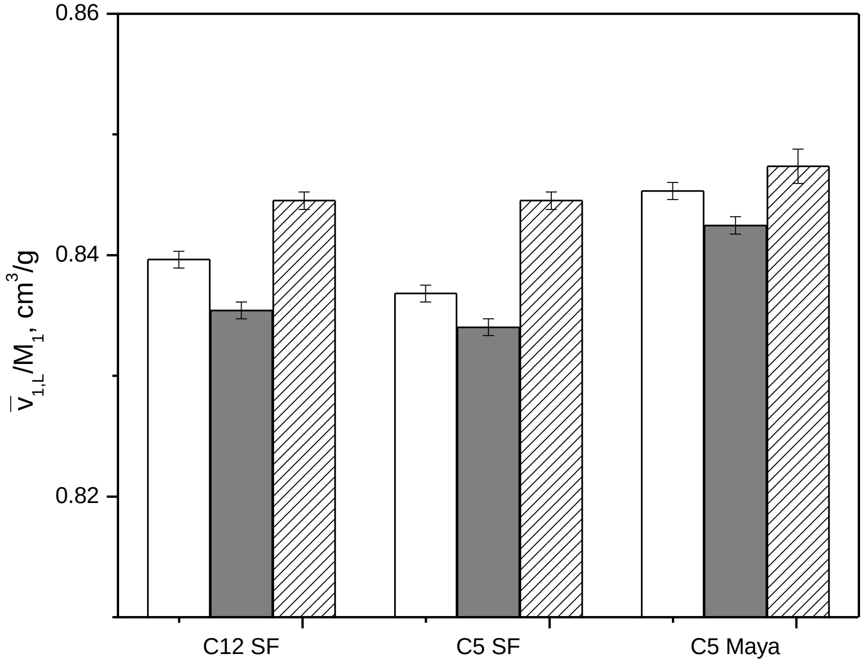

Figure 2-9 – Partial specific volume of solids free n-dodecane and n-pentane Athabasca asphaltenes and Maya n-pentane asphaltenes in toluene (☐),THF (■), and 1-MN (▨)at 20 °C.

As the phase state(s) of asphaltenes are ill-defined, the enthalpy associated with phase state change on mixing with diluents are not accessible. For example, if asphaltenes are glasses, the phase state transition enthalpy is zero. The Hildebrand solubility parameters for liquid asphaltenes are also not accessible. The possible existence of a relationship between the enthalpy of solution group $\frac{\Delta H^{sol}}{M_1} / \frac{v_{1,L}}{M_1}$ and the Hildebrand solubility parameter, $(\delta_2)$, of diluents is probed in Figure 2-10. The values of experimental enthalpy of solution per unit mass are reported in Table A-2. There is clearly no correlation between the Hildebrand solubility parameter of diluents and the enthalpy of solution group. Both positive and negative values arise at the same value of Hildebrand solubility parameter $(\delta_2)$. This result was anticipated in the preamble leading up to equation 2-10b, but it is subject to multiple interpretations.

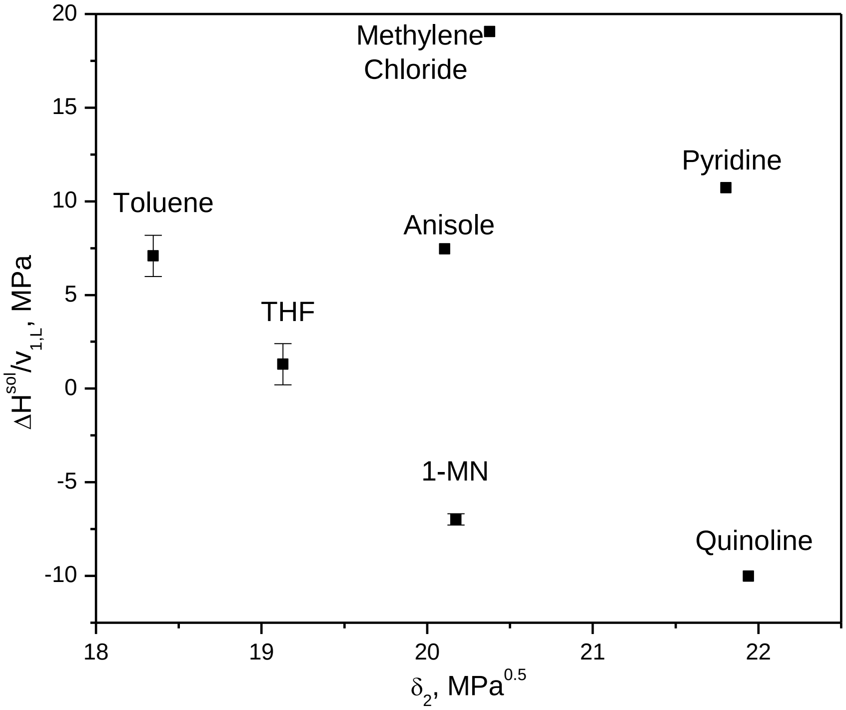

Figure 2-10- Enthalpy of solution group defined in equation 2-10b for Athabasca pentane asphaltenes versus diluent Hildebrand solubility parameter at 25 °C.

### 2.4.3 *Hansen solubility parameter*

The application of the Hansen solubility parameter to asphaltene + diluent mixtures is illustrated in Figure 2-11. Redelius[39] regressed solubility data for a set of 48 solvents with known solubility parameters to obtain Hansen solubility parameters for Venezuelan bitumen, asphaltenes and maltenes. Their parameter values are applied to enthalpy and volumetric measurements for Athabasca pentane asphaltenes obtained in this work. The values used for $\delta_d$, $\delta_p$, and $\delta_h$ of asphaltenes were 19.6, 3.4, and 3,4 MPa$^{0.5}$ respectively. From equations 2-5b and 2-10b, partial specific volume $\frac{\overline{v_{1,L}}}{M_1}$ and enthalpy of solution group $\frac{\frac{\Delta H^{sol}}{M_1}}{\frac{v_{1,L}}{M_1}}$ values are expected to correlate with $\left[(\delta_{d,1}-\delta_{d,2})^2 + {}^1\!/_4\left((\delta_{p,1}-\delta_{p,2})^2 + (\delta_{h,1}-\delta_{h,2})^2\right)\right]/\,\delta_2^2$ and $(\delta_{d,1}-\delta_{d,2})^2 + {}^1\!/_4\left((\delta_{p,1}-\delta_{p,2})^2 + (\delta_{h,1}-\delta_{h,2})^2\right)$ respectively according to this modification to Regular Solution Theory. However, even in this form, the theory does not capture the trends of partial specific volume and enthalpy of solution for these asphaltene + diluent mixtures. Restrictions inherent in the theory, as set out in the introduction, do not permit it to capture fully the physics and chemistry of pyrene + diluent mixtures, and the failure of the theory for asphaltenes + diluent mixtures should not be surprising, given the complexity of asphaltenes themselves and their behavior in diluents.

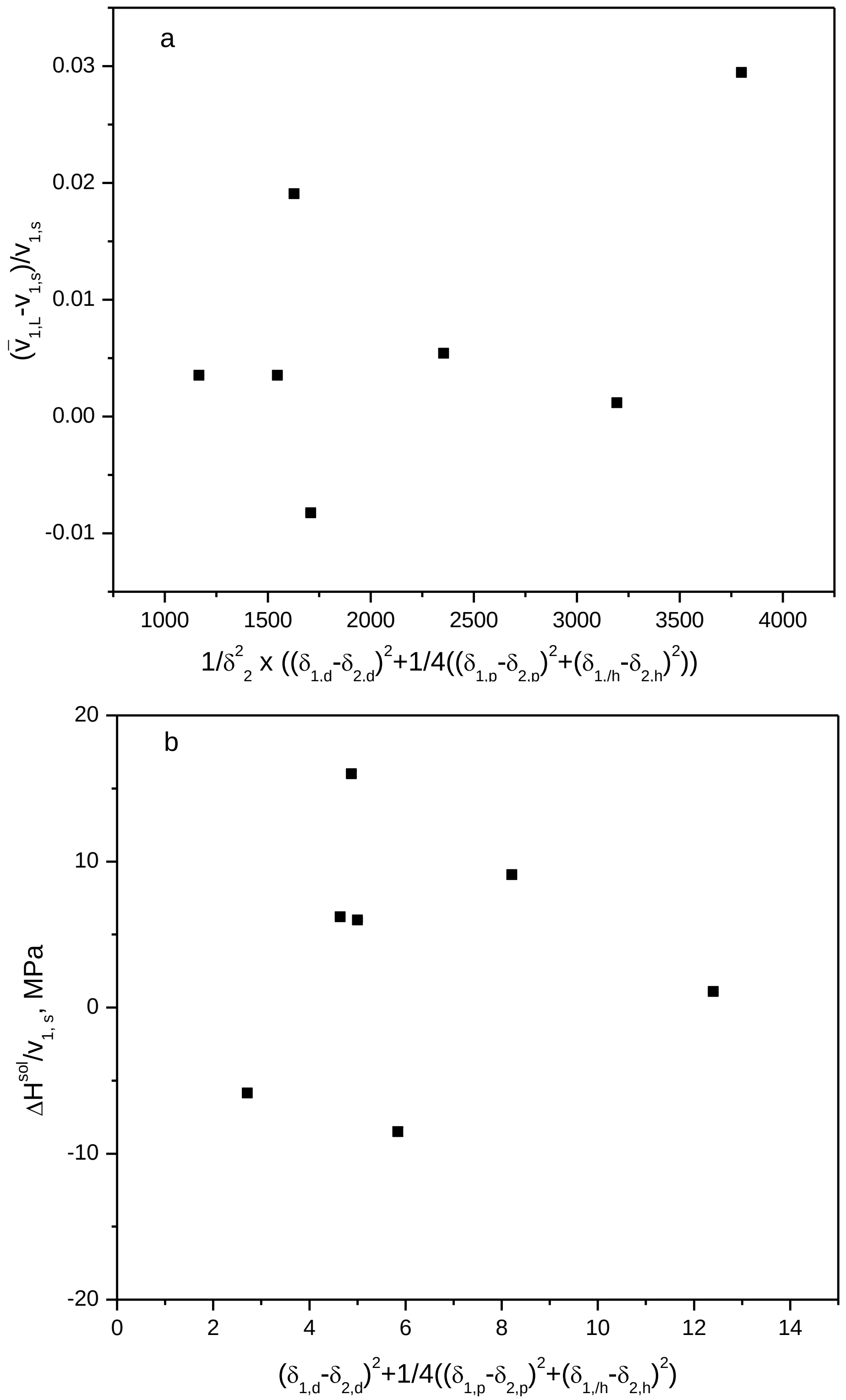

Figure 2-11- Cross plots between the partial specific volume of Athabasca heptane asphaltenes (a), and the enthalpy of solution of Athabasca pentane asphaltenes (b), with the Hansen solubility parameter for various diluents at 25 °C.

### 2.4.4 *Cross correlation of the volumetric data with enthalpy of solution and enthalpy of mixing data*

Values of partial specific volume and enthalpy of solution, at infinite dilution, both reflect the nature and the extent of the interactions between asphaltenes and diluents. Cross correlation is expected between these measures if similar or simple dissolution phenomena arise. Cross plots for the partial specific volume values of pyrene and pentane Athabasca asphaltenes versus measured enthalpy of solution values are presented in Figure 2-12a and b respectively. The enthalpy of fusion of and specific volume of subcooled liquid pyrene at room temperature, (75 J/g, 0.842 $cm^3/g$) and the fusion or glass transition enthalpy for Athabasca pentane asphaltenes and an estimated density of liquid pentane asphaltenes at room temperature (~22 J/g[41], 0.845 $cm^3/g$) also shown in Figure 2-12a and b, provide excellent reference points for the enthalpies of solution and partial specific volumes identified in this work. There is a clear correlation between the partial specific volume and enthalpy of solution for pyrene dissolution as shown in Figure 2-12a with the exception of toluene where dimer[46] formation may occur. For this latter case the enthalpy is larger for the given value of specific volume than expected. For asphaltene + diluent mixtures, divergence reflecting the complexity and diversity of the physiochemical behaviors present is observed. A trend cannot be inferred from the data in Figure 2-12b and it is clear that the behavior of asphaltene + diluent mixtures cannot be described on the basis simple solution thermodynamics. The difference between asphaltene behavior in toluene and 1-methylnaphthalene is particularly striking, as is the difference between quinoline and THF.

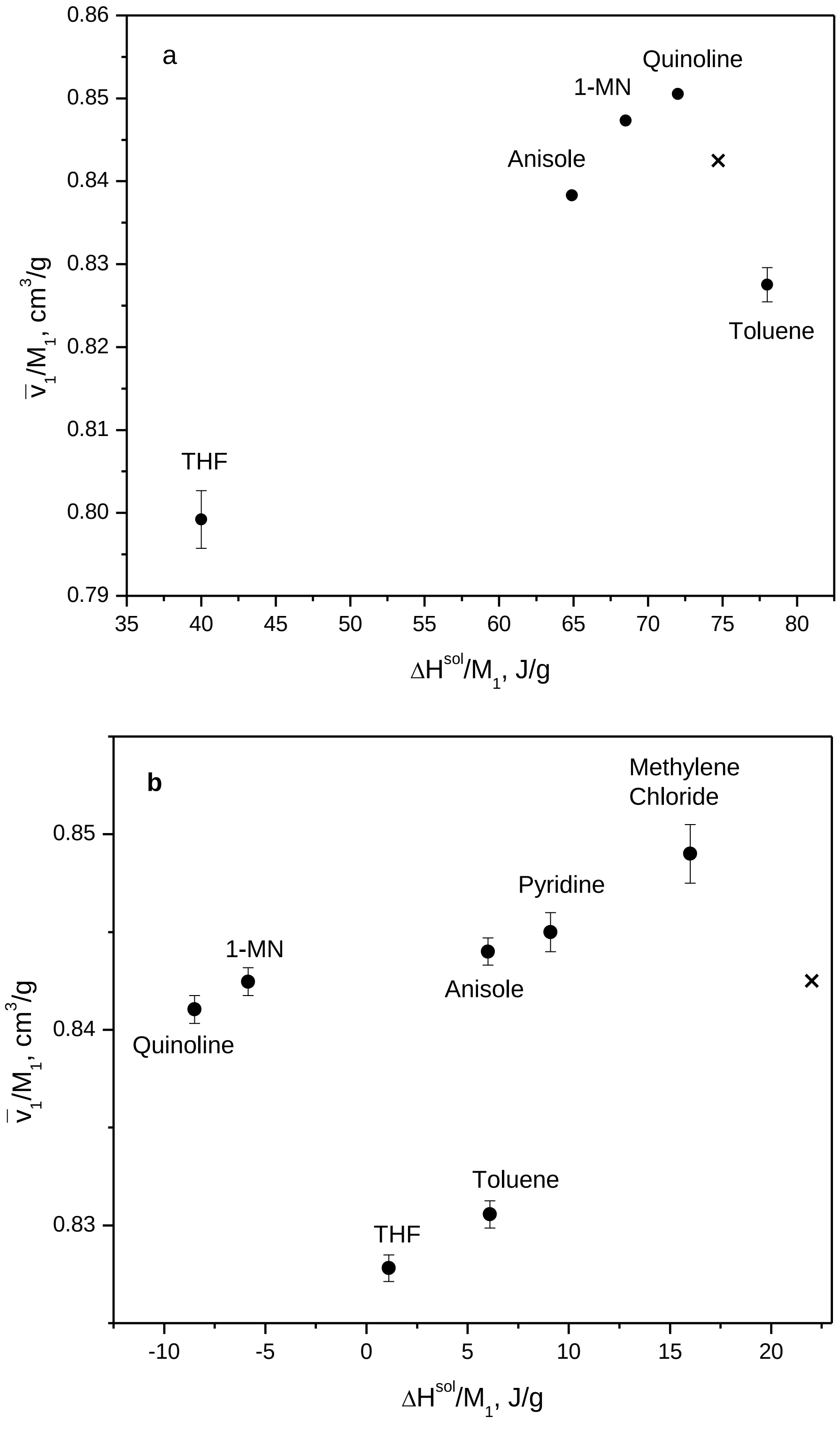

Figure 2-12- Cross correlation of the partial specific volume and enthalpy of solution per unit mass for a) pyrene and b) pentane Athabasca asphaltenes in various diluents at room temperature. Fluid reference points for pyrene and pentane Athabasca asphaltenes are denoted with an X.

Additional phenomena, from identification of the fraction of asphaltenes participating in dissolution or other phenomena, to aggregation and the nature of phase changes occurring upon mixing must be identified and quantified in order to model the observed behaviors thermodynamically. Identification and resolution of these physiochemical phenomena comprise topics for further detailed study that are actively being pursued.

## 2.5 Conclusions

The partial specific volumes and enthalpies of solution of pyrene, and various Athabasca and Maya asphaltenes at near infinite dilution in decane, toluene, 1-methylnaphthalene, quinoline, anisole, 2, 6-lutidine, pyridine, methylene chloride, and tetrahydrofuran are reported over the temperature range 20 - 80 °C. The properties of pyrene + diluent mixtures are used to illustrate the application and misapplication of regular solution theory and simple solution thermodynamics concepts to such mixtures. The partial specific volumes and enthalpies of solution of various Athabasca and Maya asphaltenes are shown to be uncorrelated with both Hildebrand and Hansen Solubility parameter values, and their values are shown to be inconsistent with the thermodynamics concepts defining regular solution theory. The results do not support the use of solubility parameter or other simple solution thermodynamic concepts to describe asphaltene + diluent mixture behavior and highlight the need for a more detailed description of physiochemical phenomena arising in such mixtures.

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# Chapter 3: Interactions between Athabasca pentane asphaltenes and n-alkanes at low concentration[a, b]

## 3.1 Introduction

Asphaltenes and related oil fractions are defined operationally based on their tendency to precipitate from petroleum upon addition of specific n-alkanes and by the details related to their separation. Examples include ASTM D3279[1], ASTM D6560[2] and the Association Francaise de Normalisation procedure[3]. The mass fraction of asphaltenes in a sample is defined by a two-stage filtration process, where samples are first diluted in an alkane solvent. The permeate from the first filtration is discarded while the retentate is mixed with toluene, or another solvent, and filtered a second time. The asphaltene content of the sample is defined as the solvent-free mass recovered from the second permeate divided by the mass of the sample. Numerous measurement techniques and variations are employed globally. The effects of temperature, contact time, solvent, solvent-to-feed ratio[4], washing procedure[5] and filter pore size[3, 6-11] on asphaltene separation results have been studied systematically, and there are data on the impact of the extent of dilution and n-alkane chain length on the yield of asphaltenes from Athabasca bitumen[12]. Small differences in procedure or differences in the application of procedure appear to cause significant differences in outcomes. For example, multi-laboratory reproducibility of the procedure in ASTM 3279 for n-heptane insoluble mass fraction determination is twice the single operator reproducibility that in turn is three times the single operator

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[a] The content of this chapter has been published in: Nikooyeh, K.; Bagheri, S. R.; Shaw, J. M., Interactions Between Athabasca Pentane Asphaltenes and n-Alkanes at Low Concentrations. *Energy & Fuels* **2012,** 26, (3), 1756-1766.

[b] All the microscopy data and text have been prepared by Dr. S. Reza Bagheri, a co-author of this paper.

repeatability. The sensitivity of mass and physical property outcomes to small procedural differences either planned or unplanned, suggests that the interaction of asphaltenes, however defined, with n-alkanes and other solvents, such as toluene, are more complex than those captured by simple notions of solubility[13-17] or even colloid behavior[18-23].

Carbognani et al.[24] reported on the swelling of asphaltene particle beds saturated with liquid n-alkanes. Beds of heptane asphaltene particles exposed to n-hexane and n-heptane swelled by 30 to 40 vol %, and swelled by 20 to 30 vol % in n-hexadecane. Mahmoud et al.[25] and Stachoviak et al.[26] using titration calorimetry of a heavy oil with a range of n-alkanes hypothesized that the enthalpy of solution is composed of endothermic and exothermic contributions, where the endothermic contribution prevails with n-hexane, and the exothermic contribution prevails with n-heptane and higher n-alkanes. They attributed the endotherm to van der Waals dispersion interactions between the diluents and the oil and the exotherm to physical interactions between n-alkanes and exterior or interior[27] asphaltene particle surfaces.

Discotic liquid crystals are typically formed in materials where the molecules comprise both fused aromatic rings and alkane chains. The details of the molecular structure are important for the formation of the liquid crystal phase[28,29] as the core provides the rigidity for the liquid crystal and the flexible chains serve to reduce the melting point so that the behavior is exhibited[30]. Sorai and Sato[31] observed that liquid crystals present in discotic liquid crystal forming materials, can be stabilized by successive melting of alkyl chains attached to their molecular core. Without delving into debates regarding asphaltene molecular structure, such groups are also associated with asphaltenes and Bagheri et al.[32]

recently reported that liquid crystalline domains form irreversibly on asphaltene particle surfaces when the particles are exposed to toluene vapor or when they are heated.[c]

In this work, the phase behavior and interactions of Athabasca pentane asphaltenes with n-alkanes at low concentration are investigated using mixture density and solution calorimetry measurements, filtration, and direct microscopic observation of asphaltene + n-alkane binary mixtures with cross-polarized and visible light. Through application of these diverse approaches, independent qualitative and quantitative data sets are obtained. These experimental results are then interpreted and modeled collectively in light of known limitations on values for thermophysical properties and processes, such as enthalpies associated with sorption, phase change and mixing of pure hydrocarbons. With this integrated approach, we expect to contribute to a deeper understanding of asphaltene properties and to methods chosen for their preparation.

