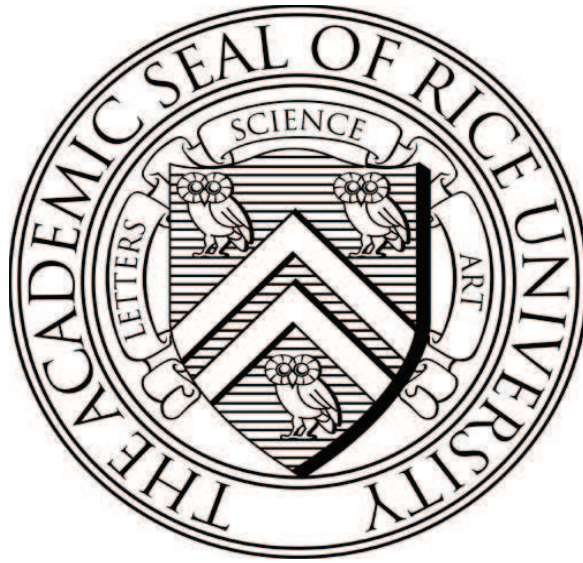




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Asphaltene Behavior in Crude Oil Systems

by

Sai Ravindra Panuganti

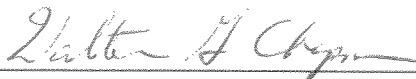
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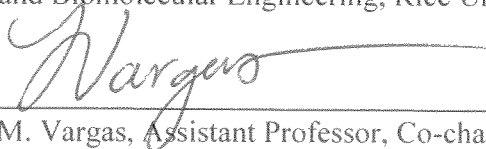
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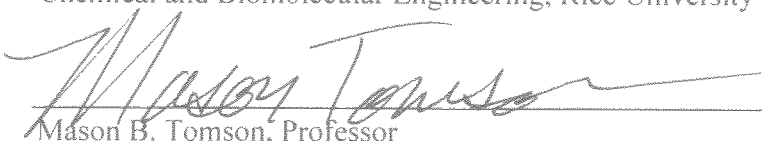
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October 2013

Abstract

Asphaltene Behavior in Crude Oil Systems

Asphaltene, the heaviest and most polarizable fraction of crude oil, has a potential to precipitate, deposit and plug pipelines, causing considerable production costs. The main objective of this study is to contribute to the thermodynamic and transport modeling of asphaltene in order to predict its precipitation, segregation and deposition. Potential calculation of some thermophysical properties of asphaltene is also explored.

Predicting the flow assurance issues caused by asphaltene requires the ability to model the phase behavior of asphaltene as a function of pressure, temperature and composition. It has been previously demonstrated that the Perturbed Chain form of Statistical Association Fluid Theory (PC-SAFT) equation of state can accurately predict the phase behavior of high molecular weight compounds including that of asphaltene. Thus, a PC-SAFT crude oil characterization methodology is proposed to examine the asphaltene phase behavior under different operating conditions.

With the fluid being well characterized at a particular reservoir depth, a compositional grading algorithm can be used to analyze the compositional grading related to asphaltene using PC-SAFT equation of state. The asphaltene compositional grading that can lead in some cases to the formation of a tar mat is studied using the same thermodynamic model.

Quartz crystal microbalance experiments are performed to study the depositional tendency of asphaltene in different depositing environments. The possibility of simulating asphaltene deposition in a well bore is discussed by modeling the capillary

data, which simultaneously accounts for asphaltene precipitation, aggregation and deposition.

The work presented is expected to contribute to the calculation of thermophysical properties of hydrocarbons and in particular of asphaltene, characterization of crude oils, improve tools to model asphaltene phase behavior, check the quality of fluid samples collected and the accuracy of (pressure, volume and temperature) PVT tests, reduce the uncertainties related to reservoir compartmentalization, optimize the logging during data acquisition, prediction of tar mat occurrence depths, improved understanding of the asphaltene deposition process, and finally optimize the wellbore operating conditions to reduce the asphaltene deposit.

Acknowledgement

Highest note of honor to Almighty God for giving me the ability to study, as well as the sustenance of my health while undertaking this study. I thank my grandparents for instilling in me the self-discipline and integrity that guide me. I thank my parents and in-laws for their support. My wife, whose love and encouragement allowed me to finish the PhD journey.

I express sincere gratitude to my adviser Prof. Walter Chapman for providing the vision and guidance necessary for me to proceed through the doctoral program and complete my dissertation. I appreciate the multiple opportunities he gave me to present my research at different conferences and meetings. I wish to thank Prof. Francisco Vargas who has been more like a senior than a co-adviser. I am grateful to Prof. George Hirasaki for introducing me to the Processes in Porous Media Consortium. I also appreciate the time and feedback from Prof. Mason Tomson, my other thesis committee member.

I am thankful to Prof. Qilin Li, Prof. Lisa Biswal and Prof. Clarence Miller for granting me access to their lab, equipment and providing space to perform the experiments. I would like to recognize Dr. Maura Puerto, Dr. Jose López, Dr. Mark Poggi and Dr. Matthew Dixon in helping me overcome the experimental bottlenecks.

The opportunities given by The Petroleum Institute in visiting them and performing research in collaboration with Abu Dhabi National Oil Company and its group of operating companies were critical in my appreciation of applied research and a

subsequent career in petroleum industry. I thank Mr. Dewayne Shirah from BP, for giving me the opportunity of a summer internship and a subsequent job offer.

I thank the DeepStar consortium with important contributions and collaboration from Dr. Jefferson Creek, Dr. Hariprasad Subramani and Dr. Jianxin Wang at Chevron and Dr. Jill Buckley from New Mexico Institute of Mining and Technology.

A special thanks to Mohammad Tavakkoli for sharing the experimental load. I appreciate other members of my research group for helpful discussions. My brother, brother-in-law and friends in USA, India and other parts of the world were sources of laughter and joy.

It has been a great privilege to spend four years in the Department of Chemical and Biomolecular Engineering at Rice University, and its members will always remain dear to me. I am grateful to the Office of International Students & Scholars at Rice University, for their indefatigable work to make all international students feel at home.

This work is undertaken with the funding from the R&D Oil Subcommittee of Abu Dhabi National Oil Company.

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Chapter 1. Introduction

The term ‘flow assurance’ was first coined by Petrobras in the early 1990s, and refers to the ability of a multiphase production system to transport produced fluids from the reservoir rock through pipelines and facilities to the sales point in a predictable manner over the life of the project [1]. Flow assurance is most critical during deep water production because of the extreme pressure and temperature involved. Flow assurance hindrances include factors such as wax and asphaltene deposition, hydrate formation, scale, slugging and corrosion. This thesis focuses on the flow assurance issues especially related to asphaltene.

Unlike wax and gas hydrates, asphaltene pose a special challenge because asphaltene are not well characterized and can deposition even at high temperature. Aspects like light oils (very low in asphaltene content and easy to flow) reporting more asphaltene deposition problems than heavy oils (high in asphaltene content and difficult to flow), makes the problem even more interesting. Thus, the ability to predict thermodynamic and transport properties of crude oil systems containing asphaltene are important in planning for and possibly eliminating asphaltene related flow assurance problems.

1.1 Objectives

The increasing incidence of flow assurance problems caused by asphaltene during oil production has motivated the development of numerous theoretical models and experimental methods to analyze this complex phenomenon. Even more challenging is the prediction of occurrence and magnitude of asphaltene deposition. It is well accepted

that the precipitation of asphaltene is a necessary condition for deposition. Hence, a significant amount of work has been devoted to the understanding of the conditions at which asphaltene precipitate from the crude oil. Although, several models seem to work well for correlating available data of onsets of asphaltene precipitation, they usually lack good prediction capabilities.

This thesis briefly reviews the properties of asphaltene and derives a few thermophysical properties. It presents a thermodynamic model based on the Perturbed Chain version of the Statistical Associating Fluid Theory equation of state, which is then proven to provide excellent prediction capabilities for the phase behavior of complex and polydisperse systems such as asphaltene, in a wide range of temperature, pressure and composition. Finally, the asphaltene compositional grading that can lead in some cases to the formation of a tar mat is studied using the same thermodynamic model. Agreement of all the predictions is checked with experimental and field data.

With asphaltene depositing on to the pipelines, effective cross sectional area will shrink continuously, which influences crude oil flow properties and threaten their safe transportation. Therefore, the deposition rate of asphaltene should be well known to safely design and operate the pipelines. An insight into the asphaltene deposition mechanism and the factors influencing it are provided based on quartz crystal microbalance experiments. The deposition process together with precipitation and aggregation is modeled in an asphaltene deposition simulator to forecast the occurrence and magnitude of asphaltene deposition in a capillary scale setup.

1.2 Thesis Structure

In the introduction chapter, an overview of the importance of asphaltene is provided in a flow assurance context. In the second chapter, the properties of asphaltene fraction of a crude oil are reviewed. Based on this background and with the advances in asphaltene science, the solubility theory with liquid-liquid equilibrium using a SAFT based equation of state is chosen as the most appropriate to model the thermodynamics of asphaltene.

In the third chapter, generalized correlations for electronic polarizability, dielectric constant, critical temperature, critical pressure, and surface tension of nonpolar hydrocarbons and their mixtures, in terms of molecular weight, mass density, and normal boiling point, are derived. In the fourth chapter, a crude oil characterization procedure is introduced by accounting for asphaltene as one of the components in order to predict the asphaltene phase behavior.

In the fifth chapter, asphaltene compositional grading is utilized to analyze the reservoir compartmentalization, wells connectivity and tar mat occurrence. The quartz crystal microbalance experiments are discussed in chapter six to study the factors influencing the deposition of asphaltene. In chapter seven, an asphaltene deposition simulator is coded. The final chapter discusses the overall conclusion, and proposes future work.

Chapter 2. Asphaltene Properties

Asphaltene are the polydisperse, heaviest and most polarizable fraction of crude oil. The term asphaltene was first introduced by Boussignault in 1837 to designate the material that precipitates out of petroleum upon addition of petroleum ether [2]. Today, it is operationally defined in terms of its solubility as the component of crude oil which is soluble in aromatic solvents, such as benzene, toluene or xylenes, but insoluble in light paraffinic solvents, such as n-pentane or n-heptane. The following aspects discuss the asphaltene properties individually.

2.1 Chemical Composition

Asphaltene primarily consist of carbon, hydrogen, nitrogen, oxygen and sulfur, as well as trace amounts of iron, vanadium and nickel. An asphaltene molecule has a carbon number in the range of 40 to 80. The carbon to hydrogen ratio is approximately 1:1.2, depending on the asphaltene source [3].

2.2 Molecular Structure

Asphaltene are polydisperse in nature, and hence do not have a specific chemical identity. In fairly early stages (1970's) of asphaltene research, Yen proposed a condensed aromatic cluster model that assumes extensive condensation of aromatic rings into large sheets with substitute side chains [4]. This type of structure was developed based on spectroscopic studies. Later on, a very different structural organization, the bridge aromatic model is proposed by Murgich and Abaner based on structural mechanics [5]. A number of other investigators also attempted to postulate model structures for asphaltene

including the recently proposed Modified Yen model and a model presented by Vargas [6-8].

The first macrostructure of an asphaltene was proposed by Dickie and Yen in 1961 and is more popularly known as the Yen model [9]. Since 2000, asphaltene science progressed dramatically and the Modified Yen Model proposed by Mullins in 2010 explained some more of the observed phenomena for asphaltene. According to the Modified Yen model, predominant part of an asphaltene structure consists of a single and moderately large polycyclic aromatic hydrocarbon, with peripheral alkanes. Asphaltene molecules form asphaltene nano-aggregates with aggregation numbers of ~ 6 and these aggregates can further cluster with aggregation numbers estimated to be ~ 8 . More recently Vargas proposed an asphaltene structural model also incorporating the aging effects, and thereby designed a new type of asphaltene deposition inhibitor with preliminary success.

2.3 Molecular Weight

Depending on the solvent, concentration and the measurement technique employed, several molecular weight ranges are reported for asphaltene. Different techniques used to estimate the molecular weight of asphaltene include vapor-pressure osmometry, viscometry, boiling point elevation, freezing point depression, light scattering, gel permeation chromatography, fluorescence depolarization, ultracentrifuge, and electron microscope studies. The vapor-pressure osmometry technique results in an asphaltene molecular weight in the range of 800 to 3000 g/mol in good solvents [10]. Alboudwarej et al., estimated an average molecular weight of asphaltene as 1800 g/mol

for heavy oil and bitumen [11]. Adopting the Modified Yen Model, Zuo et al. concluded the molecular weight of asphaltene nanoaggregate as ~ 1600 g/mol [12]. Long before the Modified Yen Model, in 1984 Hirschberg and Hermans estimated the average asphaltene molecular weight to be between 1300 and 1800 g/mol based on phase behavior studies [13].

2.4 Density

The density of petroleum derived asphaltene at ambient conditions varies between 1.1 and 1.2 g/cm³ based on the origin and methodology [14-16]. Diallo et al. estimated an average asphaltene density as 1.12 g/cc based on isothermal isobaric ensemble (NPT) molecular dynamic simulations followed by energy minimization [17]. This estimated density compares favorably with the measured density, 1.16 g/cc of petroleum asphaltene reported by Yen et al. using helium displacement [18].

2.5 Diffusion

Asphaltene diffusion coefficient is a function of concentration dependent size of the asphaltene aggregates. At low concentration, the degree of association of asphaltene is small, but increases with increase in concentration until a critical size is reached. The higher the state of association, the larger the entity size and lower the diffusion coefficient. The diffusion coefficient of asphaltene in toluene estimated by low field nuclear magnetic resonance and fluorescence spectroscopy measurements is in the order of 10^{-10} m²/s for a particle size of 1-2 nm [19]. The diffusion coefficient in toluene at infinite asphaltene dilution is 2.2×10^{-10} m²/s [20].

2.6 Interfacial Characteristics

The oil-water interfacial properties in the presence of asphaltene are peculiar. The initial rapid diffusion of asphaltene towards the interface is followed by a long reorganization and progressive building of layers. The overall adsorption process is slow, but for different oils, has similar time scales [21]. When asphaltene concentration is varied, interfacial equilibrium is reached faster at higher asphaltene concentration for good solvents and slower in the presence of poor solvents. Asphaltene molecules also adsorb at oil-air interface, forming skins which impart stability to foamy oils in which bubbles persist for long duration of time [22, 23].

In the presence of surfactant there is a co-adsorption of both surfactant and asphaltene at the oil-water interface. Surfactants being smaller molecules than asphaltene arrive at the interface before the arrival of asphaltene. At intermediate times, surface population is over compressed by surfactants adsorbed at the interface and incoming asphaltene. This over-population of the surface gives rise to a minimum in the dynamic surface tension [21]. At long enough times, the interfacial tension increases with time, a phenomenon not seen with asphaltene or surfactant alone. Such a phenomenon indicates a transfer of species across the interface, at which location other species settle [24].

2.7 Viscosity

The presence of asphaltene means additional difficulties related to transport and processing due to an increased crude oil viscosity caused by the asphaltene. Experimental results on asphaltene content and temperature affecting the crude oil viscosity are plotted in Figure 2.1, where the slurry represents an Iranian crude oil containing asphaltene. The

evidence of increased asphaltene content and low temperature significantly increasing the oil viscosity is already reported by Sirota et al. [25].

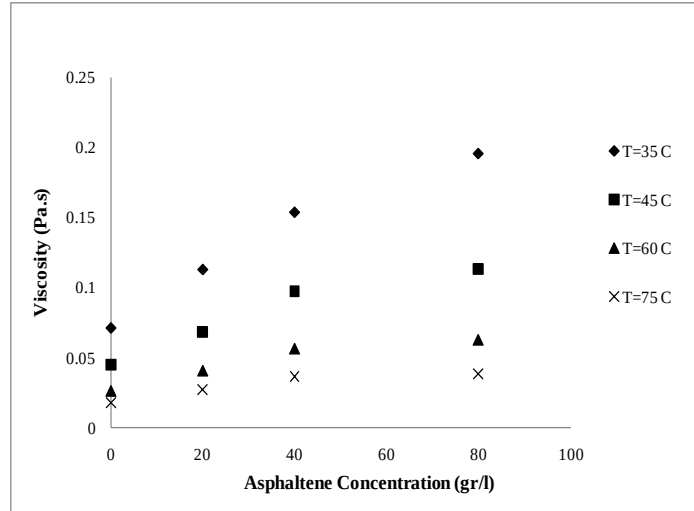


Figure 2.1. Effect of asphaltene concentration on slurry sample viscosity at different temperature.

Presence of precipitated asphaltene particles result in an increase in the viscosity of the oil. This increase becomes remarkable at and after the onset of flocculation, and hence can be used to detect the asphaltene precipitation onset conditions [26]. Compositional grading is a well-known phenomenon and with asphaltene compositional variation, the crude oil viscosity changes significantly with depth. Modeling the crude oil viscosity variation with depth due to asphaltene compositional grading, can help in predicting the occurrence of a tar mat, characterized as the highly viscous oil zone enriched in asphaltene [27].

2.8 Solubility Parameter

Considering asphaltene as a soluble species, solubility parameter (δ) can be an important tool based on which asphaltene phase behavior can be explained. The solubility

parameter for a non-polar fluid is given by Hildebrand as,

$$\delta = \sqrt{CED} = \sqrt{-\frac{U^{rsm}}{v}} \quad (2.1)$$

Where, CED is the cohesive energy density, U^{rsm} is the residual internal energy obtained by subtracting the ideal gas contribution from that of the real fluid and v is the pure liquid volume. Asphaltene has the highest solubility parameter among the crude oil components and is between 19 to 24 MPa^{0.5} [28]. If asphaltene is assumed to be dissolved in crude oil, the equilibrium can be altered by a change in temperature, pressure or composition of the oil. For example, if significant amounts of low molecular weight hydrocarbons are dissolved into the liquid phase, the solubility parameter of oil is reduced and the asphaltene precipitate may form. Changes in temperature and pressure will likewise alter the solubility parameter, thus causing conditions that induce precipitation.

2.9 Refractive Index

The refractive index (n) of an asphaltene solution can be measured in place of the solubility parameter based on the observation that London dispersion interactions dominate the asphaltene phase behavior [29]. The London dispersion properties of a material can be characterized by the wavelength dependence of the refractive index or the "dispersion" of visible light. Refractive index and solubility parameter can be inter-converted, and at 20 °C the linear correlation 2.2 holds good. Using this equation, the refractive index of pure asphaltene is observed to range from 1.54 to 1.74.

$$\delta = 52.042 \left(\frac{n^2 - 1}{n^2 + 2} \right) + 2.904 \quad (2.2)$$

2.10 Precipitation

Asphaltene precipitation is treated as the growth of primary particles from a solution due to super-saturation. Thus, asphaltene precipitation consumes super-saturation until the system reaches an equilibrium asphaltene concentration. Very limited data is available in the literature about the rate of asphaltene precipitation and the reported spectrophotometry data on 0.1 g of asphaltene/L of toluene mixed with a 50 volume % n-heptane solution, can be approximately modeled using a first order precipitation rate constant of 0.01 min^{-1} [30].

2.11 Aggregation

Aggregation does not consume super-saturation and is considered as the agglomeration of primary particles forming larger, secondary particles (asphaltene aggregate). Concentration of asphaltene aggregates less than the critical micelle concentration of 3-4 g of asphaltene/L toluene is controlled by diffusion, while at higher asphaltene concentration the aggregation is controlled by impact [31]. Most of the available literature does not consider precipitation and aggregation separately. Researchers using microscopy define the onset of asphaltene precipitation based on the resolution limit of microscopes. The redissolution kinetics of precipitated asphaltene can be considerable in the time scale of well-bore travel, while that of aggregated asphaltene is slow and hence negligible [32]. It is experimentally observed that asphaltene aggregate particle size gets saturated with time and assuming exponential approach to equilibrium, Anisimov et al. obtained that for a concentration, c [32]

$$cr^3 = c_{\infty} R_{\infty}^3 (1 - e^{-t/\tau}) \quad (2.3)$$

2.12 Deposition

Photothermal surface deformation studies of asphaltene adsorption onto surfaces revealed that the adsorption resulted in multilayer formation [33]. Recent studies performed using quartz crystal microbalance showed saturation adsorption isotherms with rapid initial response followed by slow approach to equilibrium [34]. The initial response is indicative of a diffusion controlled process. At longer timescales, the data is found to follow first-order kinetics. The overall first order rate constant is estimated as $\sim 2 \times 10^{-3} \text{ min}^{-1}$ [35]. But, all the above observations are reported for asphaltene solubilized in toluene and the deposition kinetics of precipitated asphaltene can be different.

2.13 Asphaltene - Crude Oil System

Understanding of the asphaltene stability in crude oil is based mainly on two different thermodynamic models: colloidal and solubility models. The colloidal approach describes asphaltene phase behavior assuming that the crude oil can be divided into polar and non-polar subfractions in which resins stabilize asphaltene as in micelle formation [36]. The solubility model uses the molecular solubility approach to describe an asphaltene containing fluid as a mixture of solute (asphaltene) and solvent (bulk oil) in a homogeneous liquid state [37]. The asphaltene precipitation can be treated as solid–liquid or liquid–liquid equilibrium, and is reversible. But, as discussed in the *Aggregation* section, the kinetics of re-dissolution varies depending on the physical state of the system.

The colloidal model assumes that asphaltene exist in the oil as solid particles; and, describes the stability of asphaltene in terms of micelle formation where asphaltene self-associate into an aggregate to form the core and resins adsorb onto the core (based on

polar-polar interactions) to form a steric shell shown in Figure 2.2. These points of view are based on the observation that an increase in resins content improves the stability of asphaltene. According to these models, asphaltene precipitates when a sufficient amount of diluent is added to the system because the concentration of resins is diluted, with resins becoming increasingly soluble in the liquid phase that separate them from the asphaltene micelles. However, the addition of solvents like toluene actually takes asphaltene back into solution. Using impedance analysis, Goual demonstrated that the diffusion coefficient of asphaltene is same in the presence and absence of resin [38]. Thus, resins are unlikely to coat asphaltene nanoaggregates and do not provide the steric stabilizing layer that the colloidal model proposes. Also, the polar nature of asphaltene is never confirmed in terms of charge carried by the asphaltene particles through hydrophilic-lipophilic balance [39]. While colloidal models of asphaltene were beneficial in the early stages of understanding asphaltene behavior, these analogies are not justified.

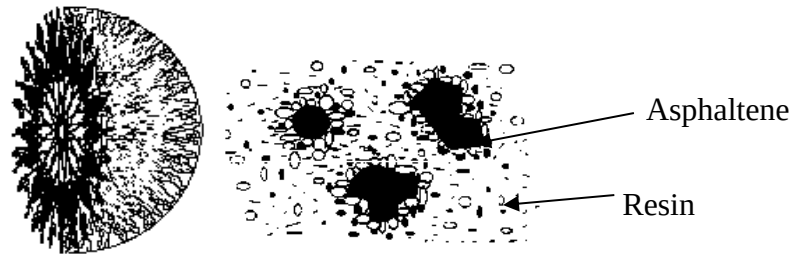


Figure 2.2. Asphaltene colloidal model [40].

Solubility models assume that asphaltene are dissolved in the crude oil. This equilibrium can be solid-liquid or liquid-liquid type. In the solid-liquid type by Nghiem and Coombe [41], precipitated asphaltene is treated as a single component residing in the solid phase, while oil and gas phases are modeled with a cubic equation of state. However, pure asphaltene is never precipitated [42]. Also asphaltene is a substance with

no defined melting point, high solubility parameter and moderately high molecular weight. Having a high aromatic content, it forms true solution in aromatic solvents. However, its molecular weight being moderately high, the entropy of mixing is not sufficient to keep it in solution if the interaction with remainder of the solution becomes unfavorable, such as upon the addition of an aliphatic fluid. The phase separation which results is thus thermodynamically driven liquid-liquid equilibrium.

The liquid-liquid treatment was initially proposed by Hirschberg, et al. [43] starting with a detailed compositional model based on the Soave equation of state to calculate liquid phase compositions and molar volumes before asphaltene precipitation. Then, using a Flory–Huggins-regular solution theory, the amount of precipitated asphaltene is estimated by calculating the solubility parameter from Hildebrand’s definition. This initial approach is difficult to extend to model the asphaltene solubility under reservoir conditions, because the solubility parameters must be corrected with correlations or an equation of state for high pressure and temperature. Also cubic equation of state models cannot describe the phase behavior of systems with large size disparities and fluid densities.

A more modern equation of state is the Statistical Associating Fluid Theory family. This equation of state based on statistical mechanics can accurately model mixtures of different molecular sizes. Thus, solubility model with liquid-liquid equilibrium using a SAFT based equation of state is the most appropriate theory for modeling asphaltene phase behavior. PC-SAFT equation of state has demonstrated excellent performance and predictive capabilities applied to a wide range of mixtures, including petroleum systems [44].

Chapter 3. Property Scaling Relations

A petroleum fraction is a mixture of different hydrocarbons, mostly nonpolar in nature, belonging to different homologous groups. A good estimation of the properties of petroleum mixtures depends on the estimation of properties of the pure compounds existing in the mixture. Thus, accurate knowledge of volumetric, physical, and thermophysical properties of pure hydrocarbons is important in the optimum design and operation of equipment related to petroleum production, processing, transportation, and related industries. Because experimental measurements of these properties are technically difficult, time consuming, and expensive, methods for property estimation are becoming increasingly important.

Estimation methods for most of the thermophysical properties of petroleum fluids are empirical, and the parameters needed to estimate a property may not be readily available or easily measurable [45]. Thus, theory based equations are required for better property estimations. Usually, measurements of the bulk properties such as molecular weight, boiling point, density, or refractive index are viable; based on the molecular theories like Liquid Hole Theory [46], One-Third Rule [47], and the Hildebrand solubility parameter of nonelectrolytes, generalized property correlations for nonpolar hydrocarbons can be derived.

The main objective of this chapter is to use readily available physical properties of hydrocarbons, such as the normal boiling temperature, density, and molecular weight, to estimate the less easily measurable properties such as electronic polarizability, dielectric constant, critical temperature, critical pressure, and surface tension of pure

nonpolar hydrocarbons. The correlations are also applied for nonpolar hydrocarbon mixtures wherever applicable. All the data references are reported in the Appendix A.

3.1 One-Third Rule

Refractometry is used extensively for crude oil characterization and petroleum product quality control. Refractive index (n) is defined as the ratio of the speed of light in space (vacuum) to its speed in a given substance. For practical purposes, the speed of light in air may be taken as equivalent to that in vacuum. Refractive index for any given substance varies with the wavelength of light and the temperature. Specific refractivity (r) is a function of refractive index divided by density (ρ). Molar refractivity (mr) is specific refractivity multiplied by molecular weight (MW).

The specific and molar refraction of individual hydrocarbons and mixtures of hydrocarbons are independent of the temperature and pressure. However, when the values of these quantities are calculated, refractive index and density are used, and these are definitely dependent on the temperature, pressure, and state of aggregation of the substance. Moreover, the molar refraction of individual hydrocarbons is additive and equal to the sum of the atomic refractions, so that they can be used for calculations in analytical practice [48]. Thus, various attempts were made to know the constant function of refractive index and density. The earliest equation relating refractive index and density is that which Newton deduced from the general laws of force [49],

$$\frac{n^2 - 1}{\rho} = \text{Constant} \quad (3.1)$$

Laplace derived the same equation from the emission theory of light and added the concept that for any one compound the constant should be independent of external

influence such as temperature and pressure [50]. Laplace's interpretation of the Newton's equation had a profound influence on the development of refraction theory, because it directed attention to the change of refractive index and density of any one compound with changes in temperature and pressure.

In the period 1805–1863, it was shown that the constant of the Newton specific refraction equation (equation 3.1) is not independent of temperature [51, 52]. Many attempts were made to modify the formula. One of the more interesting attempts is that of Schrauf [53], who proposed that n be replaced by the A of Cauchy's formula [54],

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \text{etc} \quad (3.2)$$

The A in this formula is the hypothetical refractive index for a line of infinite wavelength. No one succeeded in modifying the Newton formula to produce a constant that is independent of temperature, and the formula as such was discarded soon after the Gladstone–Dale paper published in 1863. Gladstone and Dale, in addition to confirming the dependence of the Newton equation on temperature, presented a simple empirical equation [52],

$$\frac{n-1}{\rho} = \text{Constant} \quad (3.3)$$

and justified it on the grounds that, for 90 liquids, the constant in this equation decreased less rapidly with increasing temperature than did the constant of the Newton equation.

In 1880 the Lorentz–Lorenz specific refraction equation,

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho} = \text{Constant} \quad (3.4)$$

was simultaneously derived by Lorentz, who started with Maxwell's electromagnetic theory of light, and Lorenz, who started with the undulatory theory of light [55, 56]. The specific and molar refractions given by this equation increase slightly with increasing temperature. Therefore, in the period 1880–1895, there was intensive investigation of these and many other specific and molecular refraction formulas until Eykman presented his empirical equation, which represents the relationship between refractive index and density accurately for any one liquid at various temperature [57].

$$\left(\frac{n^2 - 1}{n + 0.4} \right) \frac{1}{\rho} = \text{Constant} \quad (3.5)$$

The Lorentz–Lorenz equation in particular has been widely accepted because of its theoretical derivation. Application of this equation to hydrocarbon mixtures opens the possibility of developing novel methods to predict a wide range of thermophysical properties of crude oils [58].

Assuming the molecules of a substance are spherical perfect conductors, Maxwell's electromagnetic theory leads to the relation [59]

$$n^2 = \frac{1 + 2j}{1 - j} \quad (3.6)$$

where n is the refractive index and j is the ratio of the volume actually occupied by the molecules to that apparently occupied by the molecules. Dealing with a unit volume of a substance of density ρ ,

$$\frac{n^2 - 1}{n^2 + 2} = \text{True volume of the molecules in unit volume} \quad (3.7)$$

and therefore,

$$\frac{\rho}{\left(\frac{n^2-1}{n^2+2}\right)} = \text{True density of the molecules} \quad (3.8)$$

that is, the mass of unit volume of molecules without intermolecular spaces. The reciprocal,

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\rho} = \text{True volume of unit mass of the molecules} \quad (3.9)$$

When the refractive index is measured at the sodium D line, the Lorentz–Lorenz constant for pure nonpolar hydrocarbons is approximately one-third and, even when extended to such complex mixtures as petroleum systems, shows good agreement [58]. The one-third value does not differ significantly when measured at other wavelengths as observed from Table 3.1. The name “One-Third Rule” is used as an easy way to remember an approximate value for this relationship.

Table 3.1. Refractive index at seven different wavelengths for n-butylcyclohexane at 20 °C [60]. Density of n- butylcyclohexane is 0.799 g/cc.

Wavelength, nm	Spectral Line	Index of Refraction, n	$(n^2-1)/((n^2+2)*\rho)$
667.81	He _{red}	1.438	0.329
656.28	H _e	1.439	0.329
589.26	Na _D	1.441	0.330
546.07	Hg _e	1.443	0.331
501.57	He _{blue}	1.445	0.333
486.13	H _F	1.446	0.334
435.83	Hg _g	1.451	0.337

The validation of One-Third Rule is shown in Table 3.2. But strictly speaking it is not a constant, but a function of the mass density because molecules do not behave as hard spheres, and is expressed as

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\rho} = 0.5054 - 0.3951\rho + 0.2314\rho^2 \quad (3.10)$$

The above equation is known as the Lorentz–Lorenz (L-L) expansion, and the parameters 0.5054, −0.3951 and 0.2314 are the first three refractivity virial coefficients at 20 °C [61]. Note that equation 3.10 is fit to the data of pure n-alkanes at 20 °C. However, because the specific refractivity is nearly independent of temperature, pressure and composition, the value obtained from experimental data, from equation 3.10 or just by assuming the one-third value, can be used with confidence over a wide range of temperature and pressure.

Table 3.2. Application of One-Third Rule for nonpolar hydrocarbons and polymers.

S. No	Component	MW (g/mol)	n_D	Density (ρ , g/cc)	$\left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{1}{\rho}$	Temperature (C)
1	Cyclopentane	70.13	1.407	0.746	0.330	20
2	Diphenyl	154.21	1.588	1.010	0.333	75
3	Triphenylmethane	244.34	1.584	1.014	0.330	100
4	n-Dotriacontane	450.87	1.455	0.813	0.334	20
5	Polystyrene	-	1.592	1.040	0.325	20
6	Polypropylene	-	1.500	0.900	0.327	20

The One-Third Rule in particular has a wide range of usefulness because it provides a constant characteristic of all hydrocarbons, a constant which is practically independent of boiling point or molecular weight. In practice, the One-Third Rule has proven very valuable in calling attention to

- Errors in the transcription of data.
- Improper correction for temperature.
- Uncertainty concerning the purity of the hydrocarbon.
- Unsound data.

The subsequent sections show the usefulness of One-Third Rule in obtaining simplified expressions for thermophysical properties from the existing equations in the literature.

3.2 Electronic Polarizability

The polarizability of an atom or a molecule describes the response of its electron cloud to an external field. Technically the polarizability is a tensor quantity, but for spherically symmetric charge distributions, it reduces to a single number. For most practices, an average polarizability is adequate in calculations. Electronic polarizabilities are very slightly temperature dependent because the size of a molecule depends on its rotational and vibrational states.

The knowledge of polarizability is essential in determining the following: diamagnetic susceptibility, long range interaction energy, ion mobility in a gas, van der Waals interaction between two systems, dynamic polarizability, and Rayleigh scattering cross section. Experimentally, polarizability is determined through studies of refractive indices and relative permittivities, through Rayleigh and Raman scattering, and through the quadratic Stark effect [62]. A quantum mechanical calculation of electronic polarizability may be carried out by solving the coupled perturbed Hartree–Fock equations with electric field perturbations [63]. Thus, a simpler way of determining the electronic polarizability from easily measurable properties provides a convenience in the use of the polarizability parameter. In this regard I start with Lorentz–Lorenz equation to develop a simple expression for polarizability.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha \quad (3.11)$$

where n is the refractive index, N is the number of molecules per unit volume, and α is the mean polarizability. Both the refractive index and polarizability are independent of the amount of substance. Hence, the Lorentz–Lorenz equation can be rewritten as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{N_A}{v} \alpha \quad (3.12)$$

where N_A is the Avogadro Number (6.022×10^{23}) and v is the molar volume given by

$$v = \frac{MW}{\rho} \quad (3.13)$$

Rearranging the Lorentz-Lorenz equation for polarizability,

$$\alpha = \frac{3MW}{4\pi N_A \rho} \left(\frac{n^2 - 1}{n^2 + 2} \right) \quad (3.14)$$

From the One-Third Rule discussed in the previous section I have

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho} \cong \frac{1}{3} \quad (3.15)$$

Thus, the simple expression for obtaining mean electronic polarizability is

$$\alpha = \frac{MW}{4\pi N_A} \quad (3.16)$$

The above equation (equation 3.16) is independent of the state of the system, and the mean polarizability can be computed with a single input and conveniently measurable quantity ‘molecular weight’. If the Lorentz–Lorenz expansion is used instead of the One-Third Rule, equation 3.14 becomes equation 3.17. Figure 3.1 shows the successful comparison of the predictions with experimental data. For components which are gases at ambient conditions, the liquid densities near their boiling point is used when using equation 3.17. For components which are solids at NTP, the solid density at 20 °C is used when calculating the polarizability using expression 3.17.

$$\alpha = \frac{3MWg(\rho)}{4\pi N_A} \quad (3.17)$$

Where, $g(\rho) = 0.5054 - 0.3951\rho + 0.2314\rho^2$

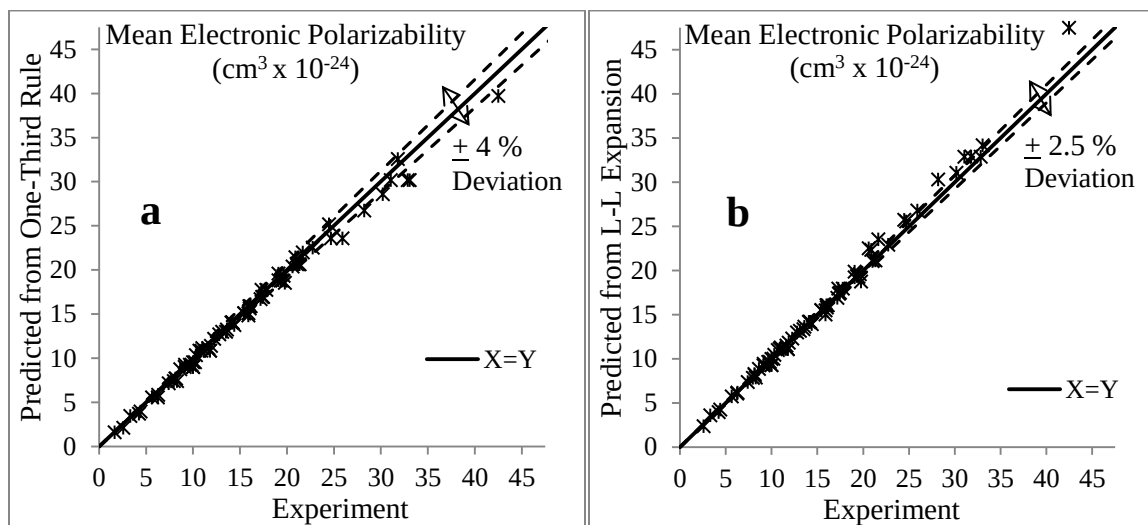


Figure 3.1. Comparison of the predicted and experimentally observed mean electronic polarizability for various nonpolar hydrocarbons belonging to different homologous series: (a) using One-Third Rule, the average absolute deviation is 4.16 % and (b) using Lorentz–Lorenz expansion, the average absolute deviation is 2.72 %.