## 3.2 Experimental

### 3.2.1 *Materials*

N-pentane precipitated asphaltenes were obtained from Athabasca bitumen supplied by Syncrude Canada Ltd. N-alkanes were obtained from Fisher, Sigma-Alrich and Acros at a minimum purity of 99%. For asphaltene preparation, n-pentane was added to bitumen at a ratio of 40 ml to 1 g of feed stock. The mixture was stirred for 24 hours at room temperature, and then filtered, using filter paper Q2, with a pore size 1-5 μm and washed with n-pentane until the liquid passing through the filter was clear. They were subsequently dried overnight in a vacuum oven at 9 kPa and 303 K. Athabasca bitumen comprises 18.7 wt% pentane asphaltenes on this basis.[33]

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[c] The preceding paragraph was written by Dr. S. Reza Bagheri.

### 3.2.2 *Density measurements*

Density measurements were performed using an Anton Paar DMA 5000 density meter with an accuracy of 0.000 01 g/cm$^3$ and values reported to 0.000 001 g/cm$^3$. For measurements with each n-alkane, 4-6 binary mixtures with asphaltene contents ranging from 1000 to 8000 ppmw (0.5-5 g/L) were prepared. Asphaltenes were mixed with the n-alkanes in a closed container and shaken using a vortex mixer at 3200 rpm for 1 minute. The mixtures were then sonicated for 10 minutes and left for 24 hours prior to measurement. Samples were re-mixed for one minute using the vortex mixer at 1000 rpm prior to each density measurement. Repeatability of the density measurements for asphaltene + n-alkane mixtures was within ± 0.000 004 g/cm$^3$.

Partial specific volumes of asphaltenes, $\bar{v}_a$ , at near infinite dilution in n-alkane mixtures were determined by linear regression of the inverse density of dilute mixtures of asphaltenes in n-alkanes versus the mass fraction of asphaltenes using equation 3-1:

$$v_a = \frac{1}{\rho_m\big|_{x_a=0}} + \frac{\partial\left(\frac{1}{\rho_m}\right)}{\partial x_a} \tag{3-1}$$

where $\rho_m$ is the mixture density and $x_a$ is the mass fraction of asphaltenes. $\left.\frac{1}{\rho_m}\right|_{x_a=0}$ and $\frac{\partial\left(\frac{1}{\rho_m}\right)}{\partial x_a}$ are the ordinate intercept and the slope of the plot respectively. An example plot is shown in Figure 3-1. For this and other cases evaluated, the R$^2$ values for the regression exceeded 0.999 and the resulting uncertainty of the partial specific volume values is 0.002 cm$^3$/g.

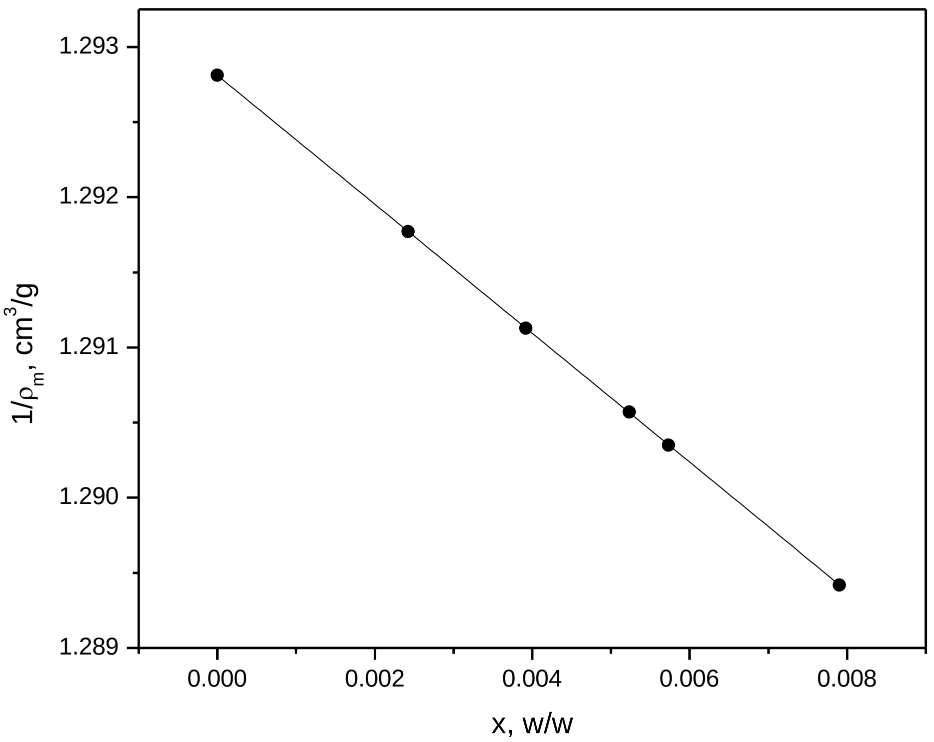

Figure 3-1 Linear regression of the plot of the inverse density of mixtures of Athabasca $C_5$ asphaltenes in n-decane versus the mass fraction of asphaltenes.

### 3.2.3 *Solution calorimetry*

For calorimetry measurements, a precision solution calorimetry module, SolCal, from TA Instruments inserted in a TAM III thermostat was used. SolCal is a semi-adiabatic system with a short-term noise of < 10 μK/5min. The module comprises a 25 ml cell, filled with n-alkane, and a 1 ml sealed glass ampoule, loaded with 30-35 mg of Athabasca $C_5$ asphaltenes or asphaltene fractions recovered from asphaltene settling experiments. As this apparatus comprises a commercial unit, and was used unmodified, equipment details are available from the supplier. The module was inserted in a thermostat, maintained at a set temperature of 25 °C, and allowed to reach a steady state or baseline condition defined as a standard deviation of an exponential fit to the temperature over 5 minutes of less than 10 μK. A temperature calibration using a heat signal of 1 J was then performed to determine system parameters. After the temperature calibration a 5 minute temperature baseline was collected. At the end of this period the glass ampoule was broken to allow for the solid to mix with the liquid. The temperature was then recorded for an additional 8 to 10 minutes, to capture the signal linked to mixing (less than 1.5 minutes in all cases), and a final baseline. A second temperature calibration was then performed. All measurements were performed within a temperature offset range of -100 mK to 100 mK, at a mixing rate of 500 rpm.

The difference between the temperature of the cell and the set temperature of the bath, (the temperature offset) during the experiment, was used to calculate enthalpies of solution according to the method of Wadso[34]. In this work, enthalpies of solution include enthalpies of sorption, phase change and mixing arising on addition of asphaltenes to n-alkanes. Measurement precision and accuracy were validated using KCl (25 mg and 2 mg) + water (25 ml). For the 25 mg KCl case, the measured enthalpy of mixing value, 232.0 J/g was within 1.1 J/g (0.5%) of the value reported in the literature, 230.9 J/g[35], based on a ~ 6 J signal. For the 2 mg KCl case, the measured enthalpy of solution value, 230.2, J/g was within 0.7 J/g (0.3%) of the value reported in the literature, based on a ~ 0.5 J signal. In this work, enthalpy of solution values are based on somewhat smaller signals (~ 0.02 to ~ 0.20) mJ. Measurement repeatability ranged from ±0.3 J/g to ±0.5 J/g. The largest uncertainties were associated with smaller signals, where the corresponding enthalpies of solution fell between -1 and 1 J/g, and with pentane, a volatile liquid.

### 3.2.4 *Sedimentation experiments*

The samples from the solution calorimetry measurements were collected and stored in a closed container for 24 h. The density of the supernatant was measured and the mass fraction of asphaltenes present in the supernatant ( $x$ ) was calculated from the supernatant, n-alkane, and mixture densities ( $\rho_{\mathrm{supernatant}}, \rho_s, \rho_{\mathrm{m}}$ ) as:

$$x = \frac{\rho_{\mathrm{supernatant}} - \rho_s}{\rho_m - \rho_s} \left[ \frac{\rho_{\mathrm{m}}}{\rho_{\mathrm{supernatant}}} \right] \qquad (3\text{-}2)$$

One sample, the supernatant from the n-decane + asphaltene mixture, was also filtered through a Millipore GSWP filter with a nominal pore size of 0.22 µm to gauge the size of the asphaltene particles, if present, in the supernatant.[d]

### 3.2.5 *Cross-polarized light microscopy*[e]

A Zeiss Axio-Observer inverted reflective microscope equipped with crossed polarizers was used to observe the interaction of asphaltene with n-alkanes. A 3 megapixel camera was connected to the microscope to record images. Figure 3-2 shows the setup for the experiments. Asphaltene samples were in the form of a powder placed on a glass slide on the microscope stage. N-alkanes were injected onto the asphaltenes using a syringe and a series of photos were taken, at room temperature, to show the progress of n-alkane-asphaltene interactions. For observation of asphaltene particle swelling, asphaltene

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[d] The fraction recovered from the supernatant was collected and its density was calculated from extrapolation of the density values to low concentrations in toluene. The calculated density was 1.15 g/cm$^3$. If this value was used in the calculations based on equation 3-2 the obtained value would be <3% higher than the current calculated values for mass fraction of the asphaltenes.

[e] The following section is written by Dr. S. Reza Bagheri.

particles were placed on an aluminum slide and then the solvent was added. The aluminum slide was then inverted and placed on the microscope stage.

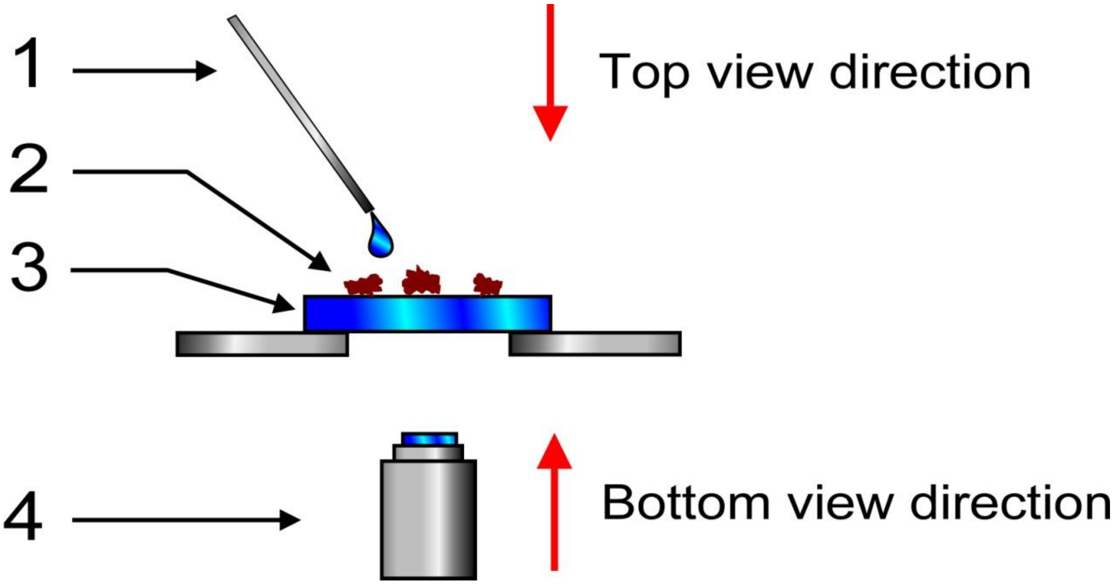

Figure 3-2 The setup for observation of solvent-asphaltene interactions using an inverted microscope. (1) syringe for solvent addition, (2) asphaltene powder, (3) glass slide placed on the microscope stage, (4) objective lens of the microscope.

### 3.3 Results and discussion

Asphaltene mass fractions in crude oils are defined as insoluble in n-alkanes, on the basis of filtration experiments. The mass fraction reported varies with the carbon number of the n-alkane used for separation. The mass fraction of heptane asphaltenes, for example, is typically smaller than the mass fraction of pentane asphaltenes. For Athabasca bitumen the difference is 5 wt % of the bitumen[13]. Such effects do not appear to play a role in the evaluations reported here as more than 80 wt % of the pentane asphaltenes settle from pentane asphaltene + n-pentane suspensions and more than 87 % settle from larger alkanes within 24 hours under the influence of gravity alone at 1-1.5 g/L, as shown in Figure 3-3. A similar behavior was observed for n-heptane asphaltenes where the fraction that remained suspended at 1-1.5 g/L is larger in n-heptane than in n-decane (~13% vs. ~8%). However, a variable fraction of fine particles, comprising a significant fraction of asphaltenes particles are at risk of being "washed away" during washing. For example, in n-decane, ~ 13 % of the pentane asphaltenes pass through a 0.220 μm filter. Different mass retention outcomes are expected if a filter cake is allowed to form or is prevented from forming on the filter surface during washing. In toluene, a diluent in which asphaltenes are defined as soluble, Athabasca asphaltenes are also separable by centrifugation from dispersions of similar composition[36]. Having noted this, given the diversity of constituents reported as asphaltenes, solubility of a small mass fraction of asphaltenes at low concentration in n-alkanes or toluene[37] cannot be precluded.

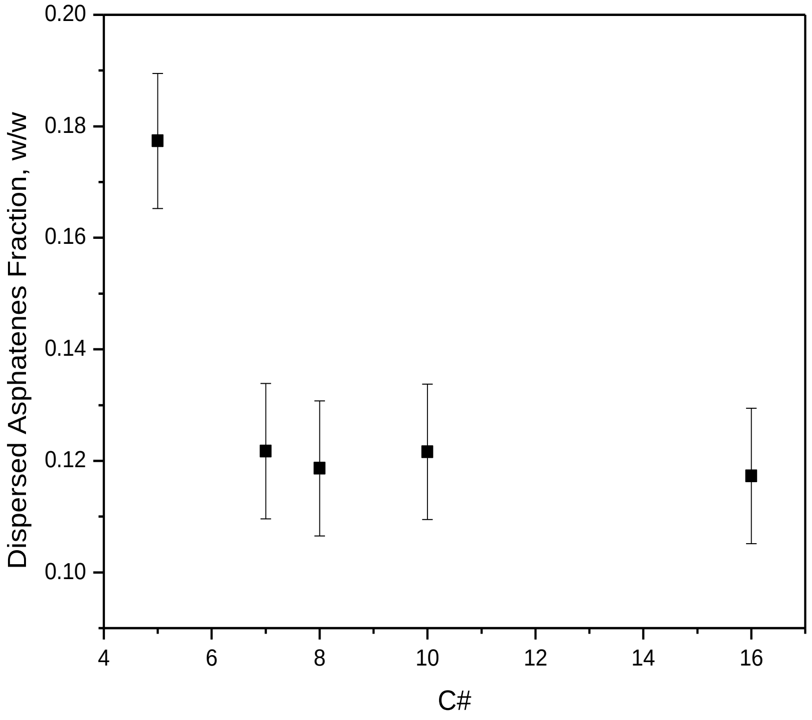

Figure 3-3 Mass of Athabasca $C_5$ asphaltenes remaining in the supernatant following 24 hrs of settling divid by the mass of asphaltenes in the mixture. The initial composition was 1-1.5g/L asphaltenes in n-alkane.

As the asphaltene fraction remaining in the supernatant comprises a mixture of soluble and fine suspended particles and these sub fractions are not discriminated, no inferences can be drawn regarding the relative solubility of asphaltenes in n-alkanes on the basis of these data.

### 3.3.1 *Partial specific volume of asphaltenes in n-alkanes*

As asphaltene particles are primarily physically dispersed and readily separable from n-alkanes by sedimentation, physical interactions between asphaltene particles and n-alkane diluents must be explored in order to explain the systematic variation of partial specific volumes of asphaltenes in n-alkanes shown in Figure 3-4a. Parkash et al.[27] showed that asphaltenes are porous solids using both mercury porosimetry and BET measurements. They found that pore volumes for pores in the size range 15-2000 Å were 0.09 to 0.12 $cm^3/g$ and that total pore volumes, reflecting the difference between the intrinsic and bulk specific volumes of asphaltene powders, were between 0.8 and 0.95 $cm^3/g$ [27]. The intrinsic specific volumes of crystalline polynuclear aromatic organic solids, the most-dense relevant class of compounds, exceed 0.7 $cm^3/g$ [38]. Thus, the specific volume of asphaltene particles is expected to exceed 0.79 $cm^3/g$. From Carbognani et al.[24], asphaltenes are expected to swell by a minimum of 20 % in n-alkanes. Thus, values for the swollen volume occupied by asphaltene particles in n-alkanes are expected to exceed 0.95 $cm^3/g$. As asphaltene particles are porous, sorption of n-alkane is also expected. The word sorption is used in this contribution because the nature of the interaction, adsorption, absorption, or both remains unclear. Consequently, measured values for partial specific volume of asphaltenes in n-alkanes are expected to be less than values linked to macroscopic observations of swollen asphaltene particles. As the partial specific volume values fall between 0.83 and 0.86 cm$^3$/g, this is clearly the case.

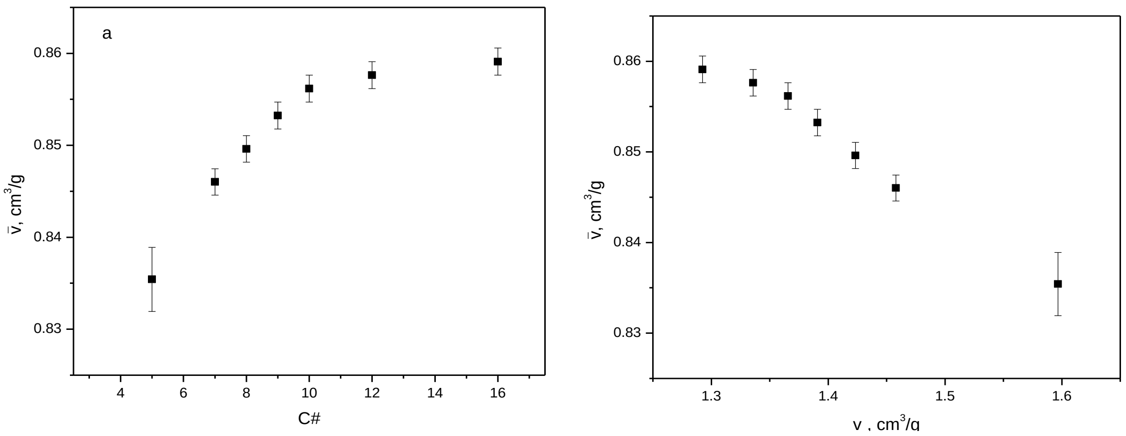

Figure 3-4 Partial specific volume of Athabasca n-pentane asphaltenes in n-alkanes from pentane to hexadecane: (a) as a function of n-alkane carbon number, (b) as a function of the specific volume of the n-alkanes

### 3.3.2 *Enthalpy of solution*

The enthalpy of solution values, reported on a per unit mass of Athabasca pentane asphaltenes basis, are plotted versus n-alkane carbon number in Figure 3-5. The sign convention employed here is that positive values indicate endothermic behavior and negative values indicate exothermic behavior. The enthalpy of solution decreases and changes sign as the hydrocarbons become larger. A related effect was also noted by Stachoviak et al[26]. Detailed examination of the heat production traces, Figure 3-6, reveals co-existing and competing exothermic and endothermic processes that sum to the net enthalpy of solution values shown in Figure 3-6. For asphaltene + n-heptane the endothermic peak dominates. For n-octane both endothermic and exothermic peaks are evident but the overall impact is endothermic. For n-decane and n-hexadecane exothermic and endothermic peaks continue to overlap but the overall impact is exothermic. From the n-octane, n-decane and n-hexadecane traces, the exothermic process clearly precedes the endothermic one, though the processes overlap significantly.

Given this complexity, one would also expect the enthalpy of solution to be a function of asphaltene concentration. As the dynamic range of the calorimetry measurements is restricted, the impact of asphaltene concentration on enthalpy of solution values was probed at 0.8, 1.5 and 3 g/L for pentane asphaltenes n-heptane. The results, 1.4, 1.3, and 1.0 J/g of asphaltene respectively appear to trend to lower values. However the differences are within the experimental uncertainty and are therefore not conclusive.