Even though equation 3.17 with Lorentz–Lorenz expansion gives a more accurate result in calculating the electronic polarizability, the usefulness of the Equation 3.16 derived from the One-Third Rule cannot be neglected because it gives close enough predictions from just knowing the overall molar mass.

3.3 Dielectric Constant

The permittivity of a substance is the ratio of electric displacement to electric field strength when an external field is applied to the substance. The dielectric constant is the ratio of permittivity of a substance to permittivity of free space. It is an expression of

the extent to which a material concentrates electric flux and is the electrical equivalent of relative magnetic permeability.

For hydrocarbons, the dielectric constant is an essential piece of information to understand the production of electrical conductance by the action of high energy radiation [64, 65]. Almost every type of electrical equipment employs dielectric materials in some form or another. Wires and cables that carry electrical current are always coated or wrapped with insulating (dielectric) material. Sophisticated electronic equipment such as rectifiers, semiconductors, transducers, and amplifiers contain or are fabricated from dielectric materials [66]. When capacitors are characterized where a material might be expected to introduce capacitance into a circuit, dielectric materials are chosen such that they are resistant to ionization. This allows the capacitor to operate at higher voltages before the insulating dielectric ionizes and begins to allow undesirable current. Dielectric constant measurements are also essential for understanding results obtained from remote-radar-sensing experiments [67]. In pharmaceutical sciences, the dielectric constant of mixed solvents is required to predict the solubility and chemical stability of a drug [68].

The dielectric constant is experimentally measured using the coaxial line technique [67], capacity bridge method [69], and free space method [70]. All the theories concerned with the dielectric constant, even though sound in derivation, cannot be applied for practical purposes because of the complexities in the expression [71-74]. Additionally, the parameters are not easily obtainable. Thus, a simpler way of determining the dielectric constant that is valid across temperature and mixtures, from an easily measurable property such as bulk density, provides a convenience in the use of the

dielectric constant parameter at the production facility. In this regard, I start with the electromagnetic theory relating refractive index and electrical permittivity.

$$n = \frac{c}{v} = \sqrt{\frac{E\mu}{E_o\mu_o}} \quad (3.18)$$

where E_o is the permittivity of vacuum and μ_o is the magnetic permeability of vacuum. In weakly magnetic materials, $\mu_o = \mu$ and the above expression at a fixed frequency simplifies to

$$n = \sqrt{\frac{E}{E_o}} = \sqrt{k} \quad (3.19)$$

where k is the dielectric constant of a material. From the One-Third Rule for nonpolar hydrocarbons it is known that the refractive index varies with the density of a material as

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho} \cong \frac{1}{3} \quad (3.20)$$

In the case of low loss materials (e.g., nonpolar hydrocarbons), $\omega\tau < 1$ (at operating frequency ω and dielectric relaxation time τ), the frequency dependent dielectric constant $k(\omega)$ can be approximated by its static value $k(0)$ [67]. Thus, the dielectric constant can be substituted in the place of the refractive index in the One-Third Rule expression

$$\left(\frac{k - 1}{k + 2} \right) \frac{1}{\rho} \cong \frac{1}{3} \quad (3.21)$$

The expression for obtaining the dielectric constant with only the density as an input parameter is

$$k = \frac{2\rho + 3}{3 - \rho} \quad (3.22)$$

Alternatively by substituting dielectric constant in the Lorentz–Lorenz expansion, the equation for calculating dielectric constant becomes

$$k = \frac{1 + 2f(\rho)}{1 - f(\rho)} \quad (3.23)$$

Where, $f(\rho) = 0.5054\rho - 0.3951\rho^2 + 0.2314\rho^3$

In the One-Third Rule and Lorentz–Lorenz expansion, the right hand side in the equations (one-third value and summation of refractivity virial coefficients respectively) represents the specific refraction of hydrocarbon molecules and is nearly independent of temperature, pressure and mixing as discussed in the *One-Third Rule* section. Because the proposed dielectric constant expressions (equations 3.22 and 3.23) are an extension of the One-Third Rule and Lorentz–Lorenz expansion, they can inherently handle pressure, temperature and composition variations. Figure 3.2 shows a successful comparison of the dielectric constant predictions with experimental data for various pressures, temperature and mixtures of nonpolar hydrocarbons including polymers. Polar compounds like water have a large and temperature dependent dielectric constant due to their permanent electric dipole.

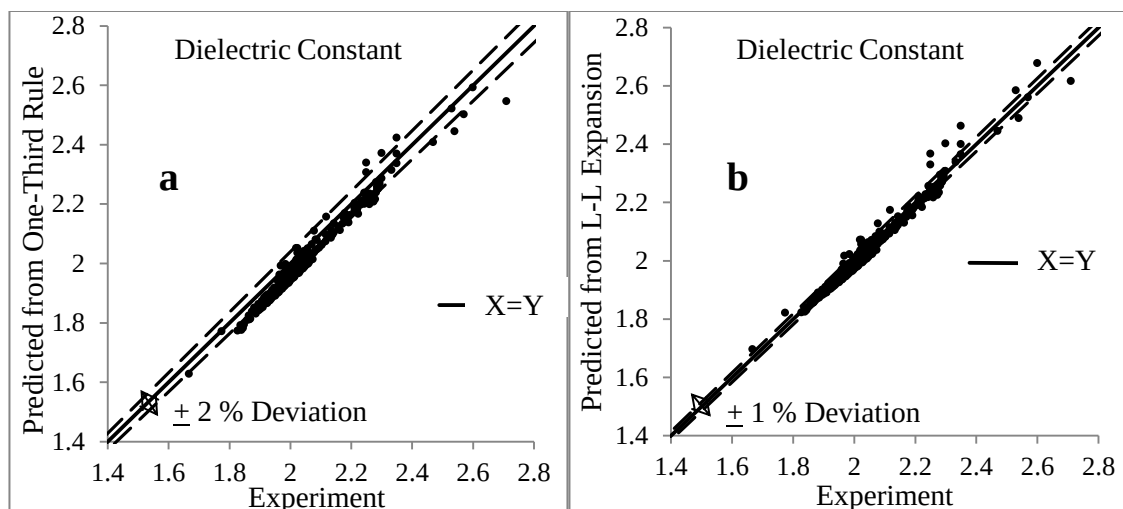


Figure 3.2. Comparison of the predicted and experimentally observed dielectric constants for a wide range of temperature, pressure and composition of various nonpolar hydrocarbons: (a) using One-Third Rule, average absolute deviation is 1.98 % and (b) using Lorentz–Lorenz expansion, the average absolute deviation is 1.00 %.

The density of gases is about one thousandth the density of solids and liquids. Therefore, gases have relatively small dielectric constants and do not vary much between them. Table 3.3 reports the values predicted by the proposed dielectric constant expressions (equations 3.22 and 3.23) for hydrocarbon gases at normal atmospheric conditions.

Table 3.3. Dielectric constants of different hydrocarbon gases at ambient conditions.

		Experiment	Predicted (1/3 rd Rule)	Predicted (L-L Expansion)
Molecule	Density (g/cc) [75]	Dielectric Constant [76]	Dielectric Constant	
Methane	0.000668	1.000818	1.000668	1.001013
Ethane	0.001264	1.001403	1.001265	1.001916
Acetylene	0.001092	1.001240	1.001092	1.001655
Ethylene	0.001178	1.001350	1.001178	1.001786
Propene	0.001748	1.002280	1.001749	1.002649
Propane	0.001882	1.002032	1.001883	1.002852
Butane	0.002489	1.002660	1.002491	1.003771
Isobutane	0.002510	1.002680	1.002512	1.003803

For both the dielectric constant expressions developed in this chapter, density at the corresponding operating condition is the only required input. Between the expressions 3.22 and 3.23, the expression based on Lorentz–Lorenz expansion is seen to have a higher degree of accuracy than the expression based on One-Third Rule.

3.4 Critical Properties

Critical properties are important input parameters for cubic equation of state and to estimate thermodynamic and transport properties. In addition, the critical temperature and pressure are important information in high pressure phase equilibrium processes such as enhanced oil recovery and supercritical fluid extraction.

Most of the measured critical data in literature are usually limited to low molecular weight compounds. Even with the advances in experimental methods for the measurement of critical properties of high molecular weight and thermally unstable fluids [77-79], the data remain scarce because of the difficulty associated with their measurement. When experimental data are not available, estimation methods are used to get an approximated value for these properties.

Available methods for the estimation of critical properties can be divided into two groups. The first group contains methods based on group contribution techniques. The first work in this regard is by Lydersen [80]. The group contribution methods represent two distinctive classes.

- The first-order group techniques, which determine the molecule by means of simple group contribution, neglecting the next-nearest neighbor's effects. The methods of Ambrose, Joback, Fedors and Somayajulu belong to this class [81-84].

- The second-order group techniques, which additionally take into consideration the influence of first- and second- level neighbors of a considered group. The methods of Daubert and Constantinou belong to this class [85, 86].

All the group contribution methods require the knowledge of molecular structure of the compound. Such methods cannot be applied to mixtures of unknown composition or even for a single component without knowing its nature. The other predictive methods (second group) use some easily measurable properties such as boiling point and specific gravity, and can be applied to undefined mixtures without the knowledge of component molecular structure. Examples of these methods are Kesler–Lee, Riazi–Daubert and Cavett [87-90]. Unfortunately, none of the equations are based on theory and these methods cannot be applied to all types of compounds as they are valid only for specific hydrocarbon systems [45]. In addition, the correlations do not cover compounds such as light hydrocarbons. Moreover, in some equations, estimating critical pressure requires critical temperature as an input parameter [91]. Therefore, any error associated with the predicted critical temperature will be propagated to much larger errors for the other critical properties.

In this section I develop a simple, reliable, and generalized method for estimating the critical properties of various nonpolar hydrocarbons using easily measurable properties and without the knowledge of chemical structure.

From fundamental thermodynamic relations:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial E}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T \quad (3.24)$$

and by substituting the Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (3.25)$$

equation 3.26 can be readily obtained

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (3.26)$$

Hildebrand measured $\left(\frac{\partial P}{\partial T}\right)_V$ for a number of liquids and realized that for most liquids below their boiling points, P is negligible in comparison with $T\left(\frac{\partial P}{\partial T}\right)_V$ [92]. Thus,

$$\left(\frac{\partial E}{\partial V}\right)_T \cong T\left(\frac{\partial P}{\partial T}\right)_V \quad (3.27)$$

During the same time, Weatwater together with Hildebrand showed that [93, 94]

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{a}{v^2} \quad (3.28)$$

where a is the molecular force term in the van der Waals equation of state. And hence,

$$\left(\frac{\partial E}{\partial V}\right)_T \cong \frac{a}{v^2} \quad (3.29)$$

For a van der Waals fluid (i.e., phase behavior is dominated by nonpolar interactions) over a small range of volumes [95],

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{\Delta E^v}{v} \quad (3.30)$$

$$\text{thus, } \frac{\Delta E^v}{v} \cong \frac{a}{v^2} \quad (3.31)$$

For nonpolar liquids, one can use $T\left(\frac{\partial P}{\partial T}\right)_V$ as a measure of the Hildebrand solubility parameter [96],

$$\left(T \frac{C_\alpha}{C_\beta} \right)^{1/2} = \left[T \left(\frac{\partial P}{\partial T} \right)_v \right]^{1/2} \cong \delta \quad (3.32)$$

Where C_α is the coefficient of thermal expansion and C_β is the isothermal compressibility coefficient. Reasonable values of the solubility parameter can be obtained from

$$\delta \cong \frac{a^{1/2}}{v} \quad (3.33)$$

Buckley et al. showed that for nonpolar compounds, the Hildebrand solubility parameter at ambient conditions varies as [97]

$$\delta = 52.042 \left(\frac{n^2 - 1}{n^2 + 2} \right) + 2.904 \quad (3.34)$$

where, n is the refractive index determined at 20 °C. Combining equations 3.33 and 3.34, one can estimate the a parameter of the van der Waals equation as

$$a^{1/2} = 52.042 \left(\frac{n^2 - 1}{n^2 + 2} \right) \left(\frac{MW}{\rho_{20}} \right) + 2.904 \left(\frac{MW}{\rho_{20}} \right) \quad (3.35)$$

Observed from the *One-Third Rule* section, the quantity of $\left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho}$ can be approximated as 1/3 independent of temperature, pressure and composition. Thus, the van der Waals a parameter, in terms of critical temperature and pressure varies as a function of molecular weight and density. The equation is expected to be linear, but not with same terms as in equation 3.35, because the molecules are not perfectly spherical as in the case with van der Waals.

$$\frac{T_c}{P_c^{1/2}} = \text{function}(MW, \rho_{20}) \quad (3.36)$$

The correlation between $\frac{T_c}{P_c^{1/2}}$ and $\left(MW + 0.1674 \frac{MW}{\rho_{20}} \right)$ for a number of nonpolar hydrocarbons (alkanes, alkenes, alkynes, aromatics, polynuclear aromatics and their corresponding isomers) is illustrated in Figure 3.3. The best fit straight line has a slope of 0.613 and an intercept 24.85. That means for any nonpolar hydrocarbon belonging to any homologous series the following is valid.

$$\frac{T_c}{P_c^{1/2}} = 0.613 p(MW, \rho_{20}) + 24.85 \quad (3.37)$$

Where, $p(MW, \rho_{20}) = \frac{MW + 0.1674 \frac{MW}{\rho_{20}}}{\rho_{20}}$

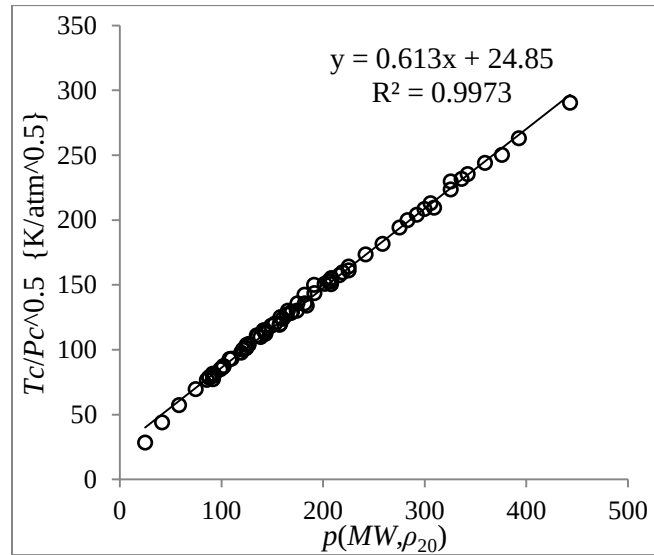


Figure 3.3. Correlation of critical temperature and pressure in terms of molecular weight and density.

The critical temperature is a measure of intermolecular attractions, and a similar temperature parameter, which provides the measure of intermolecular attractions, is the

boiling point. Thus, critical temperature in the expression 3.37 can be partially or completely replaced by normal boiling temperature and the following should also hold true

$$\left(\frac{T_C T_B}{P_C} \right)^{1/2} = \text{function}(MW, \rho_{20}) \quad (3.38)$$

The correlation between $\left(\frac{T_C T_B}{P_C} \right)^{1/2}$ and $p(MW, \rho_{20})$ for a number of nonpolar hydrocarbons belonging to different homologous series is illustrated in Figure 3.4. The best fit straight line has a slope of 0.577 and intercept 11.12. That means for any nonpolar hydrocarbon the following is valid:

$$\left(\frac{T_C T_B}{P_C} \right)^{1/2} = 0.577 p(MW, \rho_{20}) + 11.12 \quad (3.39)$$

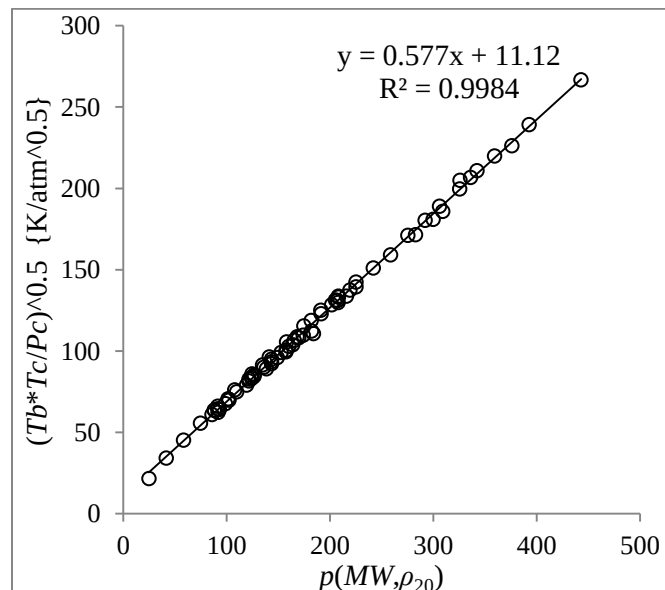


Figure 3.4. Correlation of critical temperature and pressure in terms of molecular weight, normal boiling point, and density.

Solving for the unknowns of T_C and P_C in the equations 3.37 and 3.39 the following correlations are obtained.

$$T_C = T_B \left[\frac{0.613p(MW, \rho_{20}) + 24.85}{0.577p(MW, \rho_{20}) + 11.12} \right]^2 \quad (3.40)$$

$$P_C = T_B^2 \frac{[0.613p(MW, \rho_{20}) + 24.85]^2}{[0.577p(MW, \rho_{20}) + 11.12]^4} \quad (3.41)$$

Figures 3.5 and 3.6 show the accuracy of predicted critical temperature and pressure using expressions 3.40 and 3.41 in comparison with the experimental values, respectively, for different nonpolar hydrocarbons. It is encouraging to see an increasing accuracy in the predicted critical temperature and critical pressure of high molecular weight compounds. The three most deviated points in Figures 3.5 and 3.6 correspond to methane, ethane and propane, which deviate the most from the One-Third Rule.