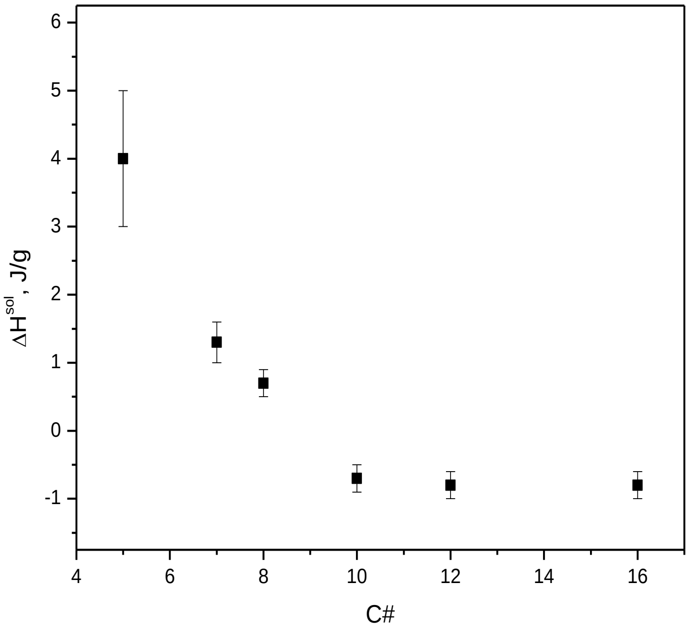

Figure 3-5 Enthalpy of solution of Athabasca C5 asphaltenes (1.5 g/l) + n-alkanes

The reversibility of the interactions between the pentane asphaltenes and n-alkanes was probed by mixing as-prepared pentane asphaltenes with n-heptane and re-drying them prior to calorimetry experiments. The enthalpies of solution of the re-dried sample in n-heptane (1.2 J/g) and in n-decane (-0.5 J/g), agree with the values for as-prepared pentane asphaltenes in the same n-alkanes, 1.3 J/g and -0.7 J/g respectively. Thus the process is reversible. This behavior contrasts with the behavior of asphaltenes with toluene, for example, where the interactions are not reversible [32].

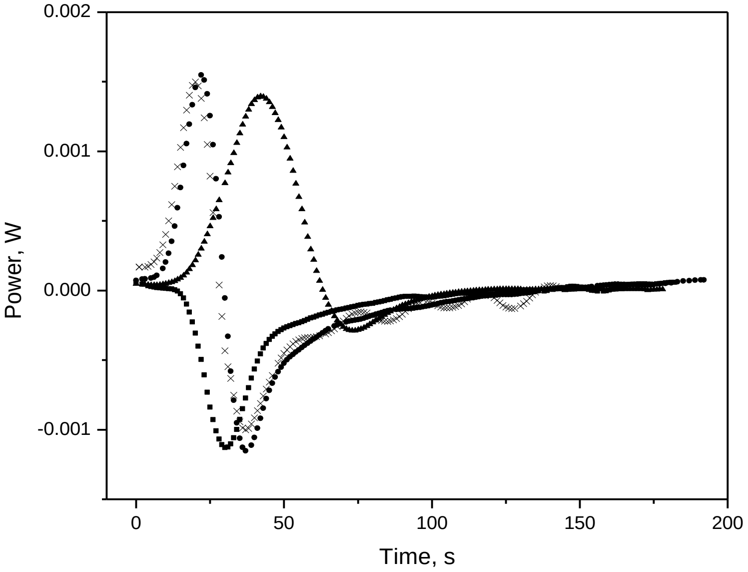

Figure 3-6 Unscaled power traces from enthalpy of solution measurements for $C_5$ Athabasca asphaltenes in n-heptane (■), n-octane (●), n-decane (×) and n-hexadecane (▲) at 1.5 g/L and 25 °C.

The enthalpy of solution values for the settled asphaltene fractions were also measured. The settled asphaltene fractions, recovered by filtration with Q2 filter paper (pore size 1-5 μm), and then dried overnight using the drying equipment and procedure for asphaltene preparation, were then remixed with the n-alkane from which they were recovered. This asphaltene fraction was expected to have a lower solubility than the asphaltenes as a whole. Unlike the asphaltenes as a whole, the enthalpy of solution values for the settled fractions, Figure 3-7, are uniformly negative and the magnitude increases with the carbon number of the solvent. The magnitude is independent of the drying period. For example asphaltenes washed with n-decane were placed under vacuum for 1, 3 and 7 days. The solution calorimetry results, were identical and all lied within -7.1 ± 0.3. Thus the settled fraction is clearly the source of the observed exotherm in the power traces, and from the energy balance, the fraction in the supernatant is the source of the endotherm in the power traces. Two cross mixtures of the settled fractions were also prepared. Here, the asphaltenes that settled in one diluent were mixed with another diluent. The enthalpy of solution of the settled fraction from $C_5$ Athabasca asphaltene + octane in decane is -7.4 J/g while the enthalpy of solution for the settled fraction from $C_5$ Athabasca asphaltene + decane in octane is -1.5 J/g. These values are similar to the enthalpy of solution values for the decane settled fraction in decane, -7.1 J/g, and for the octane settled fraction in octane, -2.5 J/g. Similarly, the enthalpy of solution of the n-decane settled asphaltene fraction in n-heptane, 0.1 J/g is comparable to the enthalpy of solution for the n-heptane settled asphaltene fraction in n-heptane, -0.5 J/g. These results highlight the similarity of the behavior of the different settled asphaltene fractions and the differences in the interactions between these asphaltene fractions and n-alkanes of different chain length at low concentration.

One can speculate on the nature and relative balance of these complex interactions. For example, sorption enthalpies are exothermic and phase transitions from solid to liquid, or to liquid crystal are endothermic. N-alkanes sorb on or within the asphaltene particles and it is conceivable that sorbed n-alkanes induce phase transitions in a fraction of asphaltene particles (individually or as a whole) at low concentration. Dissolution of solid asphaltene constituents in n-alkanes, also an endothermic process, cannot be precluded. Thus, an exotherm (i.e.: sorption) is expected to precede or be concurrent with an endotherm (phase change or phase change + dissolution). For the lower n-alkanes, phase transition and possibly dissolution appear to play greater roles, than for the larger n-alkanes. For the settled asphaltene fractions, sorption (an exothermic process) appears to play a more important role than in the asphaltenes as a whole.

No further information on the nature of possible transitions can be inferred from calorimetric measurements. Direct visual examination of the processes occurring in asphaltene + n-alkanes mixtures, at the particle level, using visible and cross-polarized light microscopy provide additional detail which permit more detailed analysis and interpretation of the enthalpy of solution and partial specific volume data.

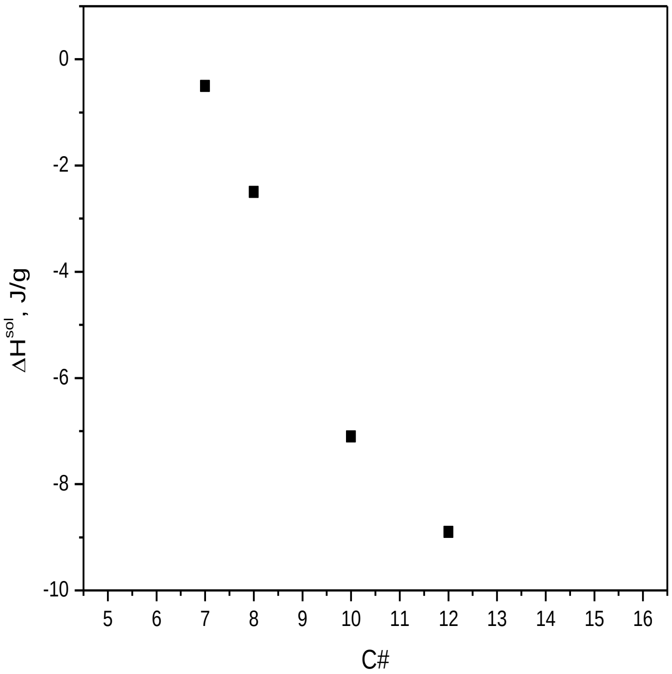

Figure 3-7 Enthalpy of solution of settled asphaltene fractions recovered and then remixed in the same n-alkane at 1 g/L.

### 3.3.3 *Microscopic observation of asphaltene + n-alkane mixtures*[f]

*Birefringence of asphaltene particles exposed to n-alkanes*

Figure 3-8 shows the interaction of n-octane with C5 asphaltenes. The asphaltene powder is amorphous and should be dark under cross-polarized light. The golden appearance is

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[f] The work presented in the following section is performed and written by Dr. S. Reza Bagheri.

due to diffuse reflection from the rough powder surface (Figure 3-8a). As soon as a drop of n-octane is added, it spreads over the asphaltene powder and birefringent spots become visible (Figure 3-8b). These birefringent spots then become isotropic once the particles are coated. Figure 3-9 shows the reverse process for the interaction of C5 Athabasca asphaltenes with n-heptane under cross-polarized light. For this case, the observations started with heptane covered asphaltene particles. There was no birefringence initially as shown in Figure 3-9a. As the heptane evaporated, a large number of birefringent spots appeared on the asphaltene particle surfaces, within 12 seconds of heptane addition (Figure 3-9b). The birefringent spots then disappeared as the evaporation of the n-heptane continued (Figure 3-9c). Similar reversible transitions were observed for n-pentane, n-heptane, n-octane, n-nonane, n-decane and n-hexadecane. For each of these experiments, the addition of solvent yields birefringent spots that then become isotropic. During the evaporation of the solvent on the reverse path, the birefringent points reappeared then disappeared as the solvent evaporated.

The appearance of birefringence under cross-polarized light is indicative of the presence of ordered structures such as crystals and liquid crystals. In the previous chapter, asphaltenes were shown to form lyotropic liquid crystalline domains irreversibly on exposure to toluene vapor that subsequently became isotropic liquid. For n-alkanes, the sequence is similar but the process is reversible and clearly dependent on the mass fraction of asphaltenes in the asphaltene + n-alkane mixtures. For n-hexadecane, evaporation was slow, and it was possible to observe the impact of n-hexadecane under both polarized and normal visible light (Figure 3-10). Quantification of the amount of liquid crystal material formed and discrimination of the relative amount of liquid crystal material formed in each n-alkane proved infeasible.

### 3.3.4 *Interpretation of cross-polarized light microscopy images*[g]

The birefringent spots were only visible from below the glass fluid interface (bottom view direction in). They were not detected or were difficult to detect from above the free fluid surface (top view direction in ). Results for a heptane + asphaltene mixture exemplify this issue. The observations reported in Figure 3-9 (bottom view) and Figure 3-11 (top view) for heptane + asphaltene only differ in this respect. Asphaltenes comprise amorphous irregularly shaped particles lacking flat or smooth surfaces. Diffuse reflection makes asphaltene particles appear bright under polarized light. Liquid crystals form as these particles contact solvents. Only a portion of individual particles undergo this transition, as the irregular shape of the particles is detectable even after complete coverage by solvent (c).

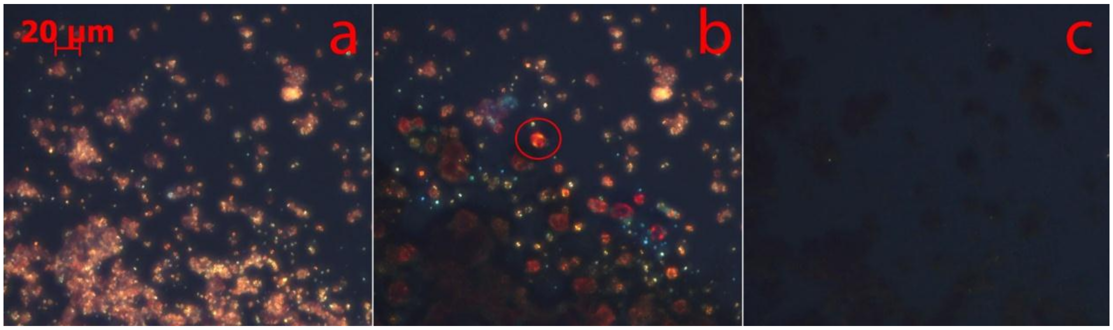

Figure 3-8 Cross-polarized light images showing the interaction between n-octane and Athabasca C5 asphaltenes: (a) asphaltene particles, (b) asphaltene + octane showing birefringent spots, (c) asphaltene particles covered by octane.

A flat surface is needed for the birefringence to be observed clearly. The flat glass surface allows particles to anchor and show birefringence clearly. At the top surface, diffuse

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[g] The work presented in the following section is performed and written by Dr. S. Reza Bagheri.

reflection from the irregular and rough shape of the particles masks the birefringence and makes it difficult to detect. At higher solvent concentrations, the liquid crystals become isotropic liquid. Once coated with a smooth film of isotropic liquid, diffuse reflection is eliminated.

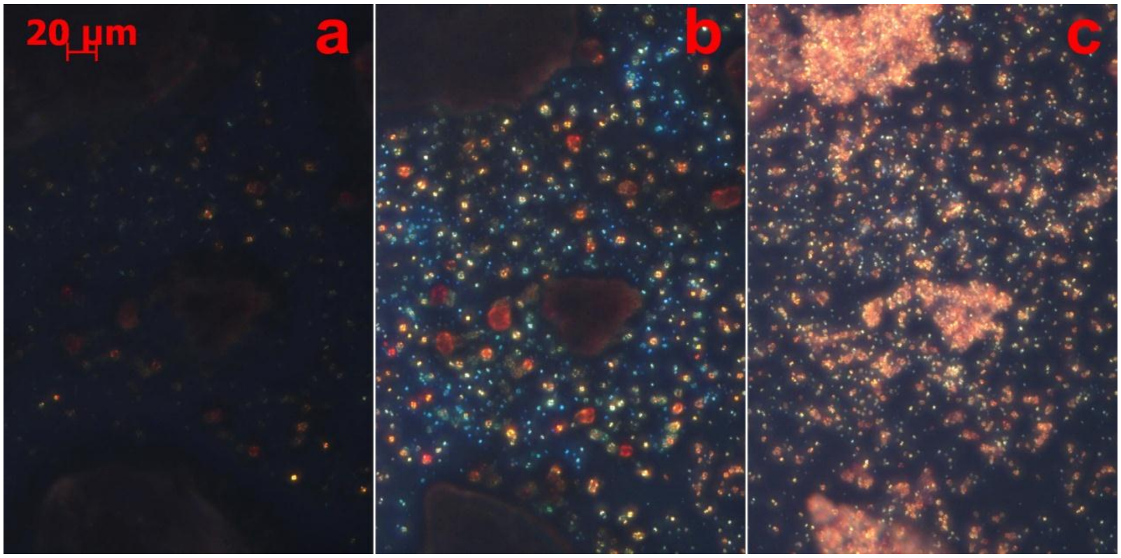

Figure 3-9 Cross-polarized light images showing the interaction between n-heptane and Athabasca C5 asphaltenes: (a) asphaltene particles covered with n-heptane, (b) asphaltene particles during n-heptane evaporation showing birefringent spots, (c) asphaltene particles following n-heptane evaporation.

### 3.3.5 *Swelling of asphaltene particles*[h]

Asphaltene particle swelling on exposure to n-alkanes has been reported previously[24,27] . Athabasca pentane asphaltene particles swell significantly on exposure to heptane (Figure 3-11a) and shrink once the heptane evaporates (Figure 3-11b). Figure 3-12a and Figure 3-12b show the same result for Athabasca pentane asphaltenes in n-decane. Addition of n-alkanes from heptane to hexadecane results in swelling. Swelling and liquid crystals were observed if asphaltene particles were coated individually with n-alkane, Figure 3-12a and b or covered with a film of n-alkane Figure 3-13a and b. Swelling also changed

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[h] The work presented in the following section is performed and written by Dr. S. Reza Bagheri.

the transparency of the asphaltene particles, under visible light, as seen in Figure 3-13a. Quantification of swelling for individual asphaltene particles in n-alkanes is difficult since the microscopic images are two-dimensional projections of three-dimensional and irregularly shaped particles. The projected area of the particles under the octane film is 8000 μm$^2$ (Figure 3-13a) and 5900 μm$^2$ once the film evaporates (Figure 3-13b). If the projected area is proportional to the square of leading dimension of the particles, then the change in the particle leading dimension during swelling is 17 %.

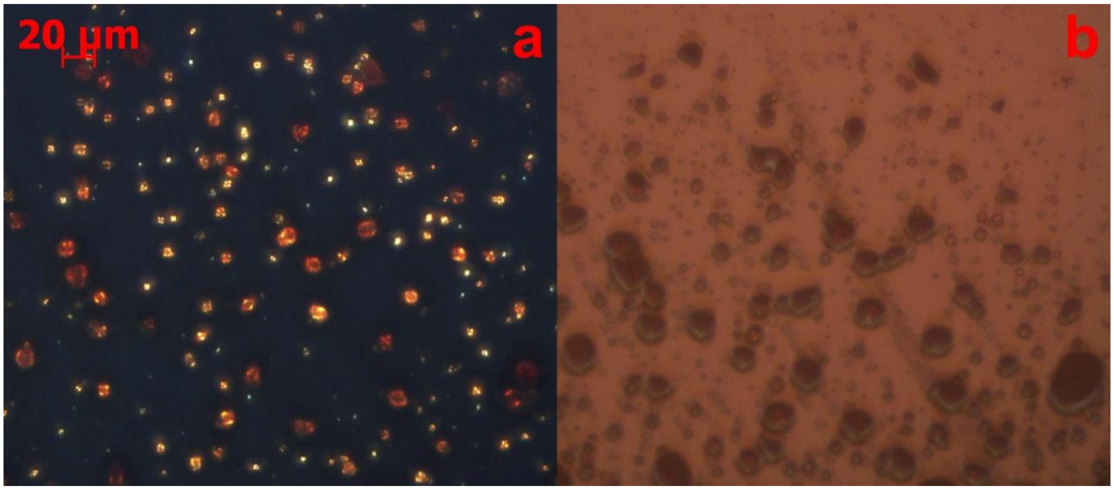

Figure 3-10 Images showing the interaction between n-hexadecane and Athabasca C5 asphaltenes: (a) under cross-polarized light, (b) under normal light.

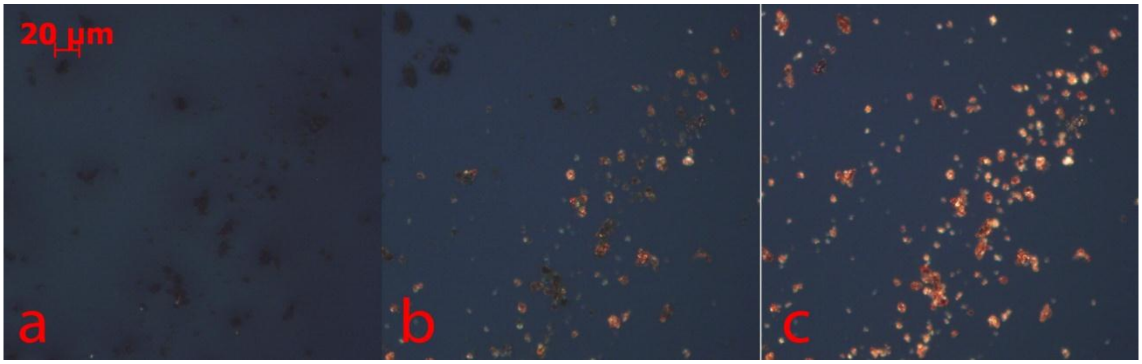

Figure 3-11 Cross-polarized light images showing the interaction between n-heptane and Athabasca C5 asphaltenes from the top view direction: (a) asphaltene particles covered with n-heptane, (b) asphaltene particles during n-heptane evaporation (c) asphaltene particles after the evaporation of n-heptane.

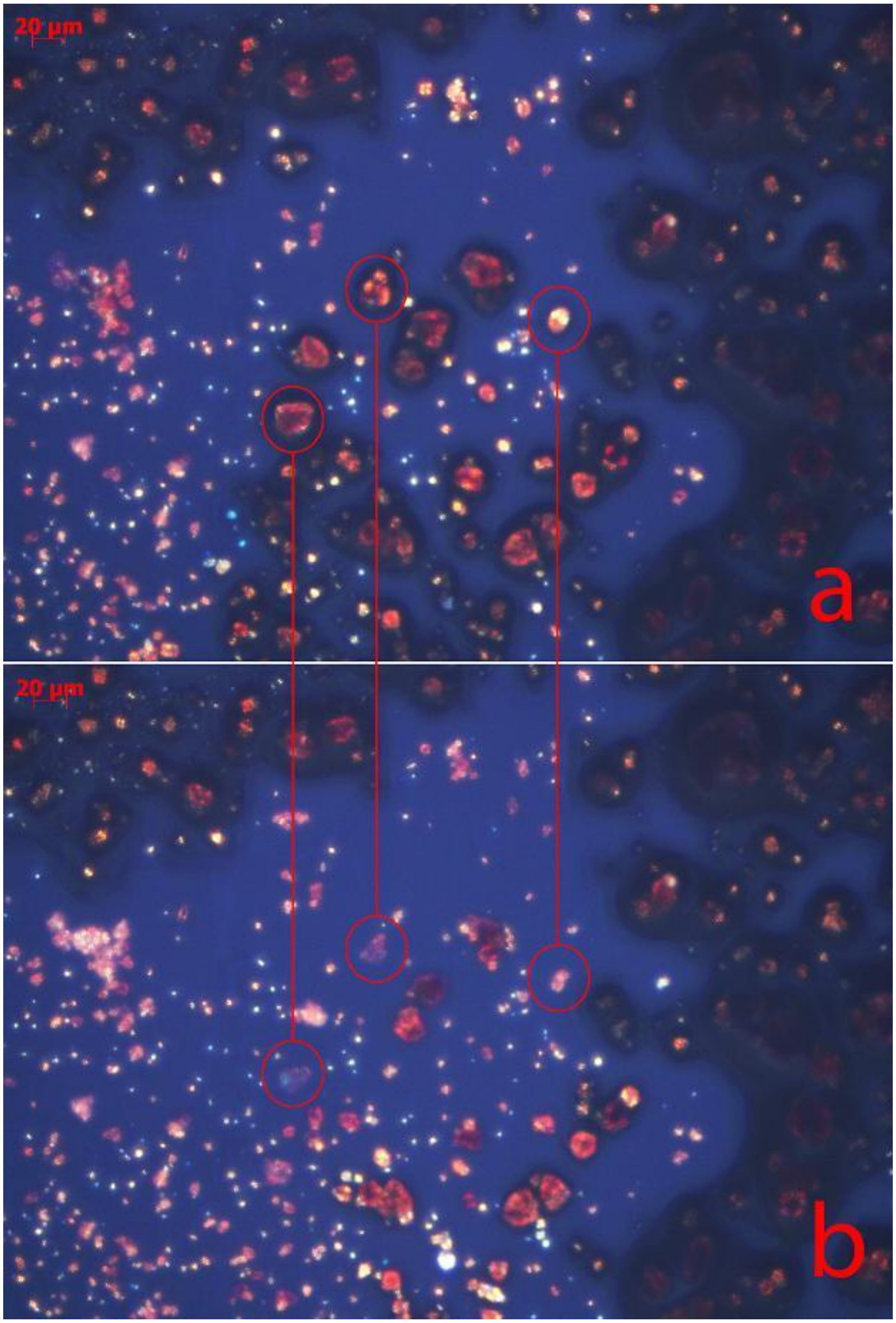

Figure 3-12 Swelling of Athabasca C5 asphaltenes in decane. Asphaltene particles (a) swell on addition of decane and (b) shrink as the decane evaporates.

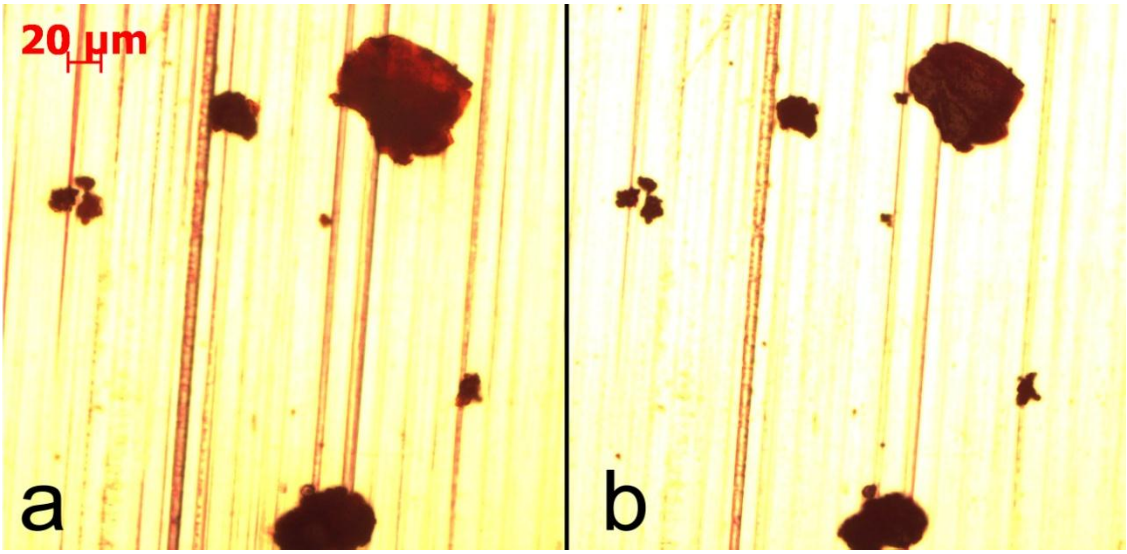

Figure 3-13 Swelling of Athabasca C5 asphaltenes submerged under a film of n-octane. Asphaltene particles (a) swell on addition of n-octane and (b) shrink once the n-octane evaporates.

### 3.3.6 *Interpretation of asphaltene + n-alkane density and enthalpy of solution measurements*

Integrating the qualitative observations and the quantitative measurements with related measurements from the literature for well-defined mixtures undergoing well-defined processes permits speculation and hypothesis testing related to possible processes arising in asphaltene + n-alkane mixtures. For example, the partial specific volume of asphaltenes in diluents, equation 3-1, can be rewritten as a function of the specific volume of asphaltene particles ($v_a^{particle}$), the swelling ratio (S), the mass of n-alkane sorbed per mass of asphaltenes (R), the mass fraction of asphaltenes undergoing phase change to liquid ($\alpha$), the mass fraction dissolving in the solvent ($\beta$), and the specific volume ($v_a^L$), and partial specific volume of liquid asphaltenes ($\bar{v}_a^L$). Starting from an expression for the mixture specific volume ($v_m$):

$$v_m = (1-\alpha)x_a v_a^{particle} S + (1-x_a)v_s - (1-\alpha)x_a v_s R + x_a(\alpha-\beta)(v_a^L - v_a^{particle}) + x_a\beta(\bar{v}_a^L - v_a^{particle})$$

(3-3a)

Differentiating with respect to the mass fraction of asphaltenes at near infinite dilution one obtains:

$$\bar{v}_a = (1-\alpha)(v_a^{particle} S - v_s R) + (\alpha-\beta)v_a^L + \beta(\bar{v}_a^L - v_a^{particle}) \qquad \text{(3-3b)}$$

As the mass fraction of asphaltenes soluble in n-alkanes, β, $v_a^L$ » $\bar{v}_a^L$ and the product $a(v_a^{particle}S - v_a^L)$ is small the second and third terms on the right side of equation 3-3b can be neglected, and one obtains:

$$\bar{v}_a \approx v_a^{particle} S - (1-\alpha)v_s R \qquad \text{(3-3c)}$$

The simplest swelling + sorption model, where $(1-\alpha)v_a^{particle}S$ and $(1-\alpha)R$ are constant, indicates a linear relationship between $\bar{v}_a$ and $v_s$ that is consistent with the plot of the partial specific volume of the asphaltenes vs the specific volume of the n-alkane diluents presented in Figure 3-4b. A linear relationship conforms with a flat orientation of the sorbed materials on the surface. These data are linearly related within experimental error. Fitted values for $v_a^{particle}S$ ~ 0.968 cm$^3$/g and $(1-\alpha)R$ ~ 0.083 g solvent/g asphaltenes appearing in equation 3c conform with exogenous measurements. The product $v_a^{particle}S$ is above the minimum anticipated swollen volume (0.95 cm$^3$/g) based on the data of Parkash et al.[27] and Carbognani and Rogel[24].

Given a fixed mass based sorption ratio, a difference of 23 % is anticipated between sorption of pentane (higher) and hexadecane (lower) on a volumetric basis. This latter result is consistent with the idea that smaller molecules penetrate the porous asphaltene particles more readily than larger ones. Further, the corresponding volume of diluents sorbed, ranging from ~ 0.11 to ~ 0.13 cm$^3$/g is comparable to reported asphaltene particle pore volumes. To a first approximation, the quantitative data and observations from this work and the literature more broadly conform with the notion that asphaltene particles swell similarly in n-alkanes, and sorb a similar mass of n-alkane per mass of asphaltene irrespective of the length of the carbon chain.

The enthalpy of solution measurements can be examined in a similar manner. From the observations they comprise a minimum of three elements - sorption of liquid n-alkanes within the asphaltene particles, swelling of the asphaltene particles, and formation of liquid crystals and drops of liquid crystal rich liquid domains. For lyotropic liquid crystals to form, n-alkane must by definition be soluble in the liquid-crystal rich phase. Although not observed, dissolution of a fraction of the asphaltenes in an n-alkane rich liquid phase cannot be precluded. Further, dissolution of asphaltenes in the n-alkanes may or may not be connected with liquid crystal and liquid formation. Allowing for these diverse physical processes, the enthalpy of solution can be expressed as:

$$\Delta h^{sol} = (1-\alpha)\left(\frac{\Delta H^{sorption}}{M}R + \Delta h^{swelling}\right) + \alpha\Delta h^{PhaseChange} + \beta\Delta h^{mixing} \tag{3-4}$$

where M is the molar mass of the n-alkane.

The term $\Delta h^{swelling}$ with the units J/g asphaltenes accounts for the energy linked to swelling. The formal name for this term is elastic energy. While not known a priori, it is expected to be small and positive, $\Delta h^{swelling} << 0.1$ J/g, for swelling of less than 40 %, if an analogy with swollen polymer networks[39, 40,41] is valid. This term is neglected relative to the sorption term.

The term $\Delta h^{PhaseChange}$ with the units J/g asphaltene accounts for the energy linked to phase change of asphaltene particles. From an energy perspective, the phase transition enthalpy from solid to liquid crystal is much greater than the transition enthalpy from liquid crystal to liquid and the difference can be neglected for this application[42]. The enthalpy of fusion of Athabasca pentane asphaltenes has been estimated as ~ 22 J/g[43]. Thus, $\Delta h^{PhaseChange}$ can be approximated as 22 J/g. This value falls below the range of the enthalpy of fusion of crystalline organic solids (50 to 250) J/g[44]. Larger values are for n-alkanes. The values for polynuclear aromatic hydrocarbons are typically in the range 80 to 160 J/g. For polynuclear aromatic hydrocarbons, specific enthalpies of fusion decrease with molar mass and with the addition of side chains.

$\Delta H^{sorption}$ is the molar enthalpy of sorption of liquid n-alkane on or within the asphaltene particles. Values obtained from enthalpy of gas sorption measurements reported in the literature, cover a broad range, 0 to -40 kJ/mol, irrespective of whether the sorbent is an ionic or organic solid. Illustrative values are listed in Table 3-1. The corresponding sorption enthalpies for liquids are variable and values can be masked by experimental error. For example, from the careful gas-based sorption enthalpies for n-alkanes on concrete reported by Widegren and Bruno[45], one obtains liquid-based sorption enthalpies that fall within the measurement error, as shown in Table 3-1. From their review of experimental studies on other ionic solids (kaolin and synthetic laponite), the sorption enthalpies of the same liquid hydrocarbons are ~ -25 kJ/mole. For organic solids such as coal subject to thermal treatment, and wood and polystyrene based char, sorption enthalpies for liquid hydrocarbons range from - 4 to -38 kJ/mole as also noted in Table 3-1. The values appear to be primarily substrate specific and sorption on inorganic matter present in asphaltenes cannot be distinguished from sorption on organic matter.

Gas-based enthalpy of sorption values typically decrease as the number of moles sorbed per unit mass of substrate increase, with lower asymptotes reached at ~ 1-10 mmole/g[46]. As the anticipated mass based sorption of hydrocarbons on asphaltenes is expected to be in the order of 0.1 g/g and the molar masses of the hydrocarbons of interest range from 72 g/mole (pentane) to 214 g/mole (hexadecane), the mole-based sorption is in the order of 1 mmole/g or less. Thus trends with carbon number cannot be inferred from asymptotic sorption enthalpy values with certainty. From the enthalpy of solution data for the remixed settled asphaltene fraction in dodecane, -9.0 J/g of asphaltenes, Figure 3-7, the enthalpy of sorption for this case is less than -17 kJ/mole or ~ -100 J/g. It is unclear whether the enthalpy of sorption can be approximated as a constant for modeling purposes either on a mass or mole basis.

$\Delta h^{mixing}$ is the energy associated with mixing liquid asphaltene constituents with n-alkane. Mixing occurs in an asphaltene rich liquid phase, and may also occur in an n-alkane rich phase. Enthalpy of mixing is expressed on a per gram of asphaltene basis in equation 3-4.

Again, the range of possible values can be derived from the literature. By transforming the enthalpy of mixing from a per mole of mixture basis in the literature into a per gram of solute basis, one obtains the values of the type listed in Table 3-1.

When expressed in this way, the maximum values arise at infinite dilution. Asphaltenes comprise primarily polynuclear aromatic and naphthenic constituents. For aromatic and naphthenic hydrocarbons dissolved in n-alkanes, the enthalpies of mixing are uniformly positive values ranging from ~ 3 J/g to ~ 35 J/g of solute. Thus, $\Delta h^{mixing}$ is expected to fall in this range for the n-alkane rich liquid, and to approach zero for asphaltene rich liquid.

Table 3-1 Sorption enthalpies for n-alkanes on diverse substrates

| source | compound | substrate | T (K) | $-\Delta H^{sorption}_{vapor}$ (kJ/mol) | $\Delta H^{vaporization}$ [47] (kJ/mol) | $\Delta H^{sorption}_{liquid}$ (kJ/mol) | Comments |
|---|---|---|---|---|---|---|---|
| Widegren and Bruno[45] | pentane | concrete | | 31.1+/-3.1 | 26.75 | -4.4+/- 3.2 | Data: assymptotic values, with expanded error (10 %) recommended by the authors |
| | hexane | | | 34.3+/-3.4 | 31.7 | -2.6 +/-3.5 | |
| | heptane | | | 36.5+/- 3.7 | 36.7 | -0.2 +/- 3.8 | |
| | octane | | | 42+/-4.2 | 41.6 | -0.4 +/-4.3 | |
| Glass and Larsen[48] | hexane | coal (# 1) | | 33 | 29 | -4 | Data |
| | | coal (# 2) | | 67 | | -38 | |
| Gordon and Glandt[49] | butane | simulated silica gel | 311 | 36 +/- 4 | < 22.4 | -13.6+/- 4 | Calculations at 0.5 mmol/g |
| | hexane | | | 50 +/- 4 | < 31.7 | -18+/-6 | |
| | octane | | | 59 +/- 8 | 41.5 | -17.5+/-8 | |
| | dodecane | | | 84 +/- 12 | 61.5 | -21.5+/-8 | |
| Fletcher and Thomas[46] | octane | wood-based active carbon (BAX950) | | 62.5 +/- 2.5 | 38.6 | -23.9+/- 3 | 1 mmol/g |
| | nonane | | | 68 +/- 2.5 | 46.4 | -21.6 +/-3 | |
| Asnin and Davankov[50] | hexane | microporous carbon adsorbent | 428 | 40 +/- 4 | | | 1 % surface coverage |
| Bruno et al.[51] | hexane | Laponite-RD packed column | 333-573 | 56.0+/-0.2 | 29.7 | 26.3 | Based on trend of retention volume vs.temperature. Very low coverage[52] |
| | heptane | | | 61.6+/-1.4 | 34.3 | 27.3 | |
| | octane | | | 65.2+/-1.6 | 40.1 | 25.1 | |
| | nonane | | | 71.3+/-1.8 | 43.6 | 27.7 | |
| | decane | | | 80.0+/-1.0 | 50.4 | 29.6 | |
| | undecane | | | 84.5+/-7.4 | 54.2 | 30.3 | |

There do not appear to be qualitative differences among the mixtures at the microscopic or macroscopic length scales. All of the asphaltene + n-alkane binaries appear to behave in a similar manner. Sorption, swelling, liquid crystal then isotropic asphaltene rich liquid formation occur reversibly. From a modeling perspective, the origin of the difference in enthalpy of solution with the size of the n-alkane, including a change of sign, is therefore linked to changes in the enthalpy of sorption with n-alkane size, to changes in the relative amount of asphaltene rich liquid produced, or to differences in solubility of asphaltenes among n-alkanes, that are large enough to change the sign of the enthalpy of solution.

Table 3-2 Enthalpies of mixing for binary and pseudo binary hydrocarbon mixtures

| source | component 1 | component 2 | $\Delta h^{mixing}$ | Comments |
|---|---|---|---|---|
| Arenosa et al.[53] | ethyl benzene | octane | 17.8 | |
| | | dodecane | 18.5 | |
| | | hexadecane | 20.1 | |
| Shiohama et al.[54] | Cis-decalin | heptane | 3.5 | |
| Auolmi et al.[55] | phenanthrene | eicosane | 20 | 118.6 C |
| | 1-phenylnaphthalene | | 17 | |
| | 9- methylanthracene | | 18 | |
| | naphthalene | octacosane | 17 | |
| | Phenanthrene | | 22 | |
| | Fluoranthane | | 22 | |
| | Pyrene | | 14 | 160 C |
| | Phenanthrene | squalane | 35 | 118.6 C |
| | fluoranthane | | 26 | |

In equation 3-4, the value for the enthalpy of fusion for asphaltenes is known exogenously, and the value for (1-$\alpha$)R, 0.083 g solvent/g asphaltene, is obtained from the partial specific volume data. The enthalpy of sorption appears to be unknown but constrained. For example, the value is ~ -17 kJ/mole for asphaltene + dodecane mixtures. The enthalpy of mixing is either zero, for an asphaltene rich liquid phase, or an unknown positive and constrained value for an alkane rich liquid phase. Thus $\alpha$ and $\beta$ are key variables of interest and the model. From this perspective, equation 3-4 possesses two asymptotes.

For the first asymptote no mixing, $\beta=0$, or mixing exclusively in an asphaltene rich liquid phase equation 3-4 becomes:

$$\Delta h^{sol} = (1-\alpha)R\left(\frac{\Delta H^{sorption}}{M}\right) + \alpha(\Delta h^{PhaseChange}) \qquad (3\text{-}5)$$

As the enthalpy of phase change and upper limits for $\alpha$ are known, the largest value for the phase change term is 2.9 to 4.4 J/g of asphaltene because $\alpha$ is constrained to be < 0.19 for pentane and < 0.135 for the other n-alkanes. This upper enthalpy of solution limit can only be realized if the enthalpy of sorption is zero, in which case negative enthalpy of solution values are precluded. No dissolution of asphaltenes in the solvent rich phase or only solvent dissolution in the asphaltene rich liquid phase is inconsistent with the experimental data.

For the second asymptote, phase change followed by mixing exclusively in an n-alkane rich liquid phase, $\alpha = \beta$, and equation 3-4 becomes:

$$\Delta h^{sol} = (1-\alpha)R\left(\frac{\Delta H^{sorption}}{M}\right) + \alpha(\Delta h^{PhaseChange} + \Delta h^{mixing}) \qquad (3\text{-}6)$$

Equation 3-6 is similar to equation 3-5 but has a broader dynamic range that can accommodate the breadth of the experimental data, shown in Figure 3-5 to Figure 3-7.

It is not possible to identify unique sets of parameters because values for enthalpy of mixing and enthalpy of sorption cross correlate with one another and with values for $\alpha$ but bounds can be identified that limit their ranges. For example, from the dodecane + asphaltene and settled asphaltene data, enthalpy of sorption values, -17 kJ/mole $> \Delta H^{sorption} >$ -18 kJ/mole, yield enthalpy of mixing values, 34 J/g $< \Delta h^{mixing} <$ 40 J/g, and dissolved fraction values $0.120 < \alpha < 0.135$ that respect the identified constraints. Clearly, this asymptote is feasible for dodecane + pentane asphaltene mixtures and by extension, solutions corresponding to mixed mode dissolution, where $0.8\ \alpha < \beta < \alpha$, are also feasible, if restrictions are imposed on the values for $\Delta h^{mixing}$. The enthalpy of mixing values and composition constraints for the other pentane asphaltene + n-alkane binaries are also well represented for $\Delta H^{sorption}$/M = -100 J/g and for enthalpies of mixing in the range 35 to 40 J/g. Thus the data sets and the model are consistent with a sorption enthalpy that is proportional to the molar mass of the sorbant, to a constant value of enthalpy of mixing and to asphaltene solubilities in n-alkane rich liquids approaching the mass fraction remaining in the supernatant. As there is no reason to expect that $\beta$ is not also a function of carbon number, the data and the model cannot be parsed with respect to the energy contributions from the mass fraction of asphaltenes soluble in n-alkanes and the fraction remaining as an asphaltene rich liquid phase. The asphaltene fraction forming liquid crystals is limited similarly, but also cannot be parsed from the dissolution behaviors on the basis of available data.

While more complex to interpret than the volumetric data, to a first approximation, the quantitative calorimetric data from this work and the literature more broadly conform with the notion that a fraction of the asphaltenes undergoes a phase transition to liquid crystal and then to liquid, and that a fraction of this asphaltene derived liquid dissolves in the n-alkane. Quantification of these physical processes, and identification of trends with n-alkane chain length are subjects of future study.