As a comparison with other methods, Tsonopoulos correlations based on the critical properties of aromatic compounds give average errors of 0.75 % and 3.5 % for the estimation of critical temperature and pressure of aromatic hydrocarbons [98]. From the method of Riazi and Daubert, the average absolute deviation for critical temperature prediction is 0.7 % and for critical pressure is 3.7 % [88]. A later work by Riazi et al. predicts the hydrocarbon's critical temperature with 0.6 % and critical pressure with 2.5 % error [90]. The nomogram-based equations of Sim and Daubert give average absolute deviations of 1 % and 1.5 % for critical temperature and pressure, respectively [45].

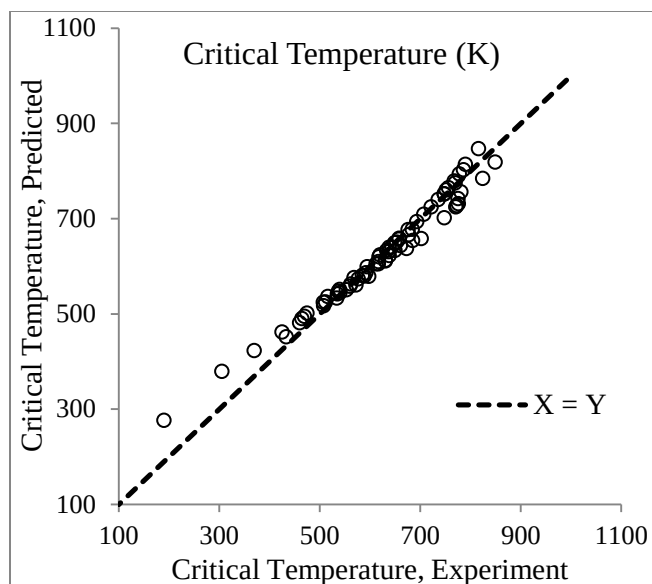


Figure 3.5. Comparison of predicted and experimentally observed critical temperatures of nonpolar hydrocarbons belonging to various homologous series. The average absolute deviation is 2.2 % excluding methane, ethane and propane.

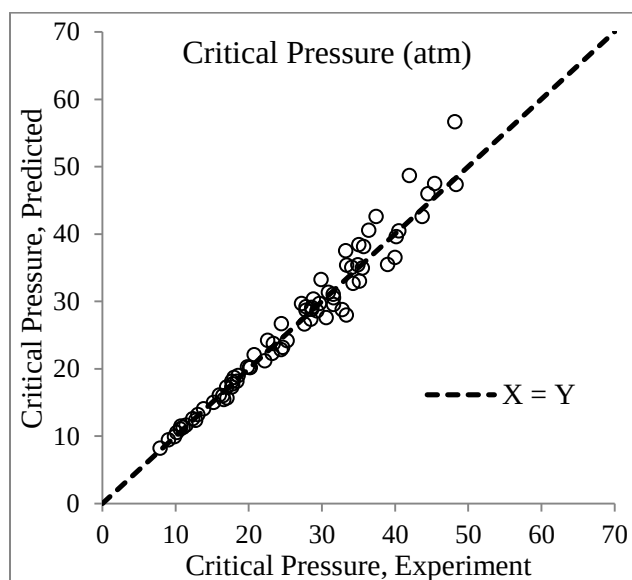


Figure 3.6. Comparison of predicted and experimentally observed critical pressures of nonpolar hydrocarbons belonging to various homologous series. The average absolute deviation is 4.5 % excluding methane, ethane and propane.

3.5 Surface Tension

Surface tension is the molecular property of a substance and is a characteristic of the interface between vapor and liquid. Surface tension is an important thermophysical property for many industrial processes. In reservoir engineering, it is mainly used for the calculation of capillary pressure. In separation units such as distillation, adsorption, or stripping columns, surface tension is a useful parameter to determine foaming characteristics. Surface tension is also needed in the calculation of the rate of oil dispersion on a seawater surface polluted by an oil spill [99]. The determination of surface tension by experimental techniques is time consuming, expensive, and prone to experimental and human errors during the interpretation of data. Thus, reliable prediction methods are highly desired.

In the literature, several approaches are used to calculate surface tensions of pure components and mixtures ranging from empirical correlations such as the parachor method [100], group contribution techniques [101], and the corresponding states principle [102] to more advanced methods such as density functional theories [103, 104], and the gradient theory [105, 106]. This section focuses on the application of Liquid Hole Theory for the calculation of surface tension of nonpolar hydrocarbons in contact with their saturated vapor.

Solving the Schrodinger wave equation for a hole in a liquid leads to an expression in the intrinsic pressure, P_o which does not contain the temperature but only contains the surface tension and difference in density between liquid and vapor [107]. For practical purposes, the density of the vapor can be neglected.

$$P_o = 3.5\sigma \left[\frac{7\pi\sigma}{15U} \right]^{1/2} \quad (3.42)$$

$$\text{where, } U = 3.1 \frac{h^{4/7} \sigma^{5/7}}{\rho^{2/7}} \quad (3.43)$$

Here, h is the Planck constant and σ is the surface tension. For hydrocarbons dominated by nonpolar attractions, the van der Waals equation can be assumed to apply to the liquid.

Thus, I have

$$P_o = (a/v^2) \quad (3.44)$$

where v is the molar volume and a is the molecular force term in the van der Waals equation.

$$a = 9.322v^2 \left[\frac{\rho\sigma^8}{h^2} \right]^{1/7} \quad (3.45)$$

$$\text{From equation 3.35 I have, } \frac{a^{1/2}}{v} \cong 52.042 \left(\frac{n^2 - 1}{n^2 + 2} \right) + 2.904 \quad (3.46)$$

$$\text{Thus, } \sqrt{9.322} \left(\frac{\rho\sigma^8}{h^2} \right)^{1/14} \cong 52.042 \left(\frac{n^2 - 1}{n^2 + 2} \right) + 2.904 \quad (3.47)$$

From the *One-Third Rule* section, the quantity of $\left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho}$ can be approximated as 1/3 and equation 3.47 at ambient temperature can be rewritten as

$$\sigma = \text{function}(w(\rho)) \quad (3.48)$$

$$\text{Where } w(\rho) = \left[\frac{(\rho + 0.1674)^{14}}{\rho} \right]^{1/8}$$

A validation of the equation 3.48 is made at an ambient temperature of 20 °C. At 20 °C, the best fit straight line for nonpolar hydrocarbons based on equation 3.48 has a slope 34.39 and intercept -7.509. Thus,

$$\sigma_{20} = 34.39w(\rho_{20}) - 7.509 \quad (3.49)$$

Figure 3.7 compares the correlated and experimentally measured surface tensions at 20 °C. Surface tension and density for other temperatures reported in Figure 3.8 show the validity of equation 3.48 for other temperatures.

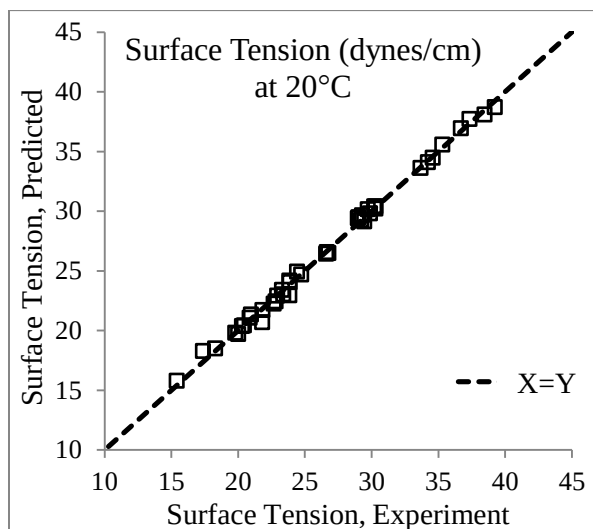


Figure 3.7. Comparison of predicted and experimentally observed surface tensions at 20 °C for nonpolar hydrocarbons. Average absolute deviation is 1.1 %.

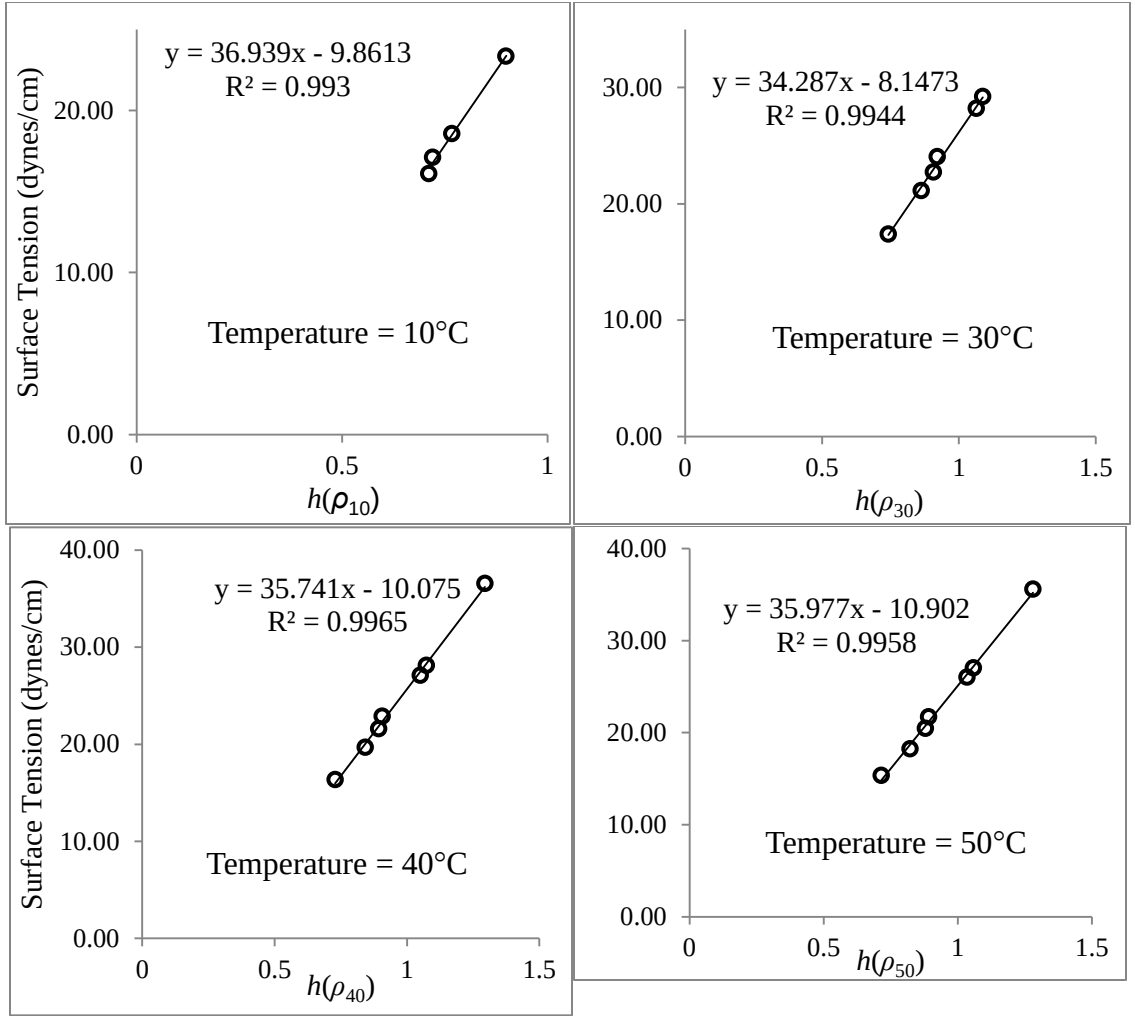


Figure 3.8. Correlation of surface tension and density at different temperature.

In Figure 3.8, trend lines are plotted showing the equation of the straight line and the average deviation of the data points from the trend line. The practical application of equation 3.48 is improved further by incorporating the temperature variation of the surface tension.

$$\sigma \propto (T_C - T)w(\rho_T) \quad (3.50)$$

Using equation 3.49 for the reference temperature of 20 °C, surface tension at any other temperature can be calculated as

$$\sigma_T = [34.39w(\rho_{20}) - 7.509] \left[\frac{T_c - T}{T_c - 293} \right] \left(\frac{w(\rho_T)}{w(\rho_{20})} \right) \quad (3.51)$$

The parameter of critical temperature can be eliminated using the equation 3.40 obtained in the *Critical Properties* section. Thus, the final expression for surface tension computed from just knowing the density, molecular weight, and normal boiling temperature of a compound is

$$\sigma_T = [34.39w(\rho_{20}) - 7.509] \left[\frac{T_B \left[\frac{0.613p(MW, \rho_{20}) + 24.85}{0.577p(MW, \rho_{20}) + 11.12} \right]^2 - T}{T_B \left[\frac{0.613p(MW, \rho_{20}) + 24.85}{0.577p(MW, \rho_{20}) + 11.12} \right]^2 - 293} \right] \left(\frac{w(\rho_T)}{w(\rho_{20})} \right) \quad (3.52)$$

Figure 3.9 compares the surface tension predicted using equation 3.52 and experimental results. Accurate prediction of the critical temperature is required for computing the surface tension near the critical point region. The Liquid Hole Theory is valid only for single component systems.

As compared with other predictive methods, the general error in Brock and Bird's correlation is 5 % [101]. A generalized correlation developed by Miqueu et al. has an average reported error of 3.5 % [108]. Another equation obtained by correlating the parachor of hydrocarbons by Tsonopoulos can predict the surface tension of pure hydrocarbons with an average deviation of about 1 % [98]. However, parachors are empirically fitted parameters and are not available for many hydrocarbons. Surface tension predictions by Escobedo and Mansoori have an average absolute deviation of 2.8 % [109]. Almost all the methods need critical constants as input parameters when predicting the surface tension.

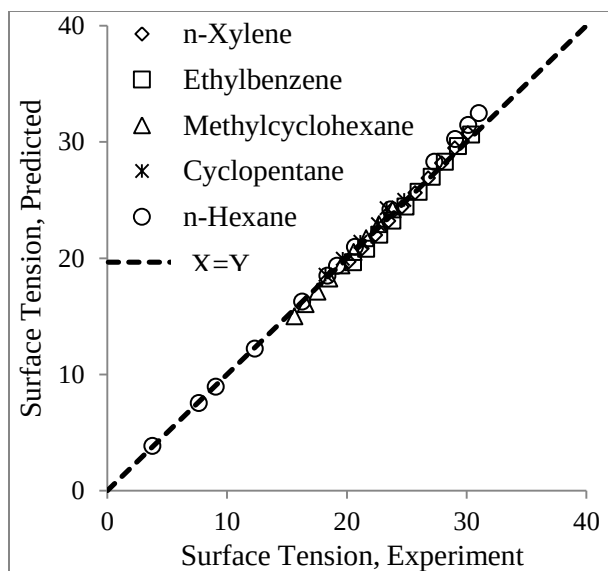


Figure 3.9. Comparison of predicted and experimentally observed surface tensions as a function of temperature for nonpolar hydrocarbons. The average absolute deviation is 1.8 %.

3.6 Predicted Asphaltene Properties

Asphaltene can be considered nonpolar because their phase behavior is dominated by London dispersion interactions [110]. Neither the polarizability nor the dielectric constant of asphaltene can be obtained using the current experimental techniques. Also, no theoretical models exist in the literature for determining those properties of asphaltene. From the electronic polarizability expression proposed in this chapter

$$\alpha = \frac{MW}{4\pi N_a} \quad (3.16)$$

the polarizability of an asphaltene molecule of molecular weight 750 g/mol will be $99.16 \times 10^{-24} \text{ cm}^3$. For a polydisperse asphaltene system, individual fractions' polarizability can be computed and utilized in determining the order of aggregation. The polarizability of an asphaltene molecule with molecular weight 750 g/mol and density 1.1 g/cm^3 , as computed using equation 3.17 is $104.28 \times 10^{-24} \text{ cm}^3$.

From the simple dielectric constant expression

$$k = \frac{2\rho + 3}{3 - \rho} \quad (3.22)$$

an asphaltene polydisperse system with density ranging between 1.1 to 1.2 g/cm³ at ambient conditions will have a dielectric constant between 2.737 and 3. That equation 3.22 is fairly independent of temperature, pressure, and composition can be utilized to understand the insulating capabilities of asphaltene-containing systems. Such information on electrical conductivity is useful in determining the asphaltene adsorption on mineral surfaces in the reservoirs [111]. The dielectric constant of asphaltene with density 1.1 g/cc as computed using equation 3.23 is 2.88.

Applying the One-Third Rule in equation 3.34 of this chapter, the solubility parameter at ambient conditions can be calculated from just the density as

$$\delta = 17.347\rho_{20} + 2.904 \quad (3.53)$$

Such an equation is helpful in calculating the solubility parameter of complex systems such as asphaltene from just the knowledge of bulk density. For example, the solubility parameter of an asphaltene-rich phase with density 1.1 g/cm³ will be 21.99 MPa. The surface tension interpreted from equation 3.49 for the same asphaltene-rich phase of density 1.1 g/cm³ will be 43.94 dynes/cm.

Even though the asphaltene substance is opaque, its refractive index can be indirectly computed from the One-Third Rule as 1.654 when its density is 1.1 g/cm³. Finally, the van der Waals ‘*a*’ parameter of asphaltene with molecular weight 750 g/mol and density 1.1 g/cc useful for cubic equation of state, as calculated from equation 3.37 is 873.6 atm L²/mol².

3.7 Chapter Summary

In this chapter, I have developed simple expressions based on theory and empirical correlations for determining the electronic polarizability, dielectric constant, critical temperature, critical pressure, and surface tension of nonolar hydrocarbons. For the dielectric constant, the equations are also applicable for mixtures. It is unfortunate that the boiling point cannot be experimentally obtained for all the hydrocarbons because of the tendency of some hydrocabons to decompose before reaching the boiling temperature. However, the ratio of critical temperature and critical pressure as observed from Figure 3.3 will be helpful as a verification whenever such experiments are conducted. For surface tension and dielectric constant, the equations are generalized to work across different operating conditions. Knowledge of the chemical structure of a hydrocarbon is not needed in these methods, and the only input parameters are normal boiling point, mass density, and molar mass. The proposed equation for the dielectric constant enables us to predict the dielectric constant for hydrocarbon mixtures without knowing the individual constituents of the mixture or the composition, and the only input parameter is the bulk density. Such an equation can be used in predicting the in situ reservoir fluid density during dielectric logging. Finally, the work as discussed in the *Predicted Asphaltene Properties* section can be applied in predicting the properties of complex, unknown, and polydisperse hydrocarbon systems.

Chapter 4. Crude Oil Characterization and Asphaltene Phase Behavior

It is well accepted that precipitation of asphaltene is a necessary condition for deposition. Hence, as a starting step prediction of asphaltene precipitation is important towards understanding deposition problems. Tendency of asphaltene to precipitate can be best understood from its phase behavior with respect to pressure, temperature and composition of the oil. However, a typical crude oil has numerous components and computing the phase behavior by considering these components individually becomes computationally expensive. On the contrary, characterizing the oil as a mixture of well-defined fractions that represent blends of similar components in oil, instead of handling the components individually can aid in significantly reducing the computational cost.

In this chapter, I present a detailed procedure to characterize crude oil, and plot the asphaltene phase envelope, using the Perturbed Chain form of the Statistical Associating Fluid Theory. This chapter also demonstrates that the proposed procedure can model the asphaltene thermodynamic phase behavior better than a cubic equation of state typically used in the industry.

4.1 Characterization of Reservoir Fluid

One of the earliest studies on crude oil characterization dates back to 1978 by Katz and Firoozabadi, where the boiling point temperature of n-paraffins are used for separating the carbon number fraction [112]. The resulting densities are for paraffinic oils and therefore very low.

A later method proposed by Whitson, as a correction of Katz and Firoozabadi, is widely applied in the industry to characterize the stock tank oil [113]. Whitson's method

is based on the average boiling point of each single carbon number cut and correlations from Riazi and Daubert [88]. Whitson's method presents a set of physical properties for the petroleum fractions C_6 through C_{45} . The calculated properties include average boiling point, specific gravity, and molecular weight based on an analysis of the physical properties of liquid hydrocarbons and condensates. However, this characterization method leads to significant errors when applied to heavier components [45].

Whitson's method is followed by the paraffins-naphthenes-aromatics method to characterize crude oil liquid phase. A new set of correlations reported by Riazi on the properties of single carbon number from C_6 to C_{50} are used to estimate the paraffins-naphthenes-aromatics composition [114]. Leelavanichkul et al. used the paraffins-naphthenes-aromatics technique to characterize different hydrocarbon fluids in a solid-liquid model to determine the asphaltene precipitation onsets [115]. However, the solubility parameter for C_{50} fraction is low to represent the heaviest fractions in a crude oil. Also, the maximum refractive index does not reach the expected 1.7 value that has been estimated for asphaltene [97].

Even with the availability of the SAFT models in commercial simulators such as PVT Sim, Multiflash and VLXE, the lack of a standard characterization procedure incorporating the heavy components such as asphaltene, hinders the industrial use of SAFT based models for asphaltene applications [116].

4.2 Proposed Characterization Methodology

The characterization procedure described below is based on saturates-aromatics-resins-asphaltene (SARA) analysis of stock tank oil. A reservoir fluid which is usually

monophasic, when flashed from reservoir to ambient conditions yields residual liquid/stock tank oil (STO) and an evolved gas phase/flashed gas. Such a flash of reservoir fluid is carried out under controlled environment in a PVT cell, and the liberated gas and residual liquid are analyzed for composition using gas chromatography. Table 4.1 reports the compositional analysis of crude oil A and Table 4.2 shows the properties of crude oil A which is used for describing the characterization.

Table 4.1. Compositional analysis of crude oil A.

Component	MW	Density	Flashed gas		STO		Reservoir fluid (GOR-787 scf/stb)	
			wt %	mol %	wt %	mol %	wt %	mol %
N ₂	28.04	0.809	0.270	0.280	0	0	0.047	0.163
CO ₂	44.01	0.817	5.058	3.340	0	0	0.874	1.944
H ₂ S	34.08	0.786	0	0	0	0	0	0
C ₁	16.04	0.300	31.858	57.716	0	0	5.503	33.600
C ₂	30.07	0.356	13.431	12.981	0.044	0.279	2.356	7.557
C ₃	44.10	0.508	17.571	11.581	0.296	1.294	3.280	6.742
iC ₄	58.12	0.567	5.280	2.640	0.251	0.835	1.120	1.884
nC ₄	58.12	0.586	11.74	5.871	0.923	3.066	2.792	4.695
iC ₅	72.15	0.625	4.593	1.850	0.999	2.673	1.620	2.195
nC ₅	72.15	0.631	5.139	2.070	1.589	4.250	2.202	2.984
C ₆	84.00	0.690	3.497	1.210	3.593	8.254	3.576	4.162
Mcyclo-C ₅	84.16	0.749	0	0	0.447	1.024	0.369	0.429
Benzene	78.11	0.876	0	0	0.143	0.354	0.119	0.148
Cyclo-C ₆	84.16	0.779	0	0	0.322	0.739	0.267	0.310
C ₇	96.00	0.727	1.222	0.370	3.604	7.245	3.193	3.251
Mcyclo-C ₆	98.19	0.770	0	0	0.619	1.217	0.512	0.510
Toluene	92.14	0.867	0	0	0.702	1.471	0.581	0.616
C ₈	107.00	0.749	0.258	0.070	3.805	6.862	3.192	2.916
C ₂ -Benzene	106.17	0.866	0	0	0.224	0.407	0.185	0.171
m&p Xylene	106.17	0.860	0	0	0.644	1.171	0.533	0.491
o Xylene	106.17	0.860	0	0	0.038	0.069	0.032	0.029
C ₉	121	0.768	0.083	0.020	3.936	6.277	3.270	2.642
C ₁₀	134	0.782	0	0	4.605	6.632	3.809	2.779
C ₁₁	147	0.793	0	0	3.787	4.971	3.132	2.083
C ₁₂	161	0.804	0	0	3.241	3.885	2.682	1.628

C ₁₃	175	0.815	0	0	3.096	3.414	2.561	1.431
C ₁₄	190	0.826	0	0	2.929	2.975	2.423	1.247
C ₁₅	206	0.836	0	0	2.83	2.651	2.341	1.111
C ₁₆	222	0.843	0	0	2.437	2.150	2.046	0.901
C ₁₇	237	0.851	0	0	2.356	1.918	1.949	0.804
C ₁₈	251	0.856	0	0	2.128	1.636	1.761	0.686
C ₁₉	263	0.861	0	0	2.231	1.637	1.845	0.686
C ₂₀	275	0.866	0	0	2.193	1.539	1.814	0.645
C ₂₁	291	0.871	0	0	1.900	1.260	1.572	0.528
C ₂₂	300	0.876	0	0	1.805	1.161	1.493	0.486
C ₂₃	312	0.881	0	0	1.628	1.007	1.346	0.422
C ₂₄	324	0.885	0	0	1.512	0.900	1.250	0.377
C ₂₅	337	0.888	0	0	1.417	0.811	1.172	0.340
C ₂₆	349	0.892	0	0	1.377	0.761	1.139	0.319
C ₂₇	360	0.896	0	0	1.269	0.680	1.050	0.285
C ₂₈	372	0.899	0	0	1.280	0.664	1.059	0.278
C ₂₉	382	0.902	0	0	1.079	0.545	0.893	0.228
C ₃₀	394	0.903	0	0	1.031	0.505	0.853	0.212
C ₃₁	404	0.907	0	0	0.937	0.448	0.775	0.188
C ₃₂	415	0.910	0	0	0.883	0.411	0.731	0.172
C ₃₃	426	0.913	0	0	0.803	0.364	0.664	0.152
C ₃₄	437	0.916	0	0	0.694	0.307	0.574	0.129
C ₃₅	445	0.919	0	0	0.666	0.289	0.551	0.121
C ₃₆ ⁺	594	0.941	0	0	27.673	8.991	22.893	3.767

Table 4.2. Properties of crude oil A.

Gas-to-Oil ratio (scf/stb)	787
MW of reservoir fluid (g/mol)	97.750
MW of flashed gas (g/mol)	29.06
MW of stock tank oil (g/mol)	192.99
Stock tank oil density (g/cc)	0.82
Saturates (wt %)	66.26
Aromatics (wt %)	25.59
Resins (wt %)	5.35
Asphaltene (wt %)	2.80

It is well known that the light components in oil significantly affect both bubble pressure and asphaltene onset pressure (AOP). Hence, considering the lightest fractions of oil individually will result in better prediction of asphaltene onset pressures. Thus, gas phase is characterized to consist of seven components: nitrogen, carbon dioxide, methane, ethane, propane and heavy gas pseudo-component that represents a mixture of hydrocarbons heavier than propane. The PC-SAFT equation of state parameters for the pure components, nitrogen, carbon dioxide and C₁–C₃, are available in literature [117]. The average molecular weight of the heavy gas pseudo-component (mostly consisting of saturates) is used to estimate the corresponding PC-SAFT parameters through correlations shown in Table 4.3 [118]. Table 4.4 represents the characterized gas phase of crude oil A. If H₂S is also present in the flashed gas, the number of components in the characterized gas phase will become seven with H₂S being considered individually.

Table 4.3. PC-SAFT parameter correlations for Saturates.

Parameter	Function
m	$(0.0257 * MW) + 0.8444$
$\sigma(A)$	$4.047 - \frac{4.8013 * \ln(MW)}{MW}$
$\varepsilon(K)$	$\exp\left(5.5769 - \frac{9.523}{MW}\right)$

Table 4.4. Characterized gas phase of crude oil A.

Component	MW (g/mol)	mol %	PC-SAFT Parameters		
			m	σ (Å)	ε (K)
N ₂	28.04	0.28	1.21	3.31	90.96
CO ₂	44.01	3.34	2.07	2.78	169.21
C ₁	16.04	57.72	1.00	3.70	150.03
C ₂	30.07	12.98	1.61	3.52	191.42
C ₃	44.10	11.58	2.00	3.62	208.11
Heavy gas	65.49	14.10	2.53	3.74	228.51

The liquid fraction characterization into saturates, aromatics, resins and asphaltene is based on stock tank oil composition and SARA analysis. Because of their similar thermodynamic effect on the asphaltene phase behavior, the aromatics and resin fractions are combined into a single lumped pseudo component defined in terms of the degree of aromaticity (γ). Table 4.5 shows the PC-SAFT parameters for the aromatics+resins pseudo fraction [118]. The aromaticity parameter determines the tendency of aromatics+resins pseudo component to behave as poly-nuclear-aromatic ($\gamma = 1$) or benzene derivative ($\gamma = 0$), and is tuned to meet the values of density and bubble point simultaneously for the entire oil.

Asphaltene exist as pre-aggregated molecules even in good solvents such as toluene, and the average molecular weight for such a pre-aggregated asphaltene is considered as 1700 g/mol [12, 119, 120]. The asphaltene PC-SAFT parameters in the recombined oil are tuned to meet the onset of asphaltene precipitation. Table 4.6 shows the characterized stock tank oil before recombining. The gas phase and stock tank oil are then recombined as per the gas-to-oil ratio (GOR) or the monophasic fluid molecular weight, and Table 4.7 represents the characterized live oil after tuning the parameters. The constant set of PC-SAFT temperature independent binary interaction parameters are established by adjusting binary vapor–liquid equilibrium for the combination of pure components (Appendix D). Further tuning of the binary interaction parameters may be necessary based on the individual case. With all the pseudo components and parameters set, PC-SAFT can be used like any other equation of state and Figure 4.1 plots the resultant asphaltene phase behavior of crude oil A. For the same crude oil A, Figure 4.2

shows the upper asphaltene onset pressure spanning the whole range. The crude oils used for asphaltene discussion in this chapter are A, B, C and D.

Table 4.5. PC-SAFT parameter correlations for aromatics+resins pseudo component as a function of molecular weight. The equations are of the form, Parameter = $(1 - \gamma)(\text{Benzene derivatives correlation}) + \gamma(\text{Poly-nuclear-aromatic correlation})$.

Parameter	Function
m	$(1 - \gamma)(0.0223 * MW + 0.751) + \gamma(0.0101 * MW + 1.7296)$
$\sigma(A)$	$(1 - \gamma)\left(4.1377 - \frac{38.1483}{MW}\right) + \gamma\left(4.6169 - \frac{93.98}{MW}\right)$
$\varepsilon(K)$	$(1 - \gamma)(0.00436 * MW + 283.93) + \gamma\left(508 - \frac{234100}{(MW)^{1.5}}\right)$

Table 4.6. Characterized stock tank oil for crude oil A.

Component	MW (g/mol)	mol %	PC-SAFT Parameters		
			m	σ (Å)	ε (K)
Saturates	167.68	75.97	5.15	3.90	249.69
Aromatics + Resins (γ = To be tuned)	253.79	23.71	6.41	3.99	285.00
Asphaltene	1700	00.32	To be tuned	To be tuned	To be tuned

Table 4.7. Characterized crude oil A.

Component	MW g/mol	Contribution from gas	Contribution from STO	Moles in live oil	PC-SAFT Parameters		
		Moles	moles	Basis 100	m	σ (Å)	ε (K)
N ₂	28.04	0.163	0	0.163	1.21	3.31	90.96
CO ₂	44.01	1.944	0	1.944	2.07	2.78	169.21
C ₁	16.04	33.600	0	33.600	1.00	3.70	150.03
C ₂	30.07	7.557	0	7.557	1.61	3.52	191.42
C ₃	44.10	6.742	0	6.742	2.00	3.62	208.11
Heavy gas	65.49	8.198	0	8.198	2.53	3.74	228.51
Saturates	167.68	0	31.743	31.743	5.15	3.90	249.69
Aromatics + Resins (γ = 0.0)	253.79	0	9.907	9.907	6.41	3.99	285.00
Asphaltene	1700	0	0.133	0.133	33.00	4.20	353.50

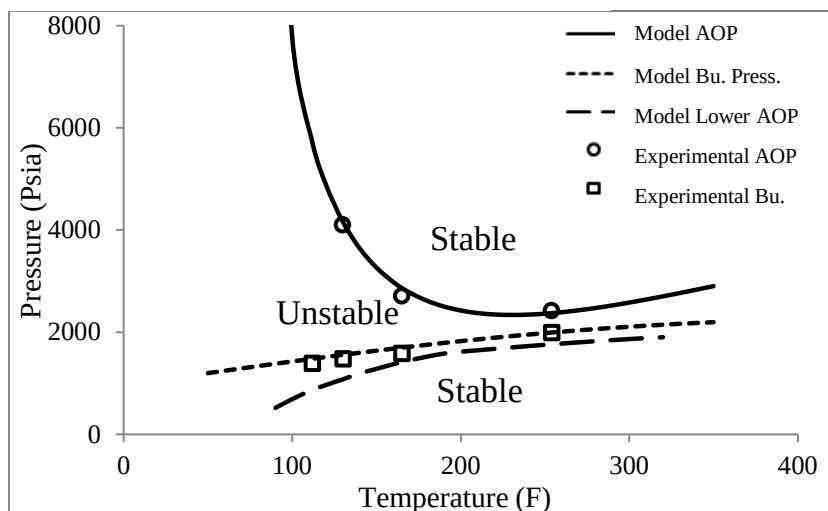


Figure 4.1. Asphaltene phase envelope for crude oil A generated by PC-SAFT.

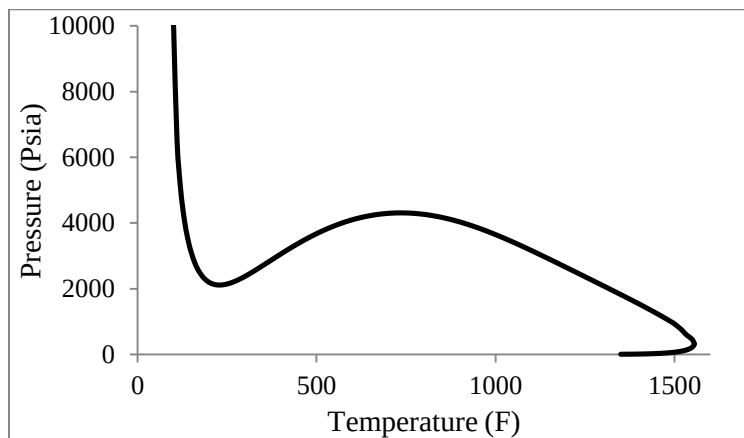


Figure 4.2. PC-SAFT generated crude oil A upper asphaltene precipitation onset pressure.

Asphaltene onset condition is the cloud point at a fixed temperature for which the crude oil will split up into two liquid phases of asphaltene rich and lean phases. Such measurements can involve depressurization of live oil or titration with a precipitant. The lower asphaltene onset represents the pressure below which asphaltene and oil coexist in a single phase.

Recently Punnapala and Vargas showed that the number of adjusted parameters of asphaltene can be reduced to two from three by estimating molecular weight and

aromaticity of the asphaltene instead of the three PC-SAFT parameters [121]. For this work aromaticity is redefined as 0 for saturates and 1 for poly-nuclear-aromatics. For asphaltene, aromaticity and molecular weight are fitted to match the asphaltene onset data reported by either near-infrared depressurization experiments or n-alkane titrations at ambient conditions.

In either of the methods, one of the important inputs on which a crude oil is characterized is the SARA. Unfortunately, a disadvantage of SARA analysis is that fraction measurements by different techniques can show large differences [122, 123]. Table 4.8 shows the SARA reported by thin layer chromatography with flame ionization detection (TLC-FID) and high pressure liquid chromatography (HPLC) for the same light crude oil B. In the process of quantifying SARA, TLC-FID lost significant amount of light ends, and hence reported a higher amount of aromatics and asphaltene than actually present. When the SARA measured by the same lab for another light crude oil C from a different field in the same region is made available through TLC-FID, the corrected weight fractions are obtained by multiplying and renormalizing the crude oil C data with the corresponding ratio of HPLC/TLC-FID obtained from crude oil B. From Table 4.9, the corrected SARA is very close to the actual SARA measured by HPLC for crude oil C. Thus, under data constraints, such SARA estimations can be used for crude oils of similar nature and origin. Alternatively, the lost fraction during TLC-FID can be assumed to be composed of mostly the saturates (because of the higher volatility of saturates compared to aromatics and other components); and the actual SARA can be estimated by adding this lost fraction to the saturates reported in SARA and renormalizing.

Table 4.8. SARA analysis as reported by TLC-FID and HPLC for the crude oil B.

	TLC-FID	HPLC (IP 143)	HPLC/TLC-FID (P)
Saturates	49.5	73.0	1.47
Aromatics	40.2	19.1	0.48
Resins	7.2	7.6	1.06
Asphaltene	3.1	0.2	0.06

Table 4.9. SARA analysis corrected for crude oil C.

	TLC-FID	Corrected (= TLC-FID*P)	HPLC (IP 143)
Saturates	44.9	69.39	67.09
Aromatics	46.3	23.05	25.84
Resins	6.7	7.41	6.92
Asphaltene	2.1	0.14	0.15

4.3 Comparison of Cubic and PC-SAFT Equation of State

Despite their poor prediction of liquid properties, cubic equations of state are widely used in the petroleum industry due to the simplicity of the models. In the thermodynamic modeling of asphaltene, it is seen that the parameters fit using a cubic equation of state for a particular data set fails to predict another situation for the same well. This is demonstrated in Figure 4.3 where the parameters for both SRK-P and PC-SAFT parameters are estimated to the saturation pressures and asphaltene onset pressures for various temperature of crude oil D with 5 mol % gas injection. The same parameters are then used to predict the saturation pressure and temperature dependence of the asphaltene onset pressure for different amounts of gas injected. The predictions made by the PC-SAFT and cubic equation of state are compared in Figures 4.3A, 4.3C and 4.3D. It is observed that only PC-SAFT does a good job in predicting the phase behavior of asphaltene even with compositional changes.