### 3.3.7 *Implications for asphaltene preparation*

Five relevant inferences can be drawn from the visual observations, the quantitative data, and the phenomenological asphaltene + n-alkane interaction model:

1. a fraction of pentane asphaltenes undergo reversible phase change on addition of n-alkanes, that requires the n-alkane to be soluble in the asphaltene in order to occur.
2. a fraction of pentane asphaltenes is soluble in n-alkanes
3. pentane asphaltenes + n-alkane mixtures include finely dispersed particles and soluble fractions that pass through a 0.220 μm filter on dilution with n-alkanes.
4. the fraction of pentane asphaltenes soluble in n-alkanes, as inferred from the solution enthalpy measurements appears to decrease with increasing carbon number.
5. settled pentane asphaltene fractions also include constituents that undergo phase change and are subject to dissolution on mixing with n-alkanes.

Thus, observations by Alboudwarej et al.[5] among others that asphaltene properties are sensitive to the details of washing procedures used during their preparation are expected.

Most common asphaltene preparation techniques require extensive washing of the solid material subsequent to filtration. The washing step includes a poorly defined end point. “Clear” filtrate may include varying mass fractions of sub micron particles, as these are transparent to visible light, and dissolved species at low concentration. Variation of the details of the washing procedure, or their application from operator to operator, is expected to lead to variation in the mass fraction and physical properties of materials ultimately recovered and reported as asphaltenes. Both the consistency and repeatability of measurements, with respect to the mass fractions recovered and the thermophysical properties derived from the asphaltene samples are expected to vary. Preparation techniques without washing appear to be preferred as the mass fractions of asphaltenes recovered are expected to be more repeatable and their properties are likely to be more consistent. Among the many asphaltene preparation procedures available, one suggested by Yarranton and Masliyah[17] that substitutes washing with mixing of filtered asphaltenes with a set ratio of n-alkane to asphaltenes offers significant advantages from the perspective of measurement repeatability and composition consistency both for a single operator and among operators.

## 3.4 Conclusions

Dilute mixtures of Athabasca pentane asphaltenes with n-alkane diluents exhibit complex reversible interactions. More than 80 % by mass of pentane asphaltenes separate rapidly under gravity alone. Suspension behaviors: alkane sorption on asphaltene particle surfaces identified indirectly by solution calorimetry, and asphaltene particle swelling identified by direct visual observation respectively, are evident. Reversible phase change and dissolution behaviors: formation of liquid crystal and isotropic liquid domains on particle surfaces was observed directly, and dissolution of asphaltenes into n-alkanes was inferred from the enthalpy of solution measurements. Pentane asphaltene + n-alkane binary mixtures from pentane to hexadecane exhibit the same particulate and phase change behaviours. Estimated values for enthalpy of sorption, enthalpy of mixing and the mass fraction of asphaltenes soluble at 2000 ppm are internally consistent and consistent with values in the relevant literatures where available. Asphaltene preparation techniques including ill-defined steps such as "washing until clear" introduce irreproducibility into asphaltene mass fraction and composition measurements because asphaltenes are present as fine particles and are partially soluble at low mass fractions in n-alkanes. Preparation techniques without washing are preferred.

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# Chapter 4: On enthalpies of solution of Athabasca pentane asphaltenes and asphaltene fractions[a]

## 4.1 Introduction

Asphaltenes, defined operationally on the basis of ASTM standards that include mixing and macroscopic filtration steps, are typically asserted to be soluble in toluene[1]. A similar definition is used to classify organic diluents as solvents and non-solvents for asphaltenes. From a solution thermodynamics standpoint, dissolution of a solid into a liquid includes a transition to liquid for the solute followed by homogeneous mixing at a molecular level[2]. The ASTM standards do not meet this thermodynamic definition for solubility because fine asphaltene particles or liquid drops pass through the 200 nm or larger filters and are not distinguished from material that is soluble. The fraction of a feedstock reporting as asphaltenes is therefore sensitive to details of the separation procedure and apparatus employed. This introduces significant variability in the asphaltene fractions obtained among different operators working with the same feedstock and equipment, or among laboratories working with the same feedstock[1, 3]. Thus, the database underlying the analysis and modeling of phase separation and deposition mechanisms for asphaltenes from crude oils and reservoir fluids, includes an uncontrolled variable, that adds to the uncertainty of computational outcomes, and to ensuing operational consequences[4].

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[a] The content of this chapter has been submitted to Energy and Fuels on July 21, 2012.

Predictive models developed for asphaltene phase separation and deposition are frequently based on thermodynamic equilibrium between asphaltenes soluble in their native crude and insoluble in diluents. Models based on regular solution theory[5-9], Flory-Huggins theory[10], cubic [11] and SAFT equations of state[12, 13] all treat asphaltene separation or precipitation as examples of liquid-liquid or liquid-solid equilibrium. Models based on the treatment of asphaltenes as colloids where particles remain stable in a hydrocarbon medium surrounded by resins have also been proposed[14-16]. These models are based in part on now refuted micellar behavior attributed to asphaltenes and the concept of such particles may in any event arise as an artifact of the analysis method used to define the fluid. For example, from nanofiltration experiments[17-19], the nanoscale domains present resemble pentane asphaltenes to a first approximation. If a heptane analysis is applied, these nanoscale domains can be interpreted as a combination of asphaltenes + resins[20]. The compositional distinction between asphaltenes and resins is ill-defined. Aggregation models[21] assume that asphaltenes are present as molecules and aggregates of varying size in solvents at low concentration. As the asphaltene concentration is increased the mean aggregate size is presumed to increase. Asphaltenes aggregate in toluene at concentrations as low as 50-100 ppm[22-26, 27]. From vapor pressure osmometry (VPO) measurements, the size of the aggregates reaches a maximum at approximately 2 wt%[8, 28]. Simple aggregation does not explain asphaltene solution behavior as an aggregate growth termination step is absent. A limitation with these models is that they typically treat asphaltenes as a single constituent and emphasize one type of behavior. Asphaltenes comprise tens of thousands different compounds with wide ranges of molecular weight[29, 30], aromaticity, heteroatom content, and structure, and therefore solution behaviors.

Recent work has addressed the complexity of asphaltene phase behavior alone, in native crudes[18, 31-34], and in organic diluents[4, 35]. These studies challenge key underlying assumptions in individual asphaltene behavioral models and suggest that both colloidal and solution phenomena co-exist in asphaltene + diluent mixtures. First, asphaltenes have been shown to be selectively filterable from native crudes, thus limiting the applicability of the assumption that asphaltenes are soluble in their native crude. Second, the appropriateness of the application of regular solution theory to asphaltene + organic diluent mixtures[35] is challenged because volume changes on mixing and enthalpies of solution for asphaltene + organic diluent binary mixtures are both shown to be independent of the solubility parameter of the organic diluent, a result that is contrary to regular solution theory. Third, n-alkanes are shown to be soluble in a fraction of pentane asphaltenes on the basis of microscopic observation. Fourth, a fraction of pentane asphaltenes is shown indirectly to be soluble in n-alkanes at low concentration[4].

Typical solution behavior measurements include partial molar volume and enthalpy of solution measurements. These are conventionally expressed on a mole basis with respect to the solute or the solution. As the molar properties of asphaltene are ill-defined, the corresponding mass based measures, partial specific volume ($\bar{v}$, $cm^3$/g asphaltenes) and a mass based enthalpy of solution ($\Delta h^{sol}$, J/g asphaltenes), are used in this work. Partial molar volume and enthalpy of solution measurements are multiply interpretable. An enthalpy of solution of zero may reflect the absence of interaction among constituents (stones in water) or a balance between competing endotherms and exotherms arising from complex processes. A partial specific volume in solution equal to the specific volume of a constituent on its own may reflect ideal mixing, the absence of mixing (stones in water), or the balance of complex processes. Measurements of different types, exogenous measurements and theory are frequently required to aid interpretation of such measurements.

In a recent publication[4] the partial specific volume and enthalpy of solution of asphaltenes were defined on the basis of observed or inferred physical phenomena. Partial specific volume was defined as:

$$\bar{v}_a = (1-\alpha)(v_a^{particle}S - v_s R) + (\alpha-\beta)(v_a^L) + \beta(\bar{v}_a^L) \qquad (4\text{-}1)$$

where $v_a^{particle}$ is the specific volume of asphaltene particles, S is the swelling ratio, R is the mass of n-alkane sorbed per unit mass of asphaltenes, α is the mass fraction of asphaltenes undergoing phase change to liquid, β, is the mass fraction dissolving in the solvent, $v_a^L$ the specific volume, and $\bar{v}_a^L$ is the partial specific volume of liquid asphaltenes. Enthalpy of solution was defined as:

$$\Delta h^{sol} = (1-\alpha)\left(\frac{\Delta H^{sorption}}{M}R + \Delta h^{swelling}\right) + \alpha\Delta h^{PhaseChange} + \beta\Delta h^{mixing} \qquad (4\text{-}2)$$

where all enthalpies are per unit mass of asphaltenes except for the sorption enthalpy which is the molar enthalpy of sorption per mole of diluent, $\Delta H^{sorption}$. It is divided by the molar mass of the diluent, M. Equations 4-1 and 4-2 include terms linked to solvent sorption by asphaltene particles, phase change of a fraction of asphaltenes, solubility of solvent in asphaltenes, dissolution of a fraction of asphaltenes in the solvent, particle swelling on enthalpies of solution for asphaltene + diluent mixtures, and reflect the breadth of observations in the literature. For example, Bagheri et al.[33] showed that even toluene vapor sorption induces a phase transition in asphaltene particles at room temperature leading to liquid crystal and eventually isotropic liquid formation for a portion of the asphaltenes. More recently[4], liquid n-alkanes were shown to induce the same behavior. Sheu at al.[36] have also reported possible solubility of toluene in asphaltenes at low toluene to asphaltene ratios based on small angle neutron scattering (SANS). The swelling of asphaltenes in toluene and 1-methlynaphthalene has been suggested by Sirota[37] and Angle et al.[38]. Evidence for swelling is based on indirect measures such as viscosity measurement, interpretation of x-ray scattering data, or direct visual observation. Partial specific volume is insensitive to the state of aggregation of asphaltenes and the enthalpy associated with changes in the state of aggregation cannot be discriminated as the energy associated with changes in mean aggregate size are small compared to the enthalpy of phase state change on a mass basis. Enthalpy changes upon dissolution of solids in liquids are generally positive (endothermic). At high temperature and low concentration where dissolution is expected to dominate, the enthalpy of solution is expected to be positive. At high concentrations and low temperatures, solvent sorption is expected to dominate and the enthalpy of solution is expected to be negative (exothermic).

For asphaltene + n-alkane mixtures[4], at ambient conditions, equations 4-1 and 4-2 were reduced to:

$$\bar{v}_a \approx v_a^{particle} S - (1-\alpha) v_s R \tag{4-3}$$

and

$$\Delta h^{sol} = (1-\alpha)\left(\frac{\Delta H^{sorption}}{M}R\right) + \alpha\Delta h^{PhaseChange} + \beta\Delta h^{mixing} \tag{4-4}$$

based on the relative magnitudes of terms appearing in the equations. For example, the specific volumes of the swollen asphaltene particles, liquid asphaltenes, and the partial specific volume of asphaltenes in diluents differ little. The enthalpy of swelling, more generally referred to as elastic energy, is negligible compared to the enthalpy of sorption. Equations 4-3 and 4-4 provide a coherent conceptual framework for the interpretation of solution behaviors of asphaltenes in diverse organic diluents as enthalpies of sorption and fusion, particle swelling and solvent sorption values appearing in the models are either known from exogenous measurements or exogenous measurements impose limits on values appearing in the model equations. In the present work, the viability of this conceptual framework as a basis for describing solution behaviors of asphaltenes in diverse organic solvents is explored.

## 4.2 Experimental

### 4.2.1 *Materials*

N-pentane precipitated asphaltenes were obtained from Athabasca bitumen supplied by Syncrude Canada Ltd.  Toluene, tetrahydrofuran and n-decane were supplied by Fisher, and quinoline was supplied by Acros. The purities of these compounds were 99% or greater. 1-methylnaphthalene was supplied by Sigma-Aldrich and had a purity of 97 wt%. Pyrene (98 wt% purity) was supplied by Sigma-Aldrich.

Asphaltenes were prepared by adding n-pentane to bitumen at a ratio of 40 ml to 1 g of feedstock. The mixture was stirred for 24 hours at room temperature, and then filtered, using filter paper Q2, with a pore size 1-5 μm and washed with n-pentane until the liquid passing through the filter was clear. The filter and retentate were subsequently dried overnight in a vacuum oven at 9 kPa and 303 K. Athabasca bitumen comprises 18.7 wt% pentane asphaltenes on this basis.[18]

### 4.2.2 *Density measurements*

Density measurements were performed using an Anton Paar DMA 5000 density meter. For each diluent, 4-6 asphaltene + diluent mixtures with asphaltene contents ranging from 200 to 5000 ppmw (0.2-5 g/L) were prepared. Asphaltenes were mixed with the diluents in a closed container and sonicated for 15 minutes followed by shaking with a vortex mixer at 3200 rpm for 1 minute. The mixtures were then left for 24 hours prior to measurement. There was no visible sedimentation in any of the mixtures and the repeatability of the density measurements for asphaltene + diluent mixtures was within ± 0.000 002 g/cm$^3$.

Partial specific volumes of asphaltenes, $\bar{v}_a$, which can be determined at any composition, if the mixture density and the derivative of mixture density with composition are known is defined as:

$$\bar{v}_a = \frac{1}{\rho_m} + \frac{\partial\left(\frac{1}{\rho_m}\right)}{\partial x_a} \tag{4-5}$$

where $\rho_m$ is the density of the mixture and $x_a$ is the mass fraction of asphaltenes. At near infinite dilution, values were determined by linear regression of the inverse density of dilute asphaltene + diluent mixtures. At infinite dilution: $\left.\frac{1}{\rho_m}\right|_{x_a=0}$ and $\left.\frac{\partial\left(\frac{1}{\rho_m}\right)}{\partial x_a}\right|_{x_a=0}$ are the ordinate intercept, which closely approximates the diluent inverse density ($1/r_s$), and the slope of the plot respectively. The uncertainty of the calculated partial specific volume measurements is <0.002 cm$^3$/g.

### 4.2.3 *Solution calorimetry*

The precision solution calorimetry module, SolCal, from TA Instruments inserted in a TAM III thermostat was used for calorimetry measurements. SolCal is a semi-adiabatic system with a short-term noise of less than 10 μK/5min. The module consisted of a 25 ml cell, filled with the diluent of choice, and a 1 ml sealed glass ampoule, loaded with 20-25 mg of Athabasca pentane asphaltenes or pyrene.

Three types of diluents were used during calorimetry measurements: pure diluents, diluents with an underlying composition of asphaltenes or pyrene, and diluents contaminated with 1 g/L of another diluent prior to measurements. The amount of solute added to the diluent was kept in the range of 20-25 mg to avoid discrepancies caused by slow dissolution of large amounts of solute.

The SoCal device was inserted into the thermostat maintained at a set temperature in the range of 288 to 353 K and allowed to reach steady state, defined as a standard deviation of an exponential fit to the temperature signal over 5 min less than 10 μK. The equipment measures the difference between the temperature of the cell and the set temperature of the bath - the temperature offset. The measurements were performed within a temperature offset range of -100 mK to 100 mK. A mixing rate of 500 rpm was used for all experiments. Temperature calibration using a heat signal of 1-1.5 J was performed at the beginning and the end of the experiments. After the first calibration a 5-minute baseline was collected. At the end of this period the glass ampoule was broken to allow for the solute to mix with the diluent. A 5-minute period was then allowed for generation or sorption of energy followed by another 5-minute period for baseline acquisition. Generation or sorption of energy was not detected more than 1.5 min from the break in any of the experiments. Enthalpies of solution were calculated using the method of Wadso[39].

Care was taken to ensure samples were well mixed, as this is a criterion for the measured enthalpy of solution to be valid. Cell and ampoule surfaces were inspected following all measurements. If adherent deposits were found, a sign of poor mixing, the measurement was rejected even if the thermal criteria were met. For example, all enthalpy of solution measurements for asphaltenes recovered by evaporation from 1-methylnaphthalene were rejected on this basis. Mechanical crushing of the asphaltene particles and higher mixing rates were not effective remedial measures.

For a single-component crystalline-solid in a liquid solvent, the enthalpy of solution, expressed on a unit solute basis,

$$\Delta h^{sol} = \Delta h^{PhaseChange} + \Delta h^{mixing} \qquad (4\text{-}6)$$

is a weak function of temperature at fixed composition and a weak function of composition at fixed temperature, below the saturation limit, due to the dominance of the enthalpy of fusion. At fixed temperature, the enthalpy of solution is a constant to a first approximation below the saturation limit and zero above the saturation limit - Figure 4-1a. The value of the enthalpy of solution, at fixed composition, is zero, at temperatures where the saturation limit is exceeded, and is a constant value, to a first approximation, at temperatures where the solubility limit is not exceeded, Figure 4-1b. For a multicomponent solid solute subject to the same interactions with a solvent, the trends in the enthalpy of solution values are similar except that the enthalpy of solution is a macroscopically continuous function of composition (Figure 4-1a) at fixed temperature, and of temperature at fixed composition (Figure 4-1 b) as long as the joint solubility limits of some of the constituents are exceeded.

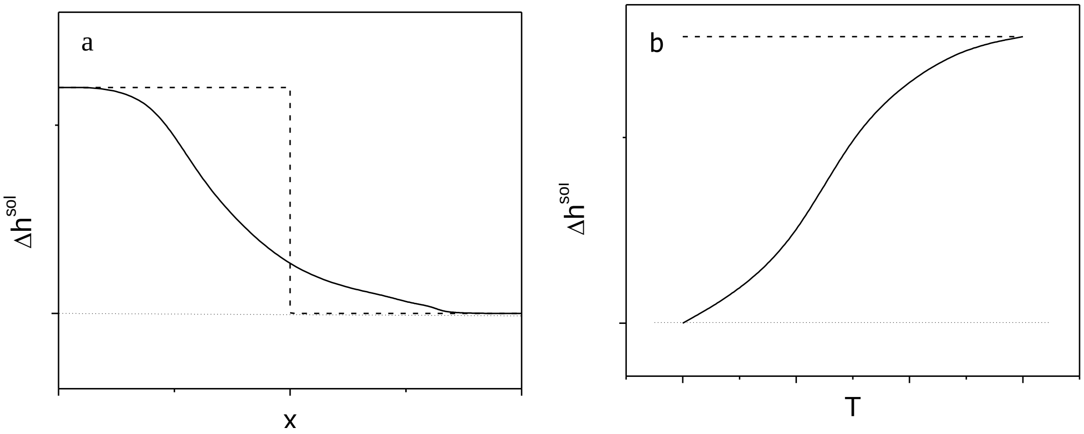

Figure 4-1 Schematics showing the enthalpy of solution of a single component solid (---) and a multi-component solid (____) in a diluent at a) constant temperature b) constant composition.

The fraction of the solute undergoing dissolution decreases with increasing solute mass fraction at fixed temperature and becomes zero once the joint solubility limits of all constituents are exceeded. At fixed composition, the enthalpy of solution approaches zero at low temperatures where the joint solubility limits for all constituents are exceeded and approaches a maximum at high temperature where the joint solubility limits are exceeded for all constituents.

### 4.2.4 *Asphaltene fractionation*

Asphaltenes are readily fractionated by adding an n-alkane to mixtures of asphaltene + aromatic or polyaromatic diluents. The addition of n-alkane induces asphaltene sedimentation. The properties of asphaltene fractions recovered from the supernatant and the precipitate, at fixed global composition, can be analyzed separately and compared to the properties of the asphaltenes as a whole. These fractions tend to be referred to as more soluble or less soluble asphaltene fractions, based on this partitioning behavior. Such asphaltene fractions were prepared by adding pentane to mixtures of Athabasca asphaltenes in toluene and 1-methylnaphthalene.

The first step comprised sonicating 3 wt % asphaltene + toluene or 1-methylnaphthalene mixtures for 10 minutes, settling them over night then centrifuging them at 3000 rpm (1000 RCF) for 5 minutes at 293K to remove inorganic solids. The clarified mixtures were then mixed with n-pentane.

Three asphaltene fractions were prepared from toluene + pentane mixtures. The first fraction comprised sediment recovered from a clarified mixture of asphaltenes in toluene + 60 vol. % pentane following sonication for 10 minutes and gravity settling overnight (a less soluble asphaltene fraction). The second fraction comprised asphaltenes recovered from the supernatant of a clarified mixture of asphaltenes in toluene + 75 vol. % pentane, following centrifugation at 3000 rpm for 5 minutes at 293 K (a more soluble fraction). The supernatant was dried at 363 K at atmospheric pressure in air for approximately 2 h. These asphaltene fractions were dried over night in a vacuum oven operated at 333K and 9 kPa. While a mass balance was not performed, Alboudwarej et al.[6] found that the two asphaltene fractions defined in this way each accounted for ~20 wt % of the Athabasca pentane asphaltenes. The third fraction comprised the sediment from the clarified mixture of asphaltenes in toluene + 75 vol. % pentane.