A major limitation of any cubic equation of state is that they cannot describe adequately the phase behavior of mixtures of molecules with large size differences, and they are unable to accurately calculate liquid densities of the precipitated phase. Accurate modeling of liquid density is essential for an equation of state to predict liquid-liquid equilibrium and their corresponding parameters, such as the solubility parameter, over a range of conditions.

The association term from SAFT can be added to a cubic equation of state to produce a non-cubic model called as the cubic plus association equation of state [124]. This cubic plus association equation of state has been applied for modeling the asphaltene phase behavior with some success. However, this model requires a lot more parameters than SAFT, and for a nonassociating system reduces to the simple cubic equation of state with the same drawbacks.

4.4 Gas Injection

Changes in crude oil composition occur during gas injection processes employed in enhanced oil recovery, reservoir pressure maintenance and gas lift. The gas injection effect on asphaltene stability is studied by the addition of increasing amounts of natural gas at different temperature for crude oil B as shown in Figure 4.4. The PC-SAFT predictions match the experimental observations of both the asphaltene onset and bubble pressures for varying amounts of the natural gas injected into the live oil. The dissolved gas decreases asphaltene solubility and the asphaltene become more unstable. Thus along with an increasing trend of bubble pressure (due to more volatiles) asphaltene onset pressure also increases. Specific effects on asphaltene precipitation onset due to nitrogen,

carbon dioxide and methane injection also show an increasing asphaltene instability with increasing amounts of gas injection [125].

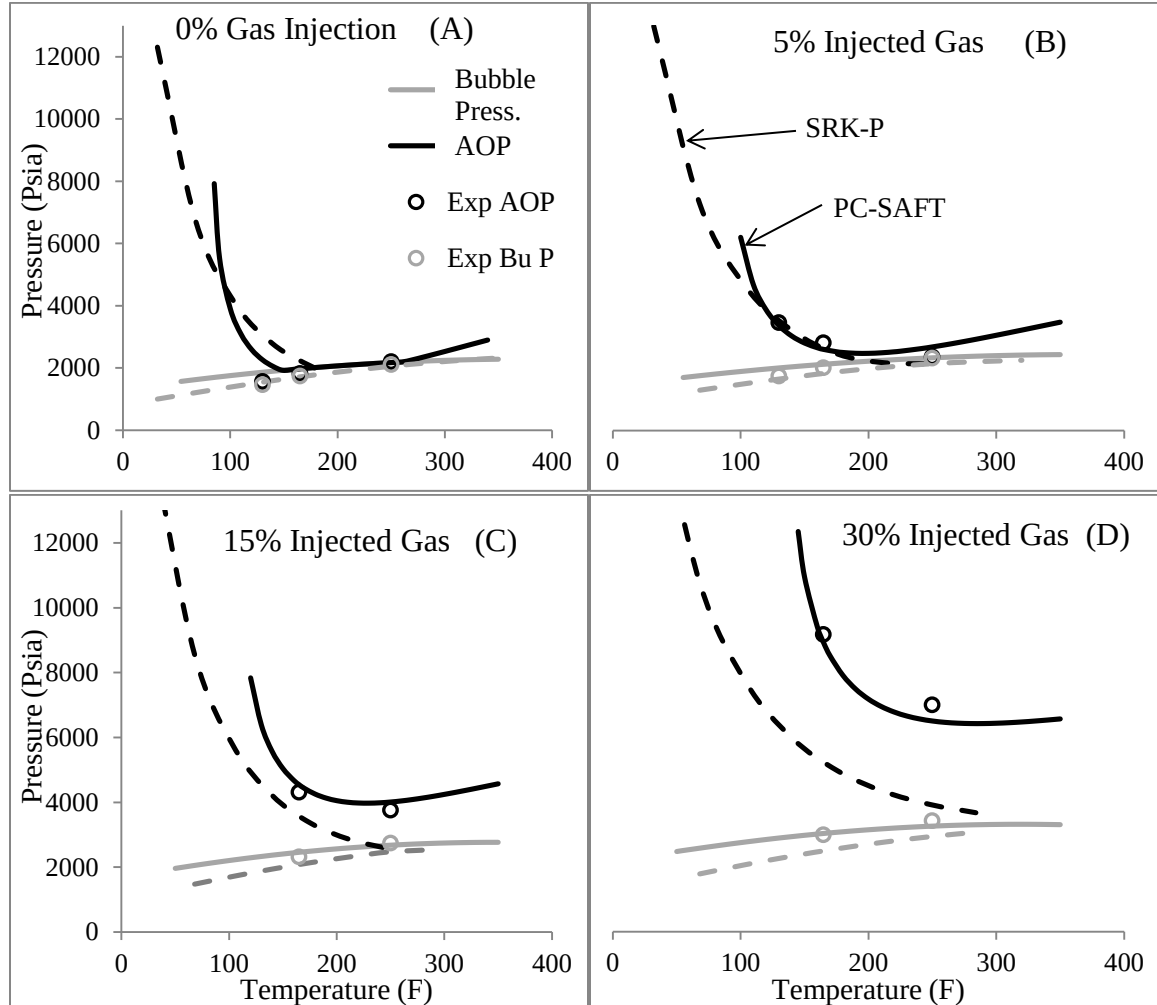


Figure 4.3. PC-SAFT and SRK-P asphaltene phase behavior predictions for crude oil D after estimating the parameters for 5 mol % of gas injection data. Injected gas composition (mol %): N_2 -0.4%, CO_2 -3.9%, C_1 -71.4%, C_2 -12%, C_3 -7.2%, heavy gas-5.1%

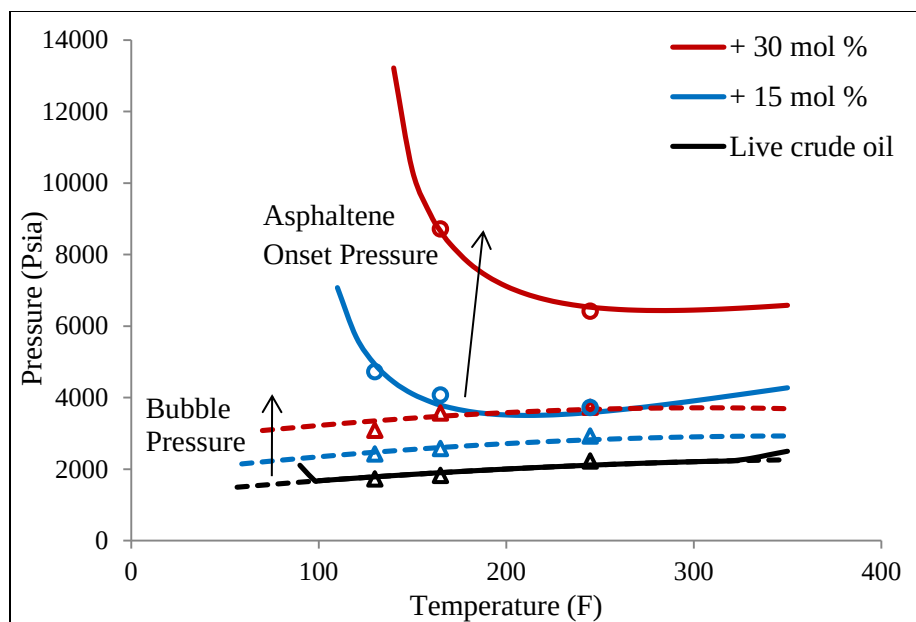


Figure 4.4. Asphaltene phase behavior in crude oil B upon the addition of natural gas.
 Injected gas composition (mol %): N₂-0.5%, CO₂-4.5%, C₁-87.4%, C₂-7.2% and C₃-0.4%

4.5 Amount of Precipitated Asphaltene

Predicting asphaltene deposit buildup is of common interest in the flow assurance community with both academic and industry actively involved in the development of asphaltene deposition simulator. For such a program, an essential initial boundary condition is the amount of asphaltene that can precipitate, and hence deposit. For the crude oil D system at bubble pressure, Figure 4.5 shows the weight percent of asphaltene precipitated in the stock tank oil with respect to gas injection. Thus the maximum percent that can be precipitated is the asphaltene content reported by SARA in Appendix B.

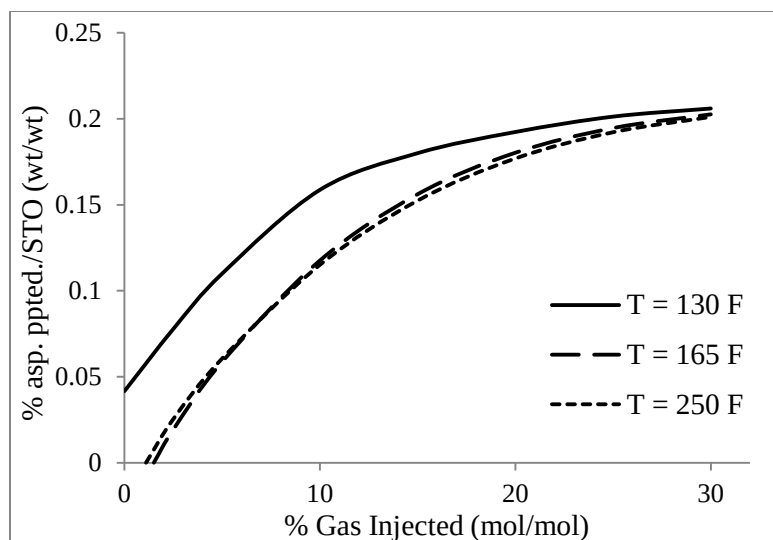


Figure 4.5. Crude oil D asphaltene precipitation curve at bubble pressure for different amounts of injected gas at three different temperatures.

The results are in accordance with the phase plots (Figure 4.3) as more asphaltene are precipitated with increasing injected gas. Also observed from Figure 4.3 is the increasing asphaltene instability at lower temperature, and hence, more amount of precipitated asphaltene in Figure 4.5 at lower temperature. Table 4.10 shows the estimated amount of asphaltene in the precipitated phase of crude oil A at the bubble pressures, and will be helpful in the design of solvent deasphalters. It is interesting to observe the enrichment of asphaltene in the precipitated phase (~ 10 mol %) from a very lean oil phase of ~ 0.1 asphaltene mol %.

Table 4.10. Amount of asphaltene in the precipitated phase of crude oil A at its bubble pressure.

Temperature (F)	Mole percentage of asphaltene in precipitated phase	Weight percentage of asphaltene in precipitated phase
130	15.2	72.45
165	11.8	66.91
254	7.9	57.24

4.6 Aging

Aging of a deposit is the change in viscoelastic behavior with time of the deposit. Asphaltene deposit hardens in the process of aging with the escape of other oil molecules from the deposit. Aging of the deposited asphaltene is a complex phenomenon with almost no study in the literature. Among the different mechanisms that can result in aging, thermodynamics can also play a role as described below.

Let us assume that the precipitated asphaltene is deposited as is on a pipe wall. The pipe surface is subjected to a different temperature than the bulk fluid because of the surroundings. Also in the process of shut down of a well, the temperature of the pipe drops more phenomenally. When such a temperature decrease occurs in the deposit adhered onto the pipe wall, the deposited asphaltene rich phase can precipitate into a more asphaltene rich phase and lean phase. This lean phase redissolves back into the crude oil. Thus, in the process of decreasing temperature, asphaltene gets enriched in the deposit which causes the hardening of the deposit. Figure 4.6 shows the increasing content of asphaltene in the deposit phase of crude oil A, with a decreasing temperature at fixed pressure.

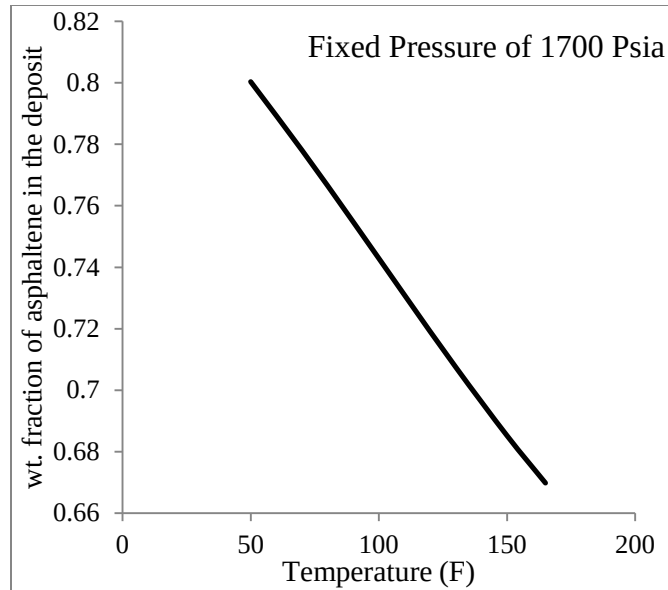


Figure 4.6. Asphaltene deposit aging in crude oil A where the asphaltene precipitate which adhered to the wall was precipitated at 165 F and 1700 Psia.

4.7 Routine and EOR PVT

While much focus of the PC-SAFT equation of state was for specialized applications like asphaltene, the versatility of the PC-SAFT for reservoir fluids has been given less attention [126]. In this section I show the successful application of PC-SAFT equation of state in predicting the overall PVT behavior of crude oils observed from different experiments. The crude oils considered in this section are B, C, E, F and G.

When characterizing crude oils without the need for individually accounting for asphaltene, the whole of stock tank oil can be considered as a single lumped pseudo-component. The gas phase consists of seven components: nitrogen, carbon dioxide, hydrogen sulfide, methane, ethane, propane, heavy gas pseudo-component (hydrocarbons C_4 and heavier in the flashed gas). The flashed gas and stock tank oil are recombined based on gas-to-oil ratio, or alternatively to match the reservoir fluid molecular weight.

Because the stock tank oil can behave anywhere between an n-alkane and a poly-nuclear-aromatic, this tendency is adjusted by the aromaticity parameter ($\gamma = 0$ for saturates and $\gamma = 1$ for poly-nuclear-aromatics) which is independently fitted to match experimental data on stock tank oil density and reservoir fluid's saturation pressure. Thus, for the whole modeling there is only a single adjustable parameter, the aromaticity of stock tank oil.

Figure 4.7 shows the measured and predicted oil density for pressure depletion at the reservoir temperature for crude oils B, C and E. Figure 4.8 shows the relative volume, defined as total volume divided by saturation point volume. Solution gas-to-oil ratio (R_s) is an important quantity measured during a differential liberation experiment. In Figure 4.9 the solution gas-to-oil ratio at any given stage is calculated by adding the standard volumes of the gas liberated in each of the subsequent stages and dividing this sum of gas volumes by the residual oil volume.

The gas gravity is defined as the average molecular weight of the gas divided by the average molecular weight of atmospheric air. The molecular weight of atmospheric air is assumed as 29 g/mol. From Figure 4.10, by expressing the molecular weight relative to that of atmospheric air, the gas gravity becomes a measure of the low pressure density of the gas relative to that of air. During a differential liberation test, knowledge on the composition of the evolved gas during different stages is useful in designing the process equipment. The accuracy of such a PC-SAFT gas composition prediction is good, and can be seen in one of my recently published article [127].

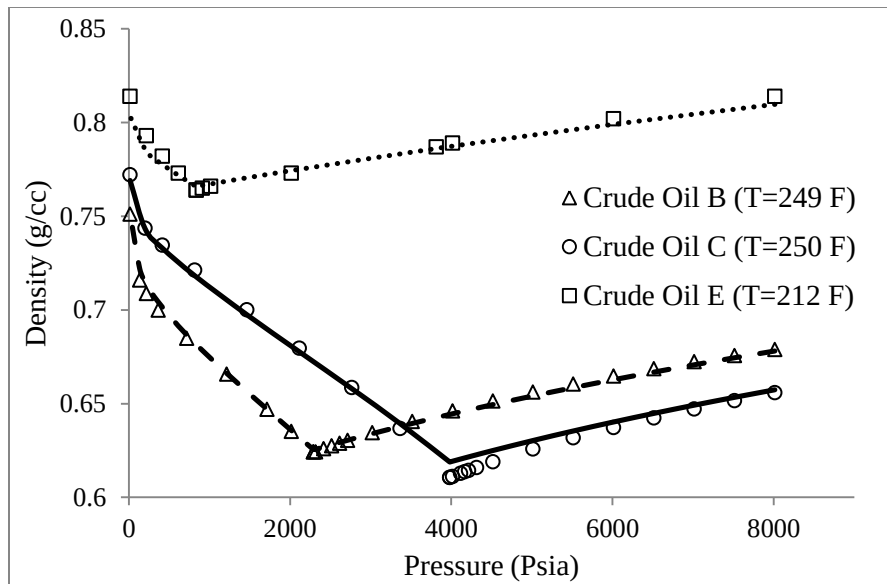


Figure 4.7. Measured and predicted liquid density as a function of pressure at constant temperature for crude oils B, C and E.

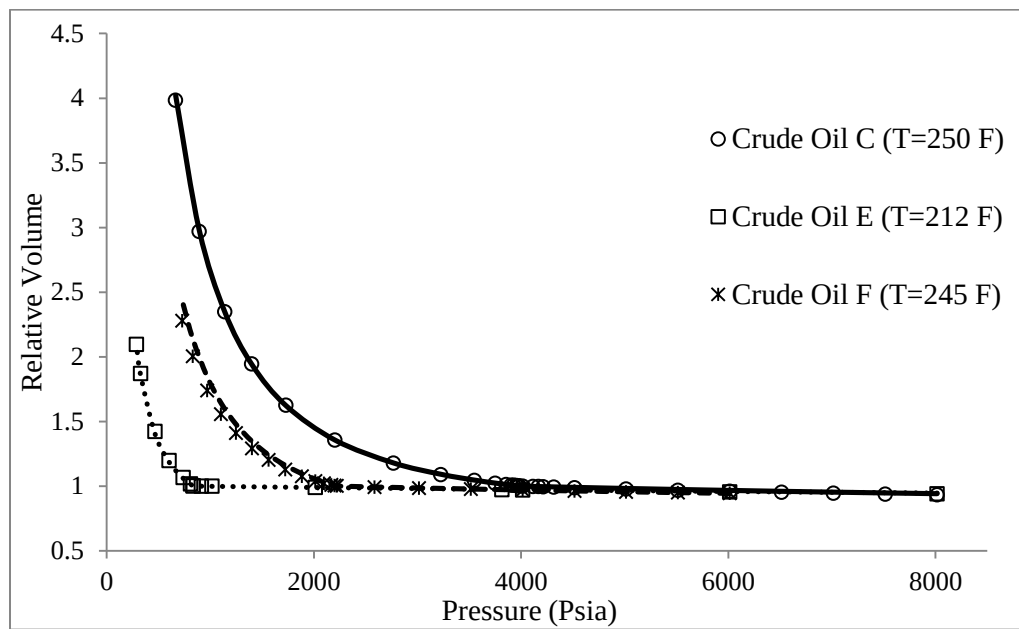


Figure 4.8. Relative volume from a constant composition expansion test on crude oils C, E and F.