For asphaltenes in 1-methylnaphthalene + pentane mixtures, asphaltene fractions were recovered from the sediment and supernatant of a clarified mixture comprising Athabasca pentane asphaltenes and 1-methylnaphthalene + 75 vol. % pentane. The sediment fraction accounted for 65 ± 5 % of the asphaltenes present in the sample. Enthalpy of solution measurements failed for the fraction recovered from this supernatant.

## 4.3 Results and discussion

### 4.3.1 *Asphaltene partial specific volume*

Partial specific volume values for Athabasca pentane asphaltenes, at near infinite dilution in toluene, tetrahydrofuran, 1-methylnaphthalene and quinoline, are plotted versus solvent specific volume in Figure 4-2. Values for pyridine and anisole drawn from chapter two for a closely related asphaltene sample are also included.

The terms $v_a^{particle}S$ and $(1-a)R$ appearing in equation 4-3 were found to be constant within experimental error for n-alkanes[4], yielding a linear relationship between

$\overline{v}_a$ and $v_s$. While some cross correlation between the extent of swelling, S, and the mass of solvent sorbed, R, is expected, the extent of dissolution is expected to be independent and variable, and there is no expectation of cross correlation for the diverse solvents employed in the current work. Consequently, the partial specific volume data are not quantitatively interpretable relative to the physical phenomena expected to arise: solvent sorption, particle swelling, asphaltene phase change and dissolution. Further, the size and possibly the physical structure of asphaltene aggregates in toluene, tetrahydrofuran, 1-methylnaphthalene and quinoline differ from the size and structure in n-alkanes. For example, the asphaltene aggregates possess nanometer size ranges [26, 27, 40-42] as opposed to macroscopic size ranges observed in n-alkanes.

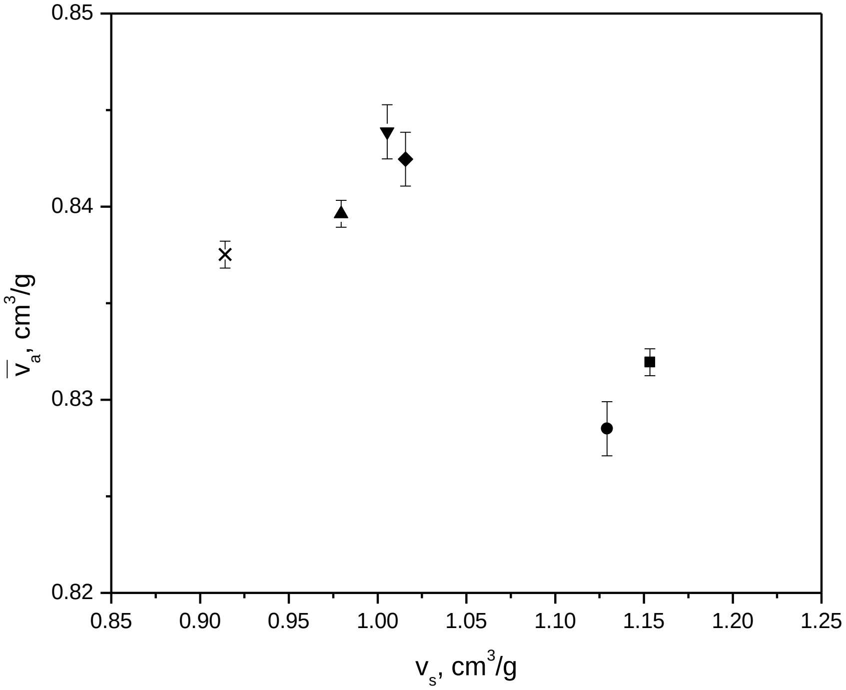

Figure 4-2 Specific partial volume of asphaltenes in toluene (■), tetrahydrofuran (●), 1-methylnaphthalene (▲), and quinoline at 293 K and near infinite dilution (current work) and for pyridine (▼) and anisole (◆)[35] versus the specific volume of the diluent.

### 4.3.2 *Enthalpy of solution for pyrene in toluene and 1-methylnaphthalene*

Pyrene, a crystalline solid with a melting temperature of 423K and a corresponding enthalpy of fusion of 86 J/g, is used to illustrate the attributes of the enthalpy of solution of a pure-crystalline solid solute in a solvent with variations of composition, temperature, and added solvent impurities, as these are key variables in this study. The enthalpy of fusion of pyrene at 298 K is ~75 J/g[35]. The enthalpy of solution values for pyrene in toluene at 1 g/L (~0.1 wt %), and at 5 wt % are 77.6 and 78.0 J/g respectively at 298 K. The addition of 1-methylnaphthalene (1 g/L) as an impurity yielded an enthalpy of solution value of 78.5 J/g at a pyrene concentration of 1g/L. All three values agree within the repeatability of the enthalpy of solution measurements with pyrene, ± 0.5 J/g. The enthalpy of mixing, $\Delta h^{mixing}$, of pyrene in toluene is + 3 ± 1 J/g according to equation 4-6.

The enthalpy of solution for pyrene in 1-methylnaphthalene at 1 g/L was found to be 69.5 J/g at 298 K and 69.2 J/g at 323 K. Again the values fall within the repeatability of the measurements, and the enthalpy of mixing of pyrene in 1-methylnaphthalene is - 6 ± 1 J/g. Thus for a pure crystalline solid undergoing dissolution, enthalpy of solution is expected to be insensitive to changes in temperature and solute mass fraction, below the melting point and the solubility limit, and the enthalpy of solution is expected to be insensitive to impurities. Enthalpies of mixing in different solvents are expected to differ, and may not possess the same sign. The enthalpies of solution of pyrene in toluene and 1-methylnaphthalene are both large and positive but differ by 9 ± 2 J/g, reflecting variation in magnitude and sign of the enthalpy of mixing of pyrene in these two solvents.

### 4.3.3 *Enthalpy of solution of asphaltene + diluent mixtures*

Thermal and concentration effects were explored using diluents, known to cover a wide range of partial specific volume and enthalpy of solution values at 298 K[35]. The results are reported in Figure 4-3 and in Figure 4-4 respectively. The impacts of impurities and significant changes in solvent composition are addressed in the text below and in Table 4-1. Enthalpies of solution for asphaltene-diluent mixtures at 1 g asphaltene /L in toluene, tetrahydrofuran, 1-methylnaphthalene and quinoline over the temperature range 288-353 K are shown in Figure 4-3. The enthalpy of solution values are sensitive to temperature, including a change of sign. Values range from -10 J/g at 288 K and exceed + 8 J/g at 353 K. Zhang et al.[2, 43] reported enthalpies of solution in the range -8 to -20 J/g for Maya, Khafji and Iranian Light heptane asphaltenes in tetralin, 1-metylnaphthalene and quinoline at 298 K and 1.5 g/L.

Although it was not possible to perform experiments over a broader temperature range, the enthalpy of solution values appear to approach common asymptotes at high temperature. The changes in the enthalpy of solution values measured for 1-methylnaphthalene and quinoline are particularly striking. In 1-methylnaphthalene the values dip from -1 J/g, at 288 K to -6 J/g, at 298 K, before rising to a value 7.8 J/g at 353K, while in quinoline the values rise monotonically from -10 J/g to + 8.7/g over the same temperature interval. Changes of sign and fluctuations in enthalpy of solution values at fixed composition are inconsistent with the pattern of values expected for simple dissolution of pure or mixed crystalline material as temperature is varied.

The impact of asphaltene mass fraction on enthalpy of solution values at fixed temperature is shown in Figure 4-4. The enthalpy of solution values appear to approach asymptotic values at low asphaltene mass fractions and to decrease with increasing asphaltene mass fraction in all four diluents at both 298 and 323 K. The variation with mass fraction is least for quinoline at 298 K, which possesses the lowest enthalpy of solution value at low asphaltene mass fraction, and is greatest for toluene for which the enthalpy of solution is greatest at low mass fraction. The enthalpy of solution values do not trend toward zero at high mass fraction. They remain or become negative. Again, the behavior of asphaltenes in toluene, tetrahydrofuran, 1-methylnaphthalene and quinoline does not conform with the simple dissolution behavior of either pure or mixed crystalline solids.

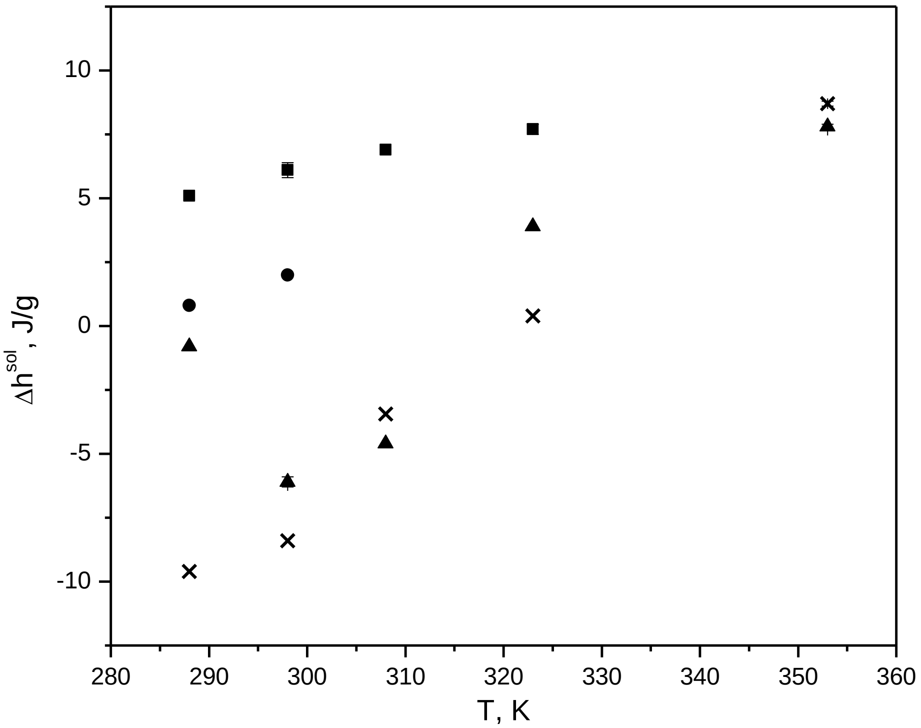

Figure 4-3 Enthalpy of solution for Athabasca pentane asphaltenes at 1 g/L in toluene (■), tetrahydrofuran (●), 1-methylnaphthalene (▲), and quinoline (×)

Impurities also appear to have a significant impact on enthalpy of solution values for asphaltenes in diluents. For example, in n-decane, where the enthalpy of solution for Athabasca pentane asphaltenes at 1 g/L and 298 K is -0.5 J/g, addition of 1g/L of tetrahydrofuran, 1-methylnaphthalene and toluene prior to solution calorimetry experiments yielded enthalpy of solution values of -1.1, -2.1, -5.5 J/g respectively. For asphaltene + toluene and asphaltene + 1-methylnaphthalene mixtures where the asphaltene concentration is 1 g/L, the addition of 1g/L of 1-methylnaphthalene to the toluene prior to calorimetry measurements lowers the enthalpy of solution from 6.1 to 4.9 J/g while addition of 1 g/l of toluene to 1-methylnaphthalene raises the enthalpy of solution from -6.3 to -5.1 J/g. These latter enthalpy differences are small but exceed their individual experimental repeatability, ±0.3 J/g.

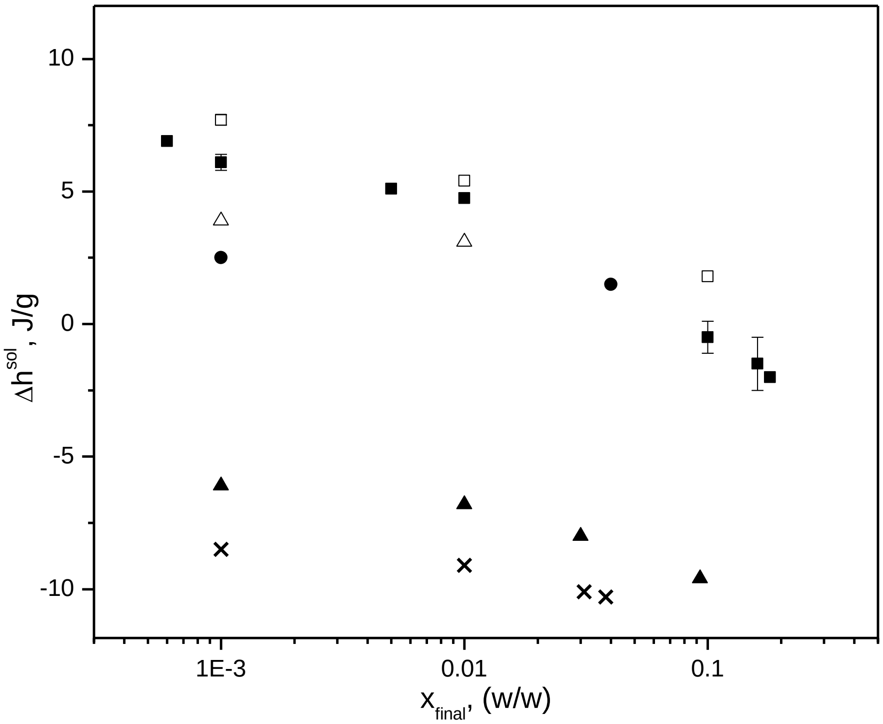

Figure 4-4 Enthalpy of solution for Athabasca pentane asphaltenes in toluene (■), tetrahydrofuran (●), 1-methylnaphthalene (▲), and quinoline (×) at 298K, and in toluene (□) and 1-methylnaphthalene (Δ) at 323 K.

Additional enthalpy of solution values for 1 g/L asphaltenes in toluene + impurities or in mixed solvents at 298 K are reported in Table 4-1. Trace water addition has by far the greatest impact on the enthalpy of solution values. This is followed by the impact of trace 1-methylnaphthalene and heptane on the enthalpy of solution values. Trace addition of Athabasca heptane maltenes and pyrene addition has little impact on enthalpy of solution values.

Table 4-1 Enthalpy of solution of Athabasca pentane asphaltenes (1 g/L) in toluene + diverse impurities at 298 K

| Added Material | $\Delta h^{sol}$, J/g asphaltenes |
|---|---|
| toluene | 6.1 |
| + water, saturated ~0.050 g/L[44] | 1 |
| + 1-methylnaphthalene, 1g/L | 4.9 |
| + n-heptane, 1 g/L | 5.1 |
| + Athabasca heptane maltenes, 3 g/L | 5.6 |
| + pyrene, 3 g/L | 6 |
| + pyrene, 9 wt % | 4.7 |
| + 1-methylnaphthalene, 25 wt % | -2.9 |

In chapter 3, it was possible to discern both endothermic and exothermic peaks in the unscaled power traces during calorimetric measurements for most Athabasca pentane asphaltene + n-alkane mixtures at 298 K. In this work, only endothermic or exothermic peaks are obtained for individual measurements even where enthalpy of solution trends with composition at fixed temperature, Figure 4-5a, and trends with temperature at fixed composition, Figure 4-5b, include a change in sign.  Individual solution calorimetry measurements, in this work, do not provide direct evidence of underlying competitive or complex processes.

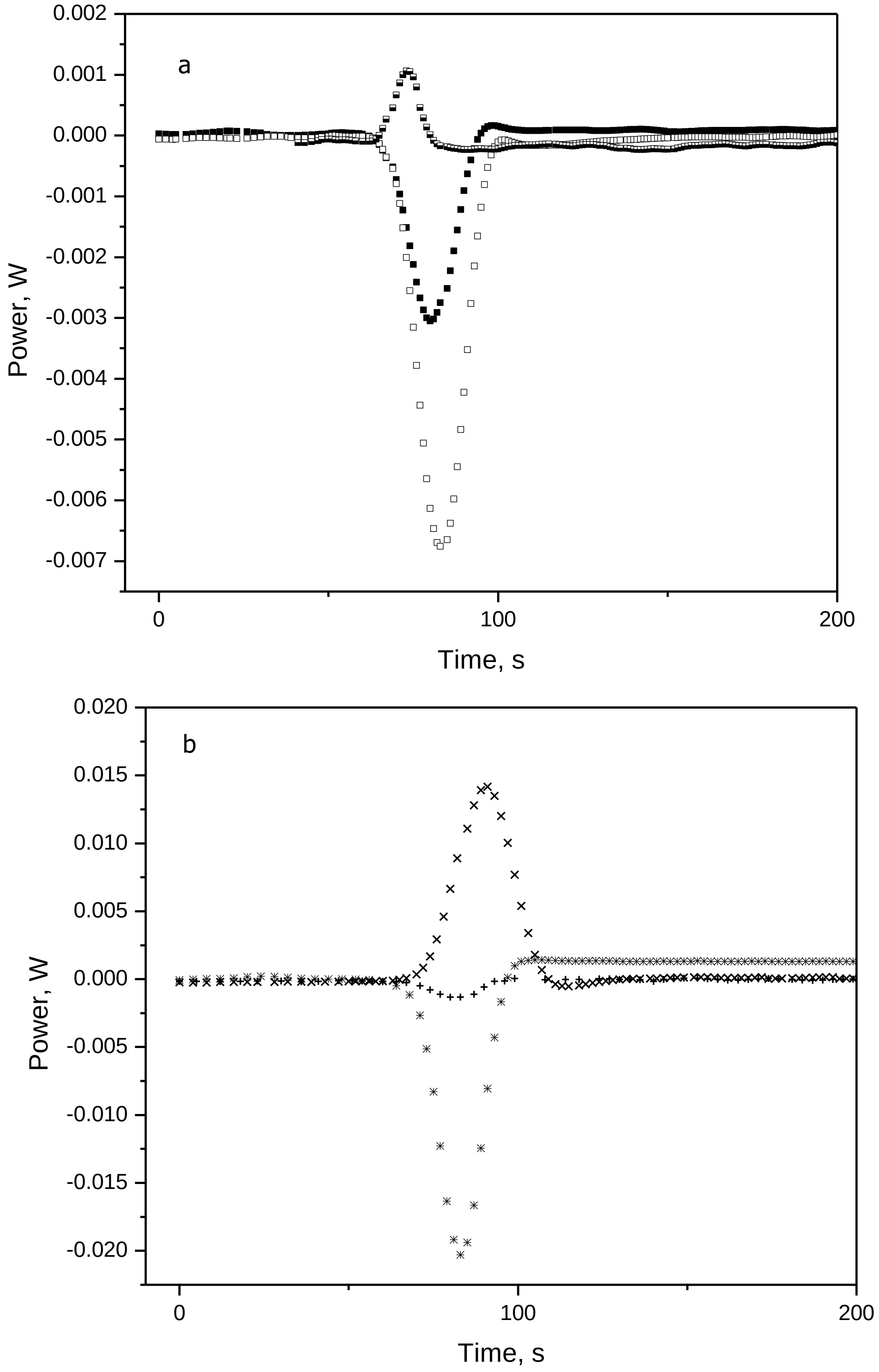

Figure 4-5 Unscaled power measurements for asphaltenes + a) toluene at 298 K and 1g/L (□), 8 wt% (■), and 16 wt% (⬒); b) quinoline at 1 g/L and 298 K (×), 323 K (+), and 353 K (*).

### 4.3.4 *Enthalpy of solution of asphaltene fractions + diluent mixtures*

As apparently competing endothermic and exothermic processes could not be discerned for whole asphaltenes, asphaltene fractions were prepared to explore whether their enthalpic responses differed significantly from whole asphaltenes. The enthalpy of solution values for the asphaltene fractions recovered from the supernatant and precipitate in a toluene (25 vol %) + pentane (75 vol %) mixture, and then dispersed in toluene at 1 g/L and 298 K, were 9.5 ± 0.5 J/g and 5.1 ± 0.3 J/g respectively, while the enthalpy of solution for the asphaltenes as a whole at the same condition, 6.1± 0.3 J/g, fell between. The enthalpy of solution value for the asphaltene fraction precipitated from a toluene (40 vol %) + pentane (60 vol %) mixture was -1.8 ± 0.3. The enthalpy of solution values for these asphaltene fractions differ by up to 11.3 ± 0.8 J/g at 298 K and include a change in sign, suggesting that these asphaltene fractions undergo different processes or a different mix of processes e.g.: sorption, phase change, dissolution when added to toluene.

As noted in the experimental section, enthalpy of solution values could only be obtained for the precipitate from a mixture of Athabasca pentane asphaltenes and 1-methylnaphthalene (25 vol %) + pentane (75 vol. %). Measurements with the fraction recovered from the supernatant failed as a result of slow kinetics as explained in detail in the experimental section. The enthalpy of solution for the precipitated asphaltene fraction in 1-methylnaphthalene at 298K and 1 g/L is -15.5 ± 0.5 J/g. For the asphaltenes as a whole at the same condition, the enthalpy of solution is -6.1± 0.3. Again, the span in enthalpy of solution values for asphaltene fractions at fixed temperature and mass fraction is large and underscores the heterogeneity of asphaltenes and their interactions with diluents.