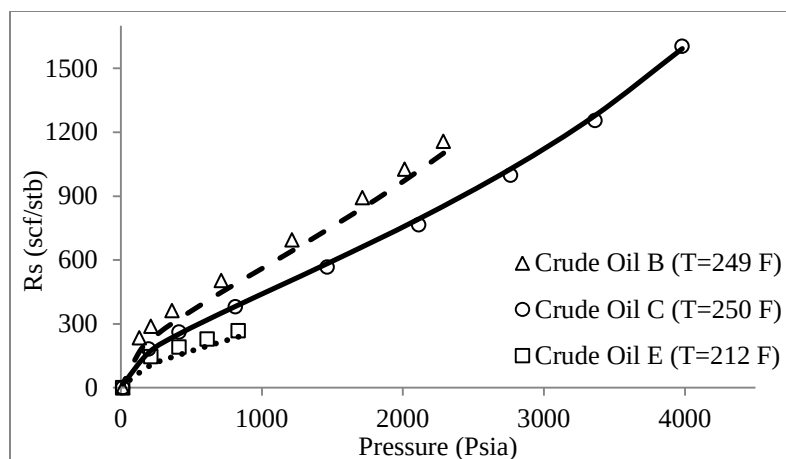


Figure 4.9. Measured and predicted solution gas-to-oil ratio during differential liberation experiment on crude oils B, C and E.

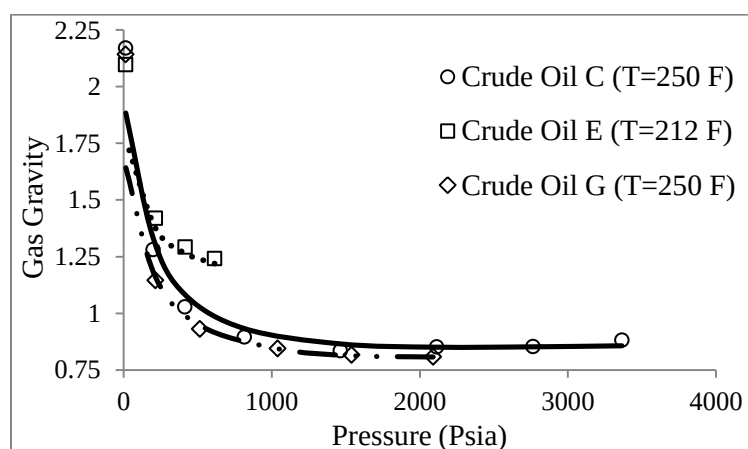


Figure 4.10. Measured and predicted gas gravities in a differential liberation experiment for crude oils C, E and G.

Carbon dioxide gas injection is seen both as a way of decreasing the release of carbon dioxide to the atmosphere and as a means of enhancing the oil recovery. An equation of state model is applicable for enhanced oil recovery purposes only if capable of matching the swelling results like bubble pressure and density. Figure 4.11 shows the increasing bubble pressure with gas injection. Symbols are the experimental data and the lines are PC-SAFT predictions. The cumulative gas injection represents the number of

moles of gas added for every 100 moles of the original reservoir fluid. For the case of crude oil B, pure carbon dioxide is injected and the composition of lean gas injected into crude oil G is given in Figure 4.11. For each of the CO₂ injected amounts into crude oil B, PC-SAFT also captured the relative volume successfully as shown in Figure 4.12.

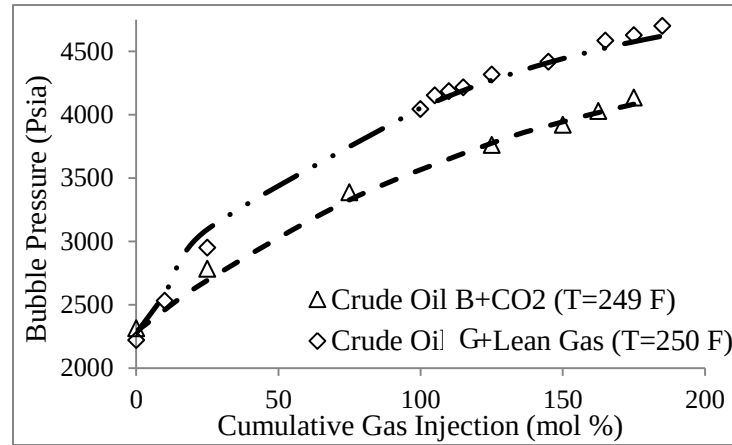


Figure 4.11. Increase in bubble pressure with gas injection during swelling experiments on crude oils B and G. Injected lean gas composition (mol %): N₂-0.3%, CO₂-3.5%, C₁-67.2%, C₂-10.9%, C₃-7.8%, heavy gas-10.3%

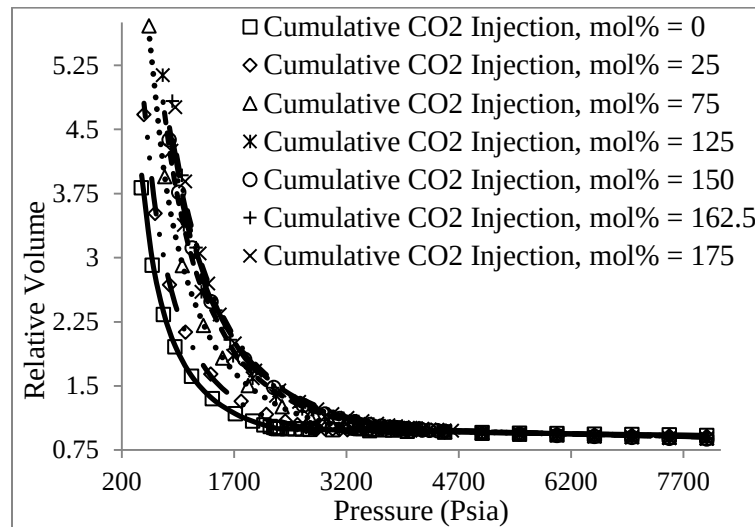


Figure 4.12. Relative volume during pressure depletion when different amounts of carbon dioxide are injected into crude oil B at 249 F.

4.8 Chapter Summary

In this chapter, I have demonstrated a brief methodology to characterize crude oils using PC-SAFT, which will facilitate easy usage of this equation of state. Among the experimental information necessary to fit the simulation parameters, SARA requires special attention. A procedure to correct the SARA values is presented, which seems to provide satisfactory results for the case of light crude oils of similar nature.

Asphaltene phase behavior calculations are performed for different crude oils in the presence of different amounts of injected gas and the results are compared against similar calculations performed with a cubic equation of state. It is observed that in case of PC-SAFT, a single set of parameters is sufficient to describe the phase behavior of oil with various compositional changes. However, for a cubic equation of state, one set of parameters failed to sufficiently describe the asphaltene experimental observations for other gas injection amounts.

Based on the predicted asphaltene phase envelope, the amount of precipitated asphaltene is computed. Such information is essential for an asphaltene deposition simulator and solvent deasphalters. This chapter also discusses about thermodynamic aging which can result in the enrichment of asphaltene in the deposit. Finally, the last section in this chapter shows that the potential of PC-SAFT equation of state in the oil industry is not limited to modeling of asphaltene precipitation and other specialized applications.

Chapter 5. Asphaltene Compositional Grading

Reservoir compartmentalization is one of the major issues on both on- and offshore reservoirs. High capital costs are involved especially in deepwater exploration and production, making it essential to assess prior to production the extent of compartmentalization within a reservoir. Within a continuous reservoir, fluid properties vary with depth because of compositional grading. Considerable fluid flow is required to attain thermodynamic equilibrium yielding compositional gradients, suggesting connectivity. In this chapter, an algorithm that makes use of the PC-SAFT equation of state is proposed to address the isothermal asphaltene compositional grading in a uniform gravitational field. The model is validated against well log and production data. The results are compared to field data to evaluate the reservoir compartmentalization. An approximate analytical solution for asphaltene compositional grading, derived from solution thermodynamics, is also presented. Asphaltene compositional grading under extreme cases can lead to tar mat formation. The PC-SAFT asphaltene compositional grading introduced in this chapter is extended to further depths to model the possibility of tar mat formation in different fields.

5.1 Introduction to Compartmentalization and Tar Mat

Compartmentalization arising because of different factors, such as impermeable layers and faults, leads to the lack of reservoir connectivity. This chapter proposes a combined solution to the individually ill-posed problems of reservoir compartmentalization and tar mat occurrence. Tar mat predominantly represents non-producible oil in place and low-permeability intrareservoir flow barrier.

Compartmentalization in a reservoir makes recovery more difficult because of poor drainage for a given number of wells. Seismic data and discontinuous variation of fluid properties (e.g., chemistry, density, and viscosity) are commonly used in an attempt to assess the level of compartmentalization. The varying fluid properties along the depth of a continuous reservoir are due to compositional grading [128]. In oil columns, considerable fluid flow is required to reach thermodynamic equilibrium, yielding such compositional gradients, and, thus, suggests reservoir connectivity better than pressure communication where little fluid flow is required. In particular, reservoir connectivity can be best understood on the basis of continuous characteristics of the asphaltene compositional gradient, because to equilibrate asphaltene, the heaviest component of crude oil with by far the least mobility, necessitates substantial permeability.

The analysis by Hoier and Whitson accounts for gas-to-oil ratio and composition of equilibrium fluids during compositional grading [129]. However, Whitson or others did not analyze compositional grading related to asphaltene because of limited knowledge of asphaltene prior to 2000. Confident from the application of PC-SAFT for asphaltene thermodynamic predictions (Chapter 4) with various operational changes, PC-SAFT equation of state is used here for the first time to model asphaltene distribution in oil columns, and compared to field data to evaluate the reservoir compartmentalization.

Many of the Middle East oil fields are rimmed by large and thick accumulation of highly viscous extra heavy oil [130]. It is termed as tar mat and represents a reservoir zone containing highly enriched asphaltene (20–60 wt %) relative to the oil column [131]. Tar mat is an important organic barrier for an oil reservoir and must be modeled as accurately as possible to obtain reliable predictive production profiles. The tar mat can be

formed by any of the mechanisms such as, biodegradation at oil-water contact, gas diffusion, oil cracking or flocculation of precipitated asphaltene. But, as long as the tar mat is in thermodynamic equilibrium with the rest of the reservoir fluid, the plot of asphaltene content with depth should be able to detect the tar mat formation depth.

5.2 Isothermal Compositional Grading Algorithm

Gibbs was the first to derive the general conditions of equilibrium for a mixture of any number of fluids, but he applied them only to ideal gas mixtures [132]. Gouy and Chaperon in 1887, Duhem in 1888 and van der Waals in 1900 considered binary mixtures, but did not present explicit formulae for the results [133-135]. Between 1930 and 1940, Muskat and Sage formulated equations for the distribution of components in hydrocarbon fluids because of the effect of the gravitational field [136, 137]. From 1940 to 1980, the petroleum industry was void of active research on compositional gradients, but observations are reported [138]. By 1980, cubic equation of state came into widespread use, enabling easy calculations of thermodynamic properties and Schulte was the first to solve the compositional gradients in reservoir fluids using an equation of state [139].

When a multi-component system is in true thermodynamic equilibrium in a gravity field, for each component in the system, the sum of the chemical potential and the gravitational potential will be constant. The condition of equilibrium is satisfied by the constraint 5.1. For an N component system, equation 5.1 represents N equations. Together with the constraint 5.2, composition, X and pressure, P can be solved simultaneously at any depth, h .

$$\mu_i(P, X, T) = \mu_i(P^o, X^o, T) + M_i g(h - h^o) \quad (5.1)$$

$$\sum_{i=1}^N X_i(h) = 1 \quad (5.2)$$

The thermodynamic equilibrium constraint 5.1 can be expressed in terms of fugacity of individual components in the system.

$$RT \ln \left(\frac{\hat{f}_i}{\hat{f}_i^o} \right) = M_i g(h - h^o) \quad \text{or} \quad \hat{f}_i = \hat{f}_i^o \exp \left(\frac{M_i g(h - h^o)}{RT} \right) \quad (5.3)$$

Montel and Gouel solved equation 5.3 for an isothermal gravity chemical equilibrium, using an incremental oliostatic head instead of solving for pressure directly [140]. Thus, the procedure was only approximate, because the compressibility effect of oil is not taken into consideration.

Whitson et al. successfully solved the gravity chemical equilibrium problem, also taking into account the compressibility effect of oil [141]. The algorithm in this chapter is based in part on the Whitson procedure, and solves the set of simultaneous nonlinear equations using Newton–Raphson update for pressure and Picard update for composition. The algorithm is solved in Microsoft Excel 2007, where the programming is in visual basic embedded in Excel Macros. PC-SAFT equation of state is used for calculating the thermodynamic properties. Figure 5.1 represents the flowchart of the algorithm, and the description is provided in the following paragraphs.

First, fugacities of the components, f_i^o at the reference depth, h^o are computed. Then, fugacities, f_i at the new depth, h are calculated from equation 5.3. This calculation needs to be made only once. Initial estimates of composition at depth, h are simply the values at reference depth, h^o .

$$X_i^{(1)}(h) = X_i^o \quad (5.4)$$

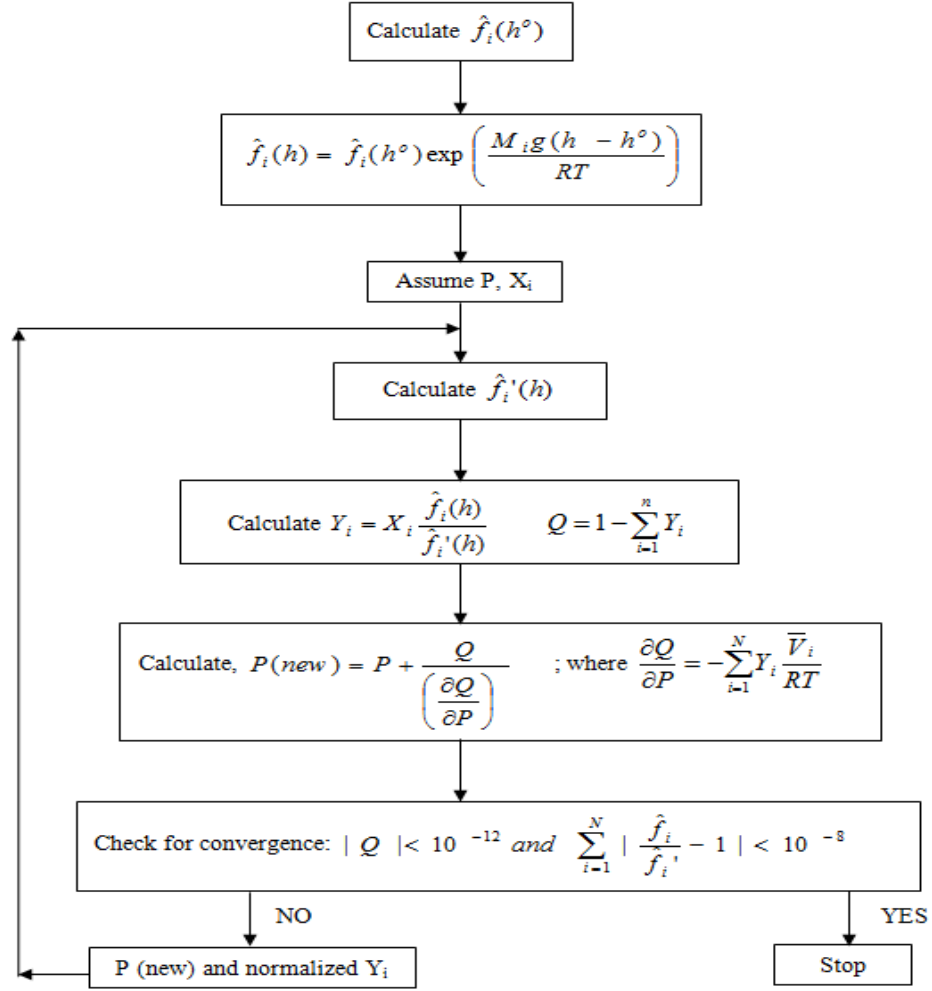


Figure 5.1. Flowchart of the isothermal gravitational compositional grading algorithm.

For initial pressure estimate at the new depth, h , it is the reference pressure added with the column head pressure at reference depth density ρ^o .

$$P^{(1)}(h) = P^o(h^o) + \rho^o g(h - h^o) \quad (5.5)$$

Now fugacities, $\hat{f}_i^{(n)}$ of the composition estimate, $X^{(n)}$ at the pressure estimate, $P^{(n)}$ are calculated. Corrected mole fractions are obtained using the Picard's update.

$$Y_i^{(n)} = X_i^{(n)} \frac{\hat{f}_i(h)}{\hat{f}_i'^{(n)}(h)} \quad (5.6)$$

However, the sum of mole fractions should add to 1.

$$Q^{(n)} = 1 - \sum_{i=1}^N Y_i^{(n)} \quad (5.7)$$

This error, $Q^{(n)}$ is computed and used to update the pressure using the Newton–Raphson method.

$$P^{(n+1)} = P^{(n)} + \frac{Q^{(n)}}{\left(\frac{\partial Q}{\partial P}\right)^n}, \quad (5.8)$$

$$\begin{aligned} \text{Where, } \left(\frac{\partial Q}{\partial P}\right)^n &= \sum_{i=1}^N X_i \hat{f}_i \frac{\partial}{\partial P} \left(\frac{1}{\hat{f}_i^{(n)}} \right) = - \sum_{i=1}^N \frac{X_i \hat{f}_i}{(\hat{f}_i^{(n)})^2} \frac{\partial \hat{f}_i^{(n)}}{\partial P} \\ &= - \sum_{i=1}^N Y_i^{(n)} \frac{\left(\frac{\partial \hat{f}_i^{(n)}}{\partial P}\right)^n}{\hat{f}_i^{(n)}} = - \sum_{i=1}^N Y_i^{(n)} \frac{\partial(\ln \hat{f}_i^{(n)})}{\partial P} = - \sum_{i=1}^N Y_i^{(n)} \frac{\bar{V}_i^{(n)}}{RT} \end{aligned} \quad (5.9)$$

It is interesting to observe that the derivative of error Q with respect to pressure can be written in terms of the mole fraction and partial molar volume of each component in the system. Thus, the updated pressure becomes

$$P^{(n+1)} = P^{(n)} - \frac{Q^{(n)}}{\sum_{i=1}^N Y_i^{(n)} \frac{\bar{V}_i^{(n)}}{RT}} \quad (5.10)$$

Convergence of solution is ensured using the following two tolerances,

$$|Q^{(n)}| < 10^{-12} \quad \text{and} \quad \sum_{i=1}^N \left| \frac{\hat{f}_i}{\hat{f}_i^{(n)}} - 1 \right| < 10^{-6} \quad (5.11)$$

Normalizing the values of $Y_i^{(n)}$ then yields the updated mole fractions, $X_i^{(n+1)}$.