The asphaltene fraction recovered from supernatants has a lower tendency to form aggregates[45-47] and possesses a lower apparent molar mass, as determined by vapor pressure osmometry[46], than the asphaltenes recovered from the sediment. Other nanostructural, thermophysical, and solution properties are also expected to vary. The literature asserts that these fractions are enriched in soluble and insoluble materials respectively. This contention is consistent with the higher enthalpies of solution for asphaltene fractions recovered from supernatants and the lower enthalpies of solution for asphaltene fractions recovered from sediments. Thus a gradation in solution and colloidal behaviors is readily anticipated for asphaltenes as a function of asphaltene mass fraction, diluent composition, and temperature.

### 4.3.5 *Interpretation of the enthalpy of solution data for asphaltenes in pure diluents*

The enthalpies of solution for asphaltene + diluent mixtures can be described as a sum of enthalpies for physical phenomena expected to arise. The model, elaborated below as Equation 4-7:

$$\Delta h^{sol} = \underbrace{(1-\alpha)\left(\frac{\Delta H^{sorption}}{M} R\right)}_{asphaltene-solid} + \underbrace{(\alpha-\beta)\Delta h^{PhaseChange}}_{asphaltene-rich-liquid} + \underbrace{\beta\Delta h^{PhaseChange} + \beta\Delta h^{mixing}}_{diluent-rich-liquid} \qquad (4\text{-}7)$$

allows for diluent sorption, by asphaltenes particles; the formation of an asphaltene rich liquid phase, where the enthalpy of mixing per unit mass of asphaltenes is negligible; and the formation of a diluent rich liquid phase, where the enthalpy of mixing of asphaltenes is not negligible. Asphaltene aggregation and disaggregation enthalpies are neglected because aggregation arises at ~ 50 ppm in diluents[35], which is well below the composition range of the experimental data and the energy released by combining aggregates to induce precipitation is small[48]. The elastic energy is also neglected. From chapter three, -40 kJ/mole < $\Delta H^{sorption}$ < 0 kJ/mole for n-alkanes on organic and inorganic substrates, $\Delta h^{Phase\ Change}$ for asphaltenes is ~ 22 J/g[31], and 3 J/g < $\Delta h^{mixing}$ < 35 J/g for aromatic compound dissolution in n-alkanes. While the sorption and mixing enthalpies are not restricted to these ranges in the present work, the formation of asphaltene-rich and diluent-rich liquid phases are both anticipated to be endothermic processes. For example adsorption enthalpies, $\Delta H^{sorption}$, of liquid toluene and other aromatic compounds on silica and zeolites are in the range of -10 to -25[49, 50] kJ/mol, and from -5 to -20 kJ/mol for toluene and benzene sorption on activated carbon[50]. The enthalpies of mixing of pyrene with tetrahydrofuran, 1-methylnaphthalene and quinoline are negative and range from -7 to -15 J/g [35] while the enthalpy of mixing pyrene in toluene is + 3 J/g. Figeys et al.[51] place the enthalpy of mixing of naphthalene in benzene at ~ -10 J/g.

At low concentration and high temperature where dissolution in the diluent rich phase dominates, equation 4-7 reduces to equation 4-6. The enthalpy of solution values per gram of asphaltenes are expected to be less than ~ 25 J/g as the enthalpy of mixing of asphaltenes, comprising polynuclear aromatic compounds, is expected to be near zero or negative (-15 to 3 J/g), in toluene, 1-methylnaphthalene, and quinoline, based on the behavior of pure compounds. From Figure 4-3, the measured enthalpy of solution at high temperature exceeds 10 J/g of asphaltenes. It is not clear if the enthalpies of solution for all of the diluents share the same high temperature asymptotic behavior but the data are suggestive and the range of probable values, 10 J/g to 25 J/g, is heavily constrained for Athabasca pentane asphaltenes.

At low enough temperatures and high enough asphaltene concentrations where both dissolution and phase change can be neglected, equation 4-7 becomes:

$$\Delta h^{sol} = \left( \frac{\Delta H^{sorption}}{M} R \right) \tag{4-8}$$

The minimum enthalpy of solution values obtained at low temperature and high asphaltene mass fraction for 1-methylnaphthalene and quinoline are less than -10 J/g as shown in Figure 4-3 and Figure 4-4. The lowest enthalpy of solution value measured for an asphaltene fraction in this work is -16 J/g and Zhang et al.[2, 43] measured values as low as -20 J/g. The lowest enthalpy of solution value measured for an Athabasca asphaltene fraction in n-alkanes was -10 J/g[4]. Thus the value of $\left( \frac{\Delta H^{sorption}}{M} R \right)$ for 1-metylnaphthalene and quinoline is expected to be less than -10 J/g. A lower bound is not readily identified, and may well be diluent dependent.

To a first approximation, the magnitudes of the enthalpy of sorption term, dominant at low temperature and high asphaltene mass fraction, and the phase change + dissolution terms, dominant at high temperature and low asphaltene mass fraction, are of comparable magnitude but of opposite sign. At intermediate conditions, both with respect to temperature and composition, the range of asphaltene interaction behaviors is diverse. The mass fractions reporting to an asphaltene rich liquid phase, α, and to a solvent rich phase, β, are not readily discriminated on the basis of the available enthalpy data.

### 4.3.6 *Impact of impurities in the diluent on the enthalpy of solution of asphaltenes*

Significant impacts of trace impurities, such as water, on enthalpies of solution of asphaltene + organic diluent + water mixtures have been attributed to interfacial interactions arising between water and asphaltene aggregates[44], as the impact of impurities on bulk properties of the diluent are negligible. Thus, within the interpretive framework, addition of impurities adds two terms to equation 4-7. One concerns de-mixing of the impurity from the diluent and the other concerns the sorption of the impurity by the asphaltenes. Thus equation 4-7 becomes:

$$\Delta h^{sol} = (1-\alpha)\left(\frac{\Delta H^{sorption}}{M}R + \frac{(\Delta H_i^{sorption} - \Delta H_i^{mixing})}{M_i}R_i\right) + \alpha\Delta h^{PhaseChange} + \beta\Delta h^{mixing} \quad (4\text{-}9)$$

The subscript *i* refers to the impurity. $\Delta H_i^{mixing}$ is the enthalpy of mixing per mole of impurity in the diluent. If the impurity is sorbed preferentially by the asphaltenes, the enthalpy of solution of the asphaltenes can be affected vis-à-vis the enthalpy of solution in the pure diluent. Further, the effect is excentuated if the absolute value of the enthalpy of mixing of the impurity is a large, and the concentration of the impurity is significant relative to the mass of diluent sorbed per unit mass of the asphaltenes. The amount of diluent sorbed by the asphaltenes relative to the amount sorbed in the absence of an impurity may also be reduced as a consequence of competition with the impurity. Thus the magnitude and sign of the impact of an impurity on the enthalpy of solution for asphaltenes is not known a priori. However, the enthalpy of mixing for n-alkanes in aromatics, for aromatics in n-alkanes, and for water in hydrocarbons is positive, and the enthalpy of sorption is negative. So, the addition of impurities is expected to reduce the enthalpy of solution of asphaltenes if impurity sorption is significant and the net impact on sorption enthalpy is small. The results reported here for enthalpy of solution measurements for Athabasca pentane asphaltenes in n-decane and toluene following impurity addition suggest that this is a common effect. Only for toluene addition to 1-methyl naphthalene is change in enthalpy of solution for asphaltenes positive.

## 4.4 Conclusions

The enthalpy of solution for pure crystalline solid solutes in pure diluents, below their solubility limit, vary with diluent composition at fixed solute mass fraction, and are largely independent of solute mass fraction, temperature and the presence of trace impurities in diluents. These well known properties of crystalline solutes are exemplified and are shown to contrast with the enthalpy of solution for Athabasca pentane asphaltenes and asphaltene fractions, which vary significantly with each of these variables, including changes of sign. The set of enthalpy of solution values for Athabasca pentane asphaltenes and asphaltene fractions in pure and mixed diluents is inconsistent with dissolution, even for a mixed solid solute, as a sole form of interaction between asphaltenes and diluents. The calorimetric results are consistent with a fraction of the asphaltenes remaining solid, permitting sorption (negative enthalpy); a fraction transitioning to an asphaltene-rich liquid (positive enthalpy and observed exogenously); and a fraction of the asphaltene-rich liquid becoming soluble in a diluent (negative or positive enthalpy). The mass fraction of asphaltenes reporting to each of these phases is a function of diluent composition, temperature and asphaltene concentration in a mixture. Quantitative assignment of asphaltene fractions to these phases remains elusive, as the enthalpies of mixing for asphaltenes and the sorption enthalpies for diluents by asphaltenes remain poorly bounded.

## 4.5 References

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# Chapter 5:Discussion

Here a broad discussion unifying the observations made in chapters 2-4 is presented. The chapter also includes speculation on the possible impact of the results and conclusions of this thesis on asphaltene research.

The results presented in chapters 2-4 all fall in the same category. Chapter two was dedicated to showing that the thermodynamic measures of mixing of asphaltenes with various diluents do not correlate even qualitatively with the solubility parameter of the diluents. Regular solution theory, despite its shortcomings, is a coherent thermodynamic model framework that once its underlying assumptions are satisfied can explain behaviors in solution qualitatively if not quantitatively. The aim of the analysis in Chapter two was not to focus on the shortcomings of individual regular solution theory based models but rather to attribute the general failure of this framework to the mismatch between the behavior of asphaltene + diluent mixtures with that of classical solutions.

Chapters 3 and 4 focused on showing why and how the asphaltene mixtures behave differently from a regular solution. Swelling of asphaltene particles, upon exposure to n-alkanes, was established is chapter 3. The difference in the behavior of Asphaltenes in n-alkanes at low and high concentrations was shown to be dramatic and the result was attributed to the presence of soluble and insoluble asphaltene fractions. The ratio of these fractions was shown to be a function of the diluent nature, temperature and composition. The current chapter is dedicated to explaining the outcome of these findings. In other words, the focus of the discussion is to provide clarification on why and how ignoring the dual nature of asphaltene containing mixtures can impact analysis of the measured data and applicability of the models developed for asphaltene containing systems.

## 5.1 Implications for asphaltene preparation and analysis of experimental data

The results described in chapters 3 and 4 illustrate the dependence of asphaltene properties on details of the preparation and measurement techniques employed in their preparation. The impact of solubility of asphaltenes in n-alkanes at low concentration on asphaltene preparation methods was discussed in chapter 3. In chapter 4 the pronounced impact of trace contaminants has on the interactions of asphaltene with the surrounding medium illustrates the importance of interfacial phenomena on their mixing behavior. This phenomenon may manifest itself in the composition or surface characteristics of the asphaltene precipitated out of oil in the presence of a certain contaminant. Asphaltene preparation in the lab is always in danger of contamination with toluene, acetone, or n-alkanes that may be residuals of cleaning steps or previous experiments.

Discrepancies may also arise if contamination occurs during property measurements. Rheological measurements, for example, can be impacted by the affinity of asphaltenes toward contaminants. Sorbed species on the surface may act as a lubricant or on the contrary as a source of friction under shear. The presence of water in asphaltene containing mixtures both in industrial and laboratory environments is always a possibility.

Aside from the impact of contaminants, the tendency of asphaltenes to sorb diluents may itself be a source of error that needs to be accounted for in interpretation of experimental data. For example, it is not clear how sorbed diluents or contaminants impact SAXS, SANS or other spectroscopic measurements. The impact of sorption on the contrast between the aggregate and the liquid phase, resolution of the borders, and the measured radii of gyration have yet to be evaluated in the literature.

Interpretation of vapor pressure osmometry results heavily rely on the assumption of ideal solution behavior. How the molar masses obtained from vapor pressure osmometry measurements may be impacted by the inter-molecular or interfacial interactions of asphaltenes with their medium is a key question. The same kinds of concerns apply to the centrifugation and filtration experiments.

The multi-component and multiphase nature of asphaltenes played a central role in the analysis performed in chapters 3 and 4. This characteristic of asphaltenes enables them to include a soluble and an insoluble portion. The coexistence of these two fractions impacts the validity of interpretation and comparison of the enthalpy of solution data such as those performed by Zhang et al[1, 2]. The strength of the diluent in dispersion of asphaltenes cannot be determined by the value of enthalpy of solution alone. Every diluent may interact strongly with a portion of the asphaltene continuum and therefore choice of the right solvent needs to be based on the application.

Lastly, there is no direct way of determining the density of asphaltenes. Density measurements require addition of a diluent and back calculation of asphaltene density from the density of the mixture. The data in chapter 2, 3, and 4 clearly show that the value measured in this way is highly dependent on the diluent and concentration used for the measurement. Therefore, the density data reported for asphaltenes need to be accompanied by information on the diluent used for their determination.

## 5.2 Implications on modeling

The data presented in chapters 3 and 4 shows that at low concentrations the portion of asphaltenes soluble in a considerably weak solvent (n-pentane) is not much different from that in a so-called strong solvent (quinoline). This is a testament to the significance of the multi-component nature of asphaltenes that is inherently ignored by common modeling approaches which represent asphaltenes as a single pseudo-component. Lumping decreases the complexity of the developed models. However, it is important to recognize that asphaltenes have a soluble and an insoluble fraction[3]. The transfer from soluble and insoluble phase upon changes in composition and temperature may be a driving force for inducing phase separation. The separation may be a result of destabilization of the colloid through change in the surface properties of the particles, their size, or their interactions with the medium.

The relative success of regular solution theory based models in capturing the precipitation trends once their parameters are tuned for a specific mixture can be explained through the relationship between solubility and phase separation. Inclusion of a minimum of two varying soluble and insoluble fractions in models for phase behavior prediction may be a good starting point to develop more generalized models without the need for tuning the parameters for each mixture. Obviously, in order for such models to reflect the colloidal and solution behaviors, intermolecular and interfacial forces should both be represented.

Aromaticity, polarity and hydrogen bonding abilities have been identified as the main sources of asphaltene interactions. Therefore, accounting for the intermolecular forces based on measures of these three characteristics may lead to more accurate representations. Application of a single solubility parameter decreases the complexity and therefore sensitivity of the developed models however fails to capture the specifics of interactions. Models similar to those based on Hansen solubility parameters, though more complex, may be modified for asphaltene systems to include their three main sources of interactions. Such models may be found beneficial in terms of generalization. Another important factor to be included is the average size of the molecules and therefore the asymmetric nature of the mixture that accounts for the entropy changes.

The main challenges in development of such inclusive models are:

1. Addition of parameters requires a larger data set for training and testing of the model
2. Defining a basis for representation of the different interactions in these models may be obscure

Phase behavior of asphaltenes in organic media is complex and is not yet well understood. Similar to many complex processes, development of models that account for every single interaction and behavior may not be plausible. Furthermore, the information that can be readily collected for oil and asphaltene samples have a limited value from a modeling perspective. This information includes: yield of pentane or heptane asphaltenes, elemental analysis, aromatic carbon ratio, average molar mass, precipitation onset upon addition of a non-solvent, densities, and in some cases distillation curves for the oil sample. These data cannot be directly used in first principles models. Therefore, the need for statistical analysis on data collected from various studies on different crudes and asphaltenes is apparent. One path forward would be to develop gray box models based on the structure of the current relatively successful models but modified to include the easily accessible auxiliary data and new types of data as they emerge. Such models have been employed in many industrial applications for complex systems and have had a significant impact on the efficiency of industrial processes.

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# Chapter 6: Contributions, conclusions and future work

## 6.1 General conclusions

This work is focused on volumetric and enthalpic studies of mixing of asphaltenes with organic diluents. Phase behavior of asphaltenes was investigated through density and solution calorimetry measurements on Maya and Athabasca asphaltenes in a series of diluents including n-alkanes, aromatics, and polar compounds.

In chapter two, the partial specific volume of asphaltenes was shown to be weakly correlated with the nature of the diluent in the temperature range of 283-353 K. The correlation between the calculated volume of asphaltenes in various diluents with the concentration was also weak and the experimental uncertainties did not allow for distinguishing between the values at low, medium and high concentration. Volumetric measurements alone proved to be of limited value in analysis of the phase state of asphaltenes and their interactions with various diluents.

The combination of solution calorimetry data with the volumetric data on asphaltenes at room temperature was shown to be inconsistent with the thermodynamic concepts defining regular solution theory. The results pointed at the possibility of variations in the distribution of phase states of asphaltenes in various diluents.

In chapter three, density measurements were proven to be valuable in analysis of asphaltene-n-alkane interactions. These measurements showed that n-alkanes appear to penetrate into the structure of asphaltenes particles. Alkane sorption on asphaltene particle surfaces was identified indirectly by solution calorimetry and asphaltene particle swelling was detected by direct visual observation. Formation of liquid crystal and isotropic liquid domains on particle surfaces was observed directly, and dissolution of asphaltenes into n-alkanes was inferred from the enthalpy of solution measurements. A significant fraction of asphaltenes were shown to be soluble in n-alkanes at low concentrations and the soluble fraction was shown to decrease with increasing n-alkane carbon number.

In chapter four, the impact of the multi-component and multi-phase nature of asphaltenes was emphasized and asphaltenes in any diluent were divided into soluble and insoluble fractions. The relative amounts of these fractions varied with temperature, composition and the diluent. The insoluble fraction was shown to have strong interfacial interactions with the surrounding medium. The enthalpies of sorption and dissolution of asphaltenes in three diluents were estimated.

Finally, calorimetric and density measurements on asphaltene – diluent mixtures over a broad range of compositions and temperatures led to development of a coherent framework for explaining the behavior of asphaltenes in organic diluents.

## 6.2 New experimental procedures

Density and solution calorimetry measurements have been used in a number of unconventional ways during the course of this study. The procedures and their applications are explained here.

### 6.2.1 *Density*

Density of slurries was measured with a vibrating U-tube density meter. The linearity of the plot of densities versus the mass fraction of the solid in liquids indicates the homogeneity of the injected samples. This technique can be used to determine the density of solid materials and because of its accuracy and flexibility in terms of temperature can be used in preference to pycnometer measurements.

Density measurements were used to determine the concentration of asphaltene containing mixtures. The technique is very simple and reliable for determination of concentration of any solid containing sample. The information required for calculations are densities of the solvent and the solid. The densities of asphaltene fractions in various diluents, at 20 °C were are all in the range 1.175 ± 0.025 g/cm$^3$. Using a common value for all fractions introduces an error of <3%. This error could be decreased significantly if the fractions were recovered and their density estimated by re-dispersion or dissolution.

### 6.2.2 *Solution calorimetry*

Performing enthalpy of solution measurements by adding a solute to a liquid with an underlying composition of the same solute was shown to be a good test for determining impact of overall composition on the behavior of asphaltenes. As discussed in chapters 4 and 5, enthalpy of solution values alone cannot be used as a basis of comparison for mixture containing complex solute such as asphaltenes. The proposed procedure is a reliable tool to show how concentration affects the behavior of a complex solute only a portion of which is soluble. The difference of enthalpy of solution of asphaltenes at different concentrations is much more pronounced than what can be shown by dilution experiments through titration calorimetry.

The test of enthalpy of solution measurements on asphaltenes in diluents + trace additives was shown to be a very sensitive measure of surface interactions of asphaltene aggregates or particles. This test can be used to assess the claims about association of materials with certain structures with asphaltenes. For example, the author's preliminary analysis, reported in chapter 4, showed an insignificant interaction of deasphalted Athabasca bitumen (containing resins) and pyrene with asphaltenes.

## 6.3 Recommendations for future work

Quantification of each of the contributions to the enthalpy of solution of asphaltenes in diluents is of great value. These contributions include: enthalpies of sorption, the amount of sorbed diluent per gram of asphaltenes, enthalpies of mixing of diluents, and enthalpies of dissolution. Some of these values may be measured directly.

The equipment used for solution calorimetry measurements also includes a titration and a relative humidity perfusion module. The former can be used for titration calorimetry measurements and the latter can be used for gas adsorption studies, following modification.

The amount of diluent sorbed on the asphaltene surface may be estimated by enthalpy measurements on adsorption of diluent vapor on solid asphaltenes. Obtaining representative values from these measurements may be challenging. Asphaltenes are known to be prone to reversible and irreversible phase transitions and oxidation upon exposure to high temperature[1, 2]. Therefore, cleaning of the solid asphaltene surface needs to be performed at lower temperature, preferably below 353 K where asphaltenes start to melt[3]. This obviously causes difficulties in degassing of the solid surface prior to adsorption measurements. Furthermore, there is no guarantee that the amount sorbed from the liquid phase by nanoaggregates be identical to what is sorbed by particles from gas phase.

Titration calorimetry measurements can be employed to determine enthalpies of mixing of diluents, and enthalpies of dilution of asphaltenes and their subfractions. This technique can also be used in calorimetric studies on asphaltene precipitation or addition of a second diluent to asphaltene + diluent mixtures. As explained in chapter one, the literature in the area of titration calorimetry applied to asphaltene systems is very rich. However, many unanswered questions remain. Of particular significance would be the calorimetric study of aggregation behavior of asphaltene subfractions to assess the claim regarding fractional solubility. These measurements which involve dilution experiments on mixtures of asphaltenes subfractions with toluene or other diluents may also be used to determine the initial aggregation concentrations of each subfraction. Such data for whole asphaltenes is not collected through calorimetry as aggregation in the whole asphaltenes starts at very low concentrations.

Titration calorimetry may also be employed in investigation of precipitation upon addition of an n-alkane to asphaltene + toluene mixtures. As shown by Verdier et al.[4] , the energy involved in this process is small and no calorimetric manifestation of the precipitation onset could be detected. In fact, the preliminary titration calorimetry work by the author of this thesis confirmed these observations. However, by subtraction of the enthalpy of mixing of n-alkanes and toluene from the enthalpy measured for asphaltene + toluene + n-alkane mixtures some useful information may be extracted.

Differential scanning calorimetry can also be used to follow the behavior of mixtures of asphaltenes during thermal cycling. Possible behavioral hystereses or irreversibilities over heating/cooling cycles would reveal whether asphaltenes, as prepared, are polymorphic, equilibrium or non equilibrium species.

The experience gained during this study on complex systems shows that common tools for analysis of mixing behaviors need to be used in a creative way to extract the maximum amount of information. This realization may well also apply to other measurement techniques. Titration calorimetry is a particularly versatile tool with great potential for evaluating the energies involved in various processes. Experimenting with various combinations of titrants and titrates may provide information of significant value on the differences in behavior of asphaltenes in various media.

## 6.4 References

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# Appendix A Tables of properties

Table A-1 Experimental partial specific volumes of pyrene and calculated values for specific volume of sub-cooled liquid pyrene [g/cm$^3$]

| Solvent | Temperature, ˚C | | | | |
|---|---|---|---|---|---|
| | **20** | **35** | **50** | **65** | **80** |
| toluene | 0.8275 | 0.8305 | 0.8333 | 0.8360 | 0.8377 |
| 1-methylnaphthalene | 0.8473 | - | 0.8605 | - | 0.8740 |
| anisole | 0.8383 | - | 0.8499 | - | 0.8594 |
| quinoline | 0.8505 | - | 0.8644 | - | 0.8784 |
| tetrahydrofuran | 0.7992 | 0.8022 | - | - | - |
| methylene chloride | 0.8271 | - | - | - | - |
| pyrene-Sub-cooled liquid[41] | 0.8425 | 0.8305 | 0.8554 | 0.8636 | 0.8718 |

Table A-2 Enthalpy of solution of pyrene in various diluents at 25 °C

| Solvent | Enthalpy of Solution, J/g | Error |
|---|---|---|
| tetrahydrofuran | 40.0 | -- |
| toluene | 78.0 | 0.5 |
| 1-methylnaphthalene | 68.5 | 0.5 |
| anisole | 64.9 | -- |
| quinoline | 72.0 | 0.5 |

Table A-3 Enthalpy of solution of Athabasca pentane asphaltenes in various diluents at 25 °C

| Diluent | Enthalpy of Solution, J/g | Error |
|---|---|---|
| quinoline | -8.5 | -- |
| 1-methylnaphthalene | -5.85 | 0.2 |
| tetrahydrofuran | 1.1 | 1 |
| toluene | 6 | 1 |
| anisole | 6.2 | -- |
| pyridine | 9.1 | -- |
| methylene chloride | 16 | -- |

Table A-4 Hansen solubility parameters

| Component | Hansen Solubility Parameter, MPa$^{0.5}$ | | |
|---|---|---|---|
| | Dispersion | Polar | Hydrogen |
| toluene[45] | 18 | 1.4 | 2 |
| quinoline[45] | 19.4 | 7 | 7.6 |
| pyridine[45] | 19 | 8.8 | 5.9 |
| tetrahydrofuran[45] | 16.8 | 5.7 | 8 |
| acetone[45] | 15.5 | 10.4 | 7 |
| Methylene Chloride[45] | 18.2 | 6.3 | 6.2 |
| 1-methylnaphthalene[45] | 20.6 | 0.8 | 4.7 |
| anisole[46] | 17.8 | 4.1 | 6.8 |

# Appendix B Calculations of solubility parameter and enthalpy of fusion of pyrene

Solubility parameter is defined in equation 2-4. Enthalpies of vaporization of pyrene at temperatures above its melting point (150.1 °C) were extracted from DIPPR database and the enthalpy-temperature curve was extrapolated to 25 °C. The resulting value was:

$$\Delta H_{vap}^{25C} = 80684\ J/mol$$

The same procedure was used for liquid density of pyrene and the value was determined as:

$$\rho_{subcooled}^{25C} = 5870\ kmol/m^3$$

The value obtained by extrapolation of the fit to the liquid density vs temperature curve was compared to linear extrapolation and also calculations based on the Peng-Robinson equation of state and volume correction using VMGsim simulation software. The deviation of the values was less than 1%.

Using equation 2-4 solubility parameter was calculated:

$$\delta^{25C} = 21.4\,MPa^{0.5}$$

The enthalpy of fusion of pyrene was determined using the following equation:

$$\Delta H_f^T = \Delta H_f^{T_m} - \left(C_p^s - C_p^l\right)\left(T - T_m\right) \qquad \text{(B-1)}$$

The term $\left(C_p^s - C_p^l\right)$ was calculated at 25 °C, 87 °C and the melting point. The average value of the three points was used.

$$\Delta H_f^{T_m} = 17.36\ kJ/mol$$

$$\left(C_p^s - C_p^l\right) = -18\ J/mol$$

$$\Delta H_f^{25C} = 15.11\ kJ/mol = 74.7\ J/g$$

# Appendix C Data and analyses not included in the papers

The following data and analyses were originally performed but were excluded from chapters 2 to 4. The data in chapters C.1, C.2, and C.3 belong to chapters 2, 3, and 4 respectively.

## C.1 Determination of maximum intake of asphaltenes by diluents

### C.1.1 *Experimental*

Asphaltenes (Athabasca $C_5$ and $C_7$, with solids, and solids-free Athabasca $C_7$) were mixed with the diluent in a closed container and shaken with vortex mixer at 3200 rpm for 1 minute. Then they were sonicated for 10 minutes and left at room temperature for 3 weeks. The samples were agitated at least once a day during this time. At the end of the 3 weeks the samples were centrifuged at 3500 rpm for 5 minutes at 20 ˚C. The supernatant liquid was centrifuged one more time using the same rate. The solubility was measured by density measurements on the sample assuming an asphaltene density of 1.18 g/cm$^3$. The maximum error associated with this assumption is 1.5%.

The samples after the density measurements were again mixed with added asphaltenes and agitated as mentioned and left for another two weeks prior to a second density measurement. At the end of week five, the same procedure was followed for another two weeks. The determined values are reported at the end of 3, 5 and 7 weeks in the results Section.

### C.1.2 *Determination of saturation concentration of asphaltenes in the diluents*

Regular solution theory does not make direct claims about volumetric behavior of the solution and its relevance to solubility parameter. In fact, the theory includes the assumption that volume of mixing is zero.

The comparison of the density of the solute on its own and the apparent density within the solvent (especially at infinite dilution) allows for comparing the solvent-solvent interactions with that of solute-solvent. These interactions directly relate to the enthalpy of mixing and through that should correlate with the solubility parameter as claimed by the regular solution theory. Basically, a solvent with a higher solubility parameter than the solute should yield an apparent density lower than the actual solute density and vice versa (if we admit that the interactions correlate with solubility parameter values). This is certainly not the case for the measured systems.

However, in order to directly investigate the relevance of solubility parameter to the asphaltene diluent system the intake of asphaltenes in a number of diluents were studied, because prediction of the solubility behavior is in fact the basic claim of the regular solution theory.

As mentioned before lutidine, anisole, pyridine and quinoline were mixed with asphaltenes and kept for 3 and 5 weeks to saturate the samples. In this part of the work, THF, Toluene and 1-methylnaphthalene were excluded as these diluents readily mix with asphaltenes at such high concentrations that density measurements were not possible due to high viscosity of the sample.

As explained in the “experimental” section every single sample was centrifuged twice prior to density measurement. For all samples a visible amount of black solids remained at the bottom of the centrifuge tubes after each round of centrifugation.

The final concentration of the samples at the end of 3, 5, and 7 weeks are summarized in Table C-1. For the cases that the values at the end of the third and fifth week were significantly different another measurement was performed at the end of the 7th week. All sample showed a consistent increase in the concentration with time indicating a slow trend towards saturation. It is also possible that the sample is saturated by a fraction of asphaltenes at the end of 3 weeks while addition of fresh asphaltenes supplies the system with the fraction that is not saturated.

Table C-1 weight percent of the asphaltenes in diluents measured at the end of 3, 5, and 7 weeks.

| Diluent | Solubility Parameter | $C_5$ Asphaltenes | | $C_7$ Asphaltenes | | |
|---|---|---|---|---|---|---|
| | | 3 weeks | 5 weeks | 3 weeks | 5 weeks | 7 weeks |
| n-heptane | 15.21 | 0.12 | - | - | - | - |
| dodecane | 15.91 | 0.49 | - | 0.061 | - | - |
| 2,6 - Lutidine | 19.29 | - | 11.77 | 12.03 | 14.93 | 17.1 |
| Anisole | 20.10 | 5.29 | 5.79 | 9.11 | 9.55 | - |
| Pyridine | 21.81 | 6.15 | 6.6 | 5.44 | 6.03 | - |
| Quinoline | 21.94 | - | - | 7.74 | 8.81 | 9.23 |

The results at the end of 5 weeks are plotted versus the solubility parameter of the diluents in

Figure C-1. The trend shown in the figure contradicts the expected trend from the solubility parameter values. As depicted in the figure at a solubility parameter lower than 20 $MPa^{0.5}$ the saturation concentration decreases by increasing the solubility parameter suggesting a solubility parameter lower than that of lutidine for the asphaltenes. At the same time, the saturation concentration increases for quinoline and pyridine as the solubility parameter is increased suggesting that asphaltenes solubility parameter should be larger than quinoline.

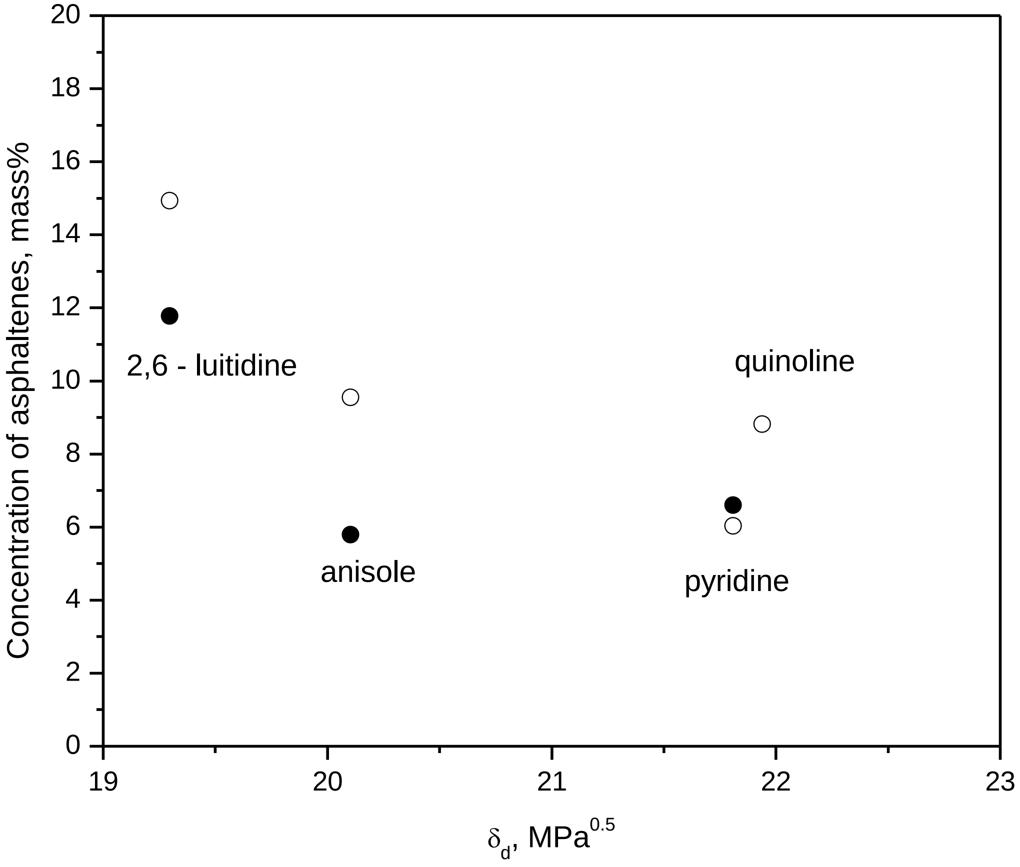

Figure C-1 Concentration of Athabasca pentane (○) and heptane (●) asphaltenes at the end of 5 weeks in 2,6 – lutidine, anisole, pyridine and quinoline versus the diluents solubility parameter.

Andersen and Speight[1] have suggested that the Scatchard-Hildebrand equation for asphaltenes at saturation can be simplified as:

$$\ln x_a = -M_a / RT\rho_a \left\lfloor \phi_d^2 \left(\delta_d - \delta_a\right)^2 \right\rfloor \tag{C-1}$$

Where $x_a$ is the mole fraction at saturation, $M_s$, $\rho_a$, and $\delta_a$ are molar mass, density and solubility parameter of asphaltenes respectively and $\delta_d$ and $\varphi_d$ are solubility parameter and volume fraction of the diluent.

Assuming a molar mass range of 500-2000 g/mol for asphaltenes, the generated data were used to calculate the solubility parameter of AB $C_7$ asphaltenes. The results of these calculations are tabulated in Table C-2.

The more relevant values are marked in bold font in the table. Except for the value from dodecane which represents only a portion of the asphaltenes that remained in dodecane upon centrifugation the rest of the values seem too large for these asphaltenes. Asphaltenes are believed to have a solubility parameter within the range of 20-22 MPa$^{0.5}$ [1].

Table C-2 Calculated solubility parameters for AB $C_7$ asphaltenes based on the measured saturation concentrations in the various diluents.

| | **MM= 500 g/mol** | | | **MM= 800 g/mol** | | | **MM= 2000 g/mol** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Diluent** | **$\delta$-$\delta_a$** | **$\delta$a** Possible Values | | **$\delta$-$\delta_a$** | **$\delta$a** Possible Values | | **$\delta$-$\delta_a$** | **$\delta$a** Possible Values | |
| **Anisole** | 5.25 | 14.85 | 25.35 | 4.37 | 15.73 | 24.47 | 3.01 | **17.09** | **23.11** |
| **dodecane** | 6.89 | 9.01 | **22.79** | 5.60 | 10.30 | **21.50** | 3.72 | 12.18 | **19.62** |
| **Lutidine** | 5.01 | 14.29 | 24.31 | 4.21 | 15.09 | **23.51** | 2.94 | 16.36 | **22.24** |
| **Pyridine** | 5.39 | 16.41 | 27.19 | 4.47 | **17.33** | 26.27 | 3.08 | **18.72** | 24.88 |
| **Quinoline** | 5.04 | 16.86 | 26.94 | 4.22 | **17.68** | 26.12 | 2.95 | **18.95** | 24.85 |

## C.2 Comparison of the solubility of pentane asphaltenes in different n-alkanes

Figure 3-5 and Figure 3-7 it appears that the soluble portion for larger n-alkanes should be larger than the smaller ones. As shown in **Figure** C-2 washing pentane asphaltenes by alkanes with larger numbers of carbons in their structures has a more pronounced impact on the enthalpy of solution of the washed asphaltenes in the same diluent. Therefore, a larger portion of material appears to be washed away in larger n-alkanes causing a more significant change in the enthalpy of solution. However, there is no reason to assume that the enthalpy of dissolution of asphaltenes is the same in all n-alkanes. Therefore, in order to measure whether the soluble portion is larger for smaller or larger n-alkanes the enthalpy of solution of n-octane washed asphaltenes in n-decane and that of n-decane washed asphaltenes in n-octane were measured. Washing of asphaltenes with these diluents is expected to remove at least a portion of the soluble material in the diluent of choice. By cross mixing of these asphaltenes with the other n-alkanes one can determine if the fraction soluble in the diluent used for measurements is completely removed by the washing diluent. If in fact the soluble fraction was larger in n-octane, the enthalpy of solution of octane washed asphaltenes in n-decane should have been more or less the same as that of decane washed asphaltenes in n-decane. On the contrary, decane washed asphaltenes would show a more endothermic behavior than octane washed asphaltenes once mixed with n-octane and vice versa.

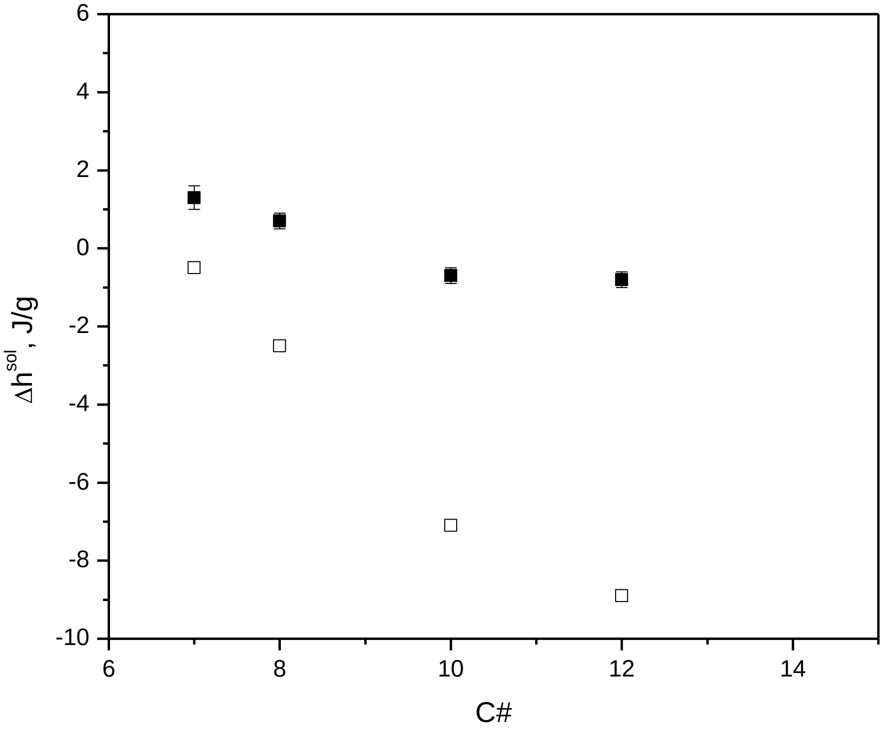

Figure C-2 Enthalpy of solution of pentane asphaltenes in n-alkanes (■) and n-alkane washed asphaltenes in the same n-alkane (□) as a function of the number of carbons in the diluent

The results of the four measurements are shown in the matrix in Table C-3. As is obvious by comparison of the numbers, a part of the fraction of asphaltenes that are soluble in n-octane are not removed by mixing with n-decane while there is no residual soluble asphaltenes in n-decane within the octane washed asphaltenes. Therefore, it appears that the smaller n-alkane solubilizes more asphaltenes than the larger one.

Table C-3 Matrix of the enthalpy of solutions in J/g of two asphaltenes in n-octane and n-decane

| **Type of Asphaltene** | | C8 Washed | C10 Washed |
|---|---|---|---|
| **Diluent** | n-octane | -2.5 | -1.5 |
| | n-decane | -7.4 | -7.1 |

## C.3 Indirect measurement of enthalpies of solution of asphaltenes at lower concentrations

Direct measurements at asphaltene concentrations much lower than 1 g/L showed a large error due to the small magnitude of energy produced/consumed during the mixing process. Therefore the enthalpies of solution of asphaltenes in toluene and 1-MN were indirectly calculated using the enthalpy of solution values measured for Athabasca bitumen and Athabasca bitumen pentane maltenes. For these calculations the inherent assumption is that the maltenes and asphaltene fractions do not interact with one another. The enthalpies of solution of Athabasca bitumen in toluene and 1-MN at 25 °C and 1 g/L were 8.4 and 6.9 J/g respectively. The enthalpy values for the maltenes fraction at the same conditions and in the same diluents were 7.8 and 6.4 J/g. Setting the composition of pentane asphaltenes in the bitumen to 0.186 and assuming a 0.2 J/g repeatability range for the solution calorimetry measurements, the calculated values for asphaltenes in toluene and 1-MN at a concentration of 200 ppm (150-200 mg/L) were 11.9 ± 2.5 and 3.8 ± 1.9 respectively. The first value is well within the expected range for enthalpy of dissolution of the whole asphaltenes in toluene while the value for 1-MN is significantly smaller showing that even at that low of a concentration a rather significant portion of the asphaltenes remain as solids in this diluent.

## C.4 References

1. Andersen, S. I.; Speight, J. G., Thermodynamic Models for Asphaltene Solubility and Precipitation. *Journal of Petroleum Science and Engineering* **1999,** 22, (1-3), 53-66.