5.3 Approximate Analytical Solution

Because of gravity, the reservoir fluid composition and properties vary with depth in a reservoir at thermodynamic equilibrium. Under negligible temperature gradient, for

each component in the system, the sum of chemical and gravity potentials will be constant. In comparison to the usual liquid–liquid equilibrium condition, which requires the chemical potential for each component to be equal in both phases, there is now an additional term because of the gravity, and the overall equilibrium can be expressed by

$$d\mu_i = M_i g dh \quad (5.12)$$

The difference in chemical potentials can be expressed in terms of fugacities of components in the system (equation 5.13). These fugacities can also be written in terms of fugacity coefficients, resulting in the expression 5.14.

$$RT \ln \left(\frac{\hat{f}_i}{\hat{f}_i^o} \right) = M_i g dh \quad (5.13)$$

$$RT \ln \frac{Z}{Z^o} + RT \ln \frac{\hat{\phi}_i}{\hat{\phi}_i^o} + RT \ln \frac{\rho_i}{\rho_i^o} = M_i g dh \quad (5.14)$$

In the limit of infinite dilution of asphaltene in oil, the partial molar volume of asphaltene can be considered independent of the concentration. Also, if the system is far away from its critical point, the partial molar volume can be assumed independent of pressure changes. Thus, expression 5.14 becomes simplified as follows [136].

$$RT \ln \frac{\rho_i^0}{\rho} + \bar{V}_i^\infty (P - P^o) + RT \ln \frac{\rho_i}{\rho_i^o} = M_i g dh \quad (5.15)$$

Assuming negligible change in the density of crude oil with depth, the pressure difference can be expressed in terms of head height and the resultant expression becomes

$$RT \ln \frac{\rho_i}{\rho_i^o} = [M_i g - \bar{V}_i^\infty \rho g](h - h^o) \quad \text{or} \quad \frac{\rho_i}{\rho_i^o} = \exp \left[\frac{(M_i - \bar{V}_i^\infty \rho)}{RT} g(h - h^o) \right] \quad (5.16)$$

A similar form of the expression 5.16 was first deduced by Muskat in 1930 [136], but was applied to understand the role of asphaltene in compositional grading only in 1988 by Hirschberg [27]. In the Hirschberg paper, the Huggins theory developed for a large linear molecule was applied for a bulky asphaltene molecule, resulting in the effective molar volume being significantly lower than the actual volume. Thus, expression 5.16 was never successfully used to determine the asphaltene gradient with depth. Using an accurate partial molar volume obtained from PC-SAFT, the successful implementation of expression 5.16 to model the asphaltene compositional gradient is demonstrated in this chapter.

Mullins et al. modified and extended the Flory–Huggins regular solution theory to derive an asphaltene compositional gradient model, where the parameters are estimated by matching field measurements of the asphaltene gradient [142]. The parameters in this work are estimated on the basis of asphaltene onset measurements in a laboratory, and all of the asphaltene compositional grading plots presented here are pure predictions.

5.4 Reservoir Compartmentalization and Wells Connectivity

Observed from expression 5.1, a considerable elevation difference produces the thermodynamic drive creating a composition difference. Equation 5.16 is similar to the buoyancy term, where on the basis of the particle mass and system density, heavier components accumulate at the base and lighter components accumulate at the top of the column. For both the A and H reservoir fields considered in this section, negligible temperature gradient and equilibrium are assumed during the measurement of field data. Field A consists of crude oil A and field H consists of crude oil H.

With the fluid being well characterized at a particular depth, the isothermal compositional grading algorithm is used to analyze the compositional grading related to asphaltene using PC-SAFT equation of state. Like all other crude oils used in this thesis, the properties of crude oils A and H are reported in Appendix B, while Appendix C shows the characterized crude oils A and H with the PC-SAFT parameters.

The molecular weight of pseudocomponents changes with depth, because individual fractions in the pseudocomponents have individual degrees of compositional grading. However, the overall thermodynamic properties can be predicted well by PC-SAFT even without considering such complex changes, as shown by the differential liberation results in the previous chapter.

5.4.1 Field H

Black and heavy oil reservoirs are characterized by a very small gas-to-oil ratio gradients. The largest gradient for these oils is often in the asphaltene, and can be used to evaluate connectivity and other complexities in the reservoir. The H field is offshore, in the Gulf of Mexico. It is a tilted reservoir with large horizontal ($k_h = 600$ mD) and vertical permeabilities ($k_v/k_h \sim 0.6$), enabling good convection. However, the reservoir is against a salt canopy and involves the risk of compartmentalization because of the faulting induced by salt buoyancy.

Successful working of the proposed PC-SAFT compositional grading algorithm is ensured by comparing the gas-to-oil ratio variation prediction to the H field data. The results are shown in Figure 5.2. The reservoir has only a small gas-to-oil ratio gradient, resulting in a small density change along the depth (3.4 % over 3000 ft). The reservoir

condition (~ 20000 psia and 200°F at 26151 ft depth) ensures that the system is far away from the critical and bubble points [12].

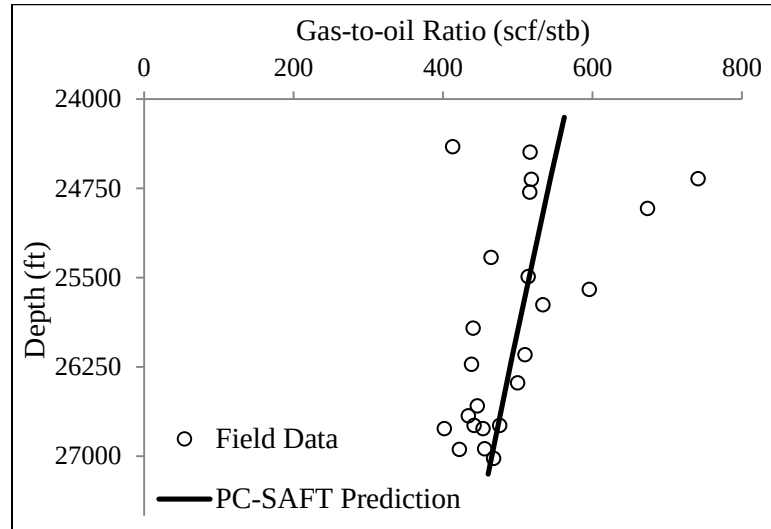


Figure 5.2. Variation of gas-to-oil ratio with depth in the H field.

Figure 5.3 shows the PC-SAFT and approximate analytical solution predictions of the slopes of crude oil optical density for the H field. The continuous lines are the predictions by PC-SAFT, and the broken lines are of analytical solution. A close match is observed between the predicted asphaltene concentration gradient and field data procured by down hole fluid analysis. The optical density measurements are performed with an infrared wavelength of 1070 nm and directly infer the asphaltene content in the system.

From the PC-SAFT-generated asphaltene compositional grading curve, it is observed that the asphaltene content varies by a factor of 2 over 2500 ft vertically. All zones belong to the same reservoir, because the respective PC-SAFT asphaltene gradient curves have similar slope resulting from bulk crude oil properties. The north part of M21A has a much lower asphaltene concentration than the other parts of M21A. This implies that the north part of M21A is disconnected from the M21A central and south

sands acknowledged by seismic and geochemistry data [142]. The M21A and M21B sands are the two primary reservoir sands. The M21B sand is in a different compartment than the M21A sands determined by formation pressure gradient and geochemistry fingerprinting of crude oil samples [142]. Thus, they are not in flow communication, and asphaltene compositional gradient analysis is consistent in this assessment. The wells along the curves are connected because of the equilibrated asphaltene.

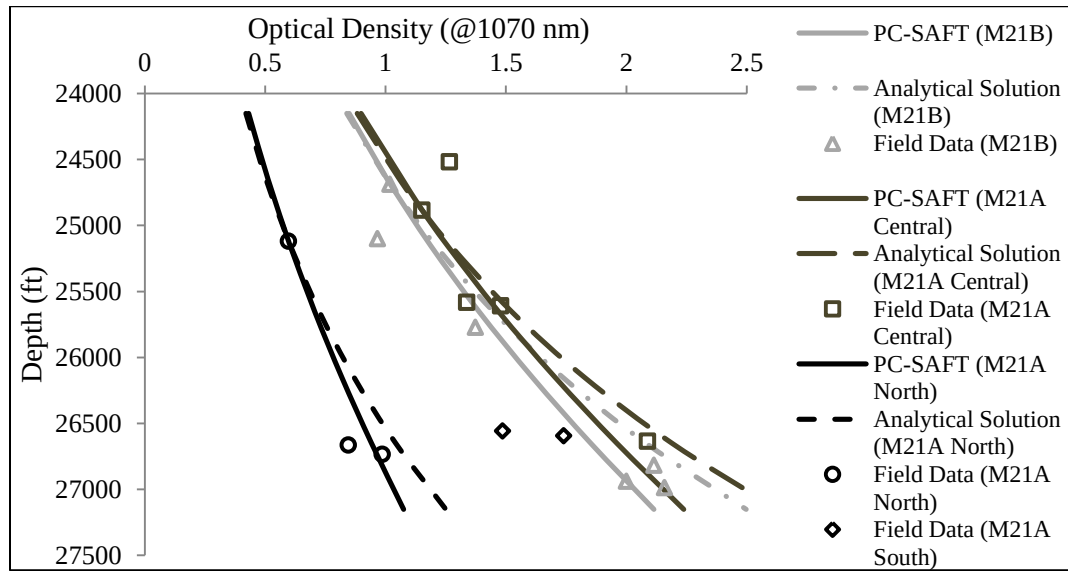


Figure 5.3. Optical density profile of crude oil H with depth in the H field.

The partial molar volume of asphaltene calculated by PC-SAFT is 1932 cm^3 with 0.1 % variation over the range of depth considered (3000 ft). Thus, the average spherical diameter of an asphaltene particle is 1.83 nm and is in good agreement with the literature [12]. The crude oil H from the H field at down hole conditions also satisfies the assumptions of the analytical solution: (i) Observed from Figure 5.2, the H field has a low gas-to-oil ratio gradient resulting in low crude oil density variations (3.4%) over the range of depth considered (3000 ft). (ii) The system is far away from the critical and bubble points. (iii) The asphaltene concentration is low enough (observed from

characterized crude oil H in Appendix C) to assume the asphaltene partial molar volume to be independent of the species concentration.

For each of the zones, analytical solution is plotted together with field data and PC-SAFT-generated asphaltene compositional grading. The results are observed as broken lines in Figure 5.3, showing the working of the simple analytical solution. Therefore, for any crude oil satisfying the above assumptions, the analytical solution can be used for an approximate estimate of the asphaltene compositional grading and sensitivity analysis of the gradient curves.

In curve M21B, the reference depth was 24687 ft. The deviation of analytical solution was only after ~25500 ft and is accounted for compressibility effects when far away from the reference depth. In curves M21A central and north, the reference depths are 24884 and 25120 ft, respectively. There is a closer agreement of M21A north analytical solution with PC-SAFT-generated asphaltene compositional grading throughout the considered depth. The asphaltene partial molar volume and density of live oil inputted into the analytical solution are nearly the average of the system, giving better results over the depth considered.

5.4.2 Field A

Equilibrium distribution of light crude oils in a reservoir is characterized by a large gradient of gas-to-oil ratio. The light crude oil considered here is from an onshore A field in the Middle East. The formation is mainly of carbonate rocks, with porosity ranging from 10 to 30 %. The A field is a northeast–southwest elongated domal anticline structure, 16 miles long and 6 miles wide, with 160 km² of closure. The field is thought to

result from pillows formed from movement of deeply buried Homruz salt. The faults are believed to have formed in response to salt piercement or compression forces because of the close proximity of the field to the orogenic zone [143].

The A field is subdivided into an upper high-permeability layer (40–400 mD) and a lower low-permeability layer (10–15 mD). Production first commenced from the upper layer, which became flooded with water during the course of time, leaving a large amount of oil in the lower layer unproduced. Later on, several wells were drilled in this layer to produce the unproduced crude. Two of such wells are X and Y, respectively. Thus, understanding the connectivity of X and Y wells is important for the enhanced production of crude oil through flooding processes.

With the successful incorporation of asphaltene as one of the characterized crude oil A components at down hole conditions, the compositional grading algorithm is employed to predict the continuous properties of fluid. The dimensionless concentration of asphaltene is plotted in terms of dimensionless optical density with the help of Beer–Lambert’s law for low-concentration species, resulting in Figure 5.4. The normalization of the asphaltene concentration for the black curve is with respect to well Y, and the normalization of the asphaltene concentration for the gray curve is with respect to well Z.

The A field oil being light in nature produces a high asphaltene compositional grading in the order of 1.6 over 300 ft of depth. From the PC-SAFT asphaltene compositional grading, wells X and Y can have flow communication in the reservoir because they fall on the same gradient curve. The formation pressure of wells X and Y is ~4000 psia, and the formation pressure of well Z is 2854 psia. Thus, well Z is not in flow

communication with wells X and Y, also corroborated by the PC-SAFT asphaltene compositional grading curve of well Y not passing through well Z. However, all wells belong to the same field because the slopes of corresponding asphaltene compositional gradient curves are similar, resulting from bulk crude oil properties.

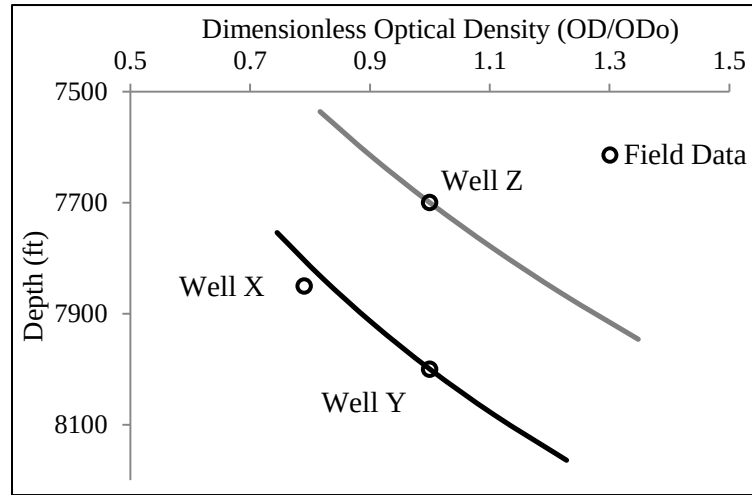


Figure 5.4. PC-SAFT-predicted asphaltene gradient in the A field.

The analytical solution cannot be applied for the A field because of high-density changes of 1.5 % over the range of depth considered (450 ft). Also, the partial molar volume of asphaltene (average = 1460 cm^3) is dependent upon depth (variation of 1.3 % for 450 ft depth).

5.5 Tar Mat

A tar mat is in general associated with paraffinic oils, because a high degree of compositional grading and asphaltene precipitation problems are chiefly related to paraffinic oils. Tar mat is differentiated from heavy oil in that tar mat is characterized by high oil saturation associated with high residual oil saturation during logging [144]. Fields A and H consisting of crude oils A and H respectively are considered for this study.

The PC-SAFT asphaltene compositional grading when extended to further depths to model the possibility of tar mat formation resulted in Figure 5.5 for field A. After a depth of ~9050 ft in the model, the asphaltene content suddenly increased from 15 wt % to 48 wt %. Asphaltene measurements of the tar mat samples report between 26 to 80 weight percent [145].

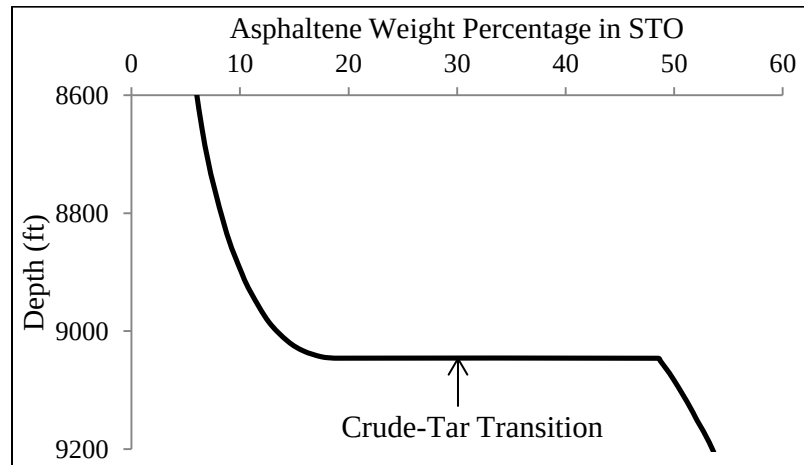


Figure 5.5. PC-SAFT prediction of tar mat in the field A consisting of crude oil A.

The high and sudden contrast of the asphaltene content represents the transition from oil leg to a tar mat and is analogous to gas–oil contact depths in a reservoir. Above 9000 ft asphaltene is stable in the oil even with increasing asphaltene content with depth. But by 9050 ft, asphaltene concentration increased to an extent of phase separation. Thus, the tar mat formed can be explained in terms of the transport of asphaltene in oil along chemical and gravitational potential gradients in the reservoir to the zone of asphaltene enrichment at the site of tar mat.

The PC-SAFT observed tar mat formation is in accordance with the field observation of tar mat depth (Figure 5.6) and the asphaltene content of the tar mat. Hence, the PC-SAFT model successfully predicted the tar mat occurrence depth from just

knowing the pressure, temperature and reservoir oil composition at a reference depth in the upper parts of the formation. Such a prediction is possible only with an equation of state, because along with asphaltene phase splitting the compressibility of oil needs to be taken into consideration. Even under valid assumptions, tar mat cannot be predicted by the approximate analytical solution because it does not implicitly take into account the coexistence of another phase.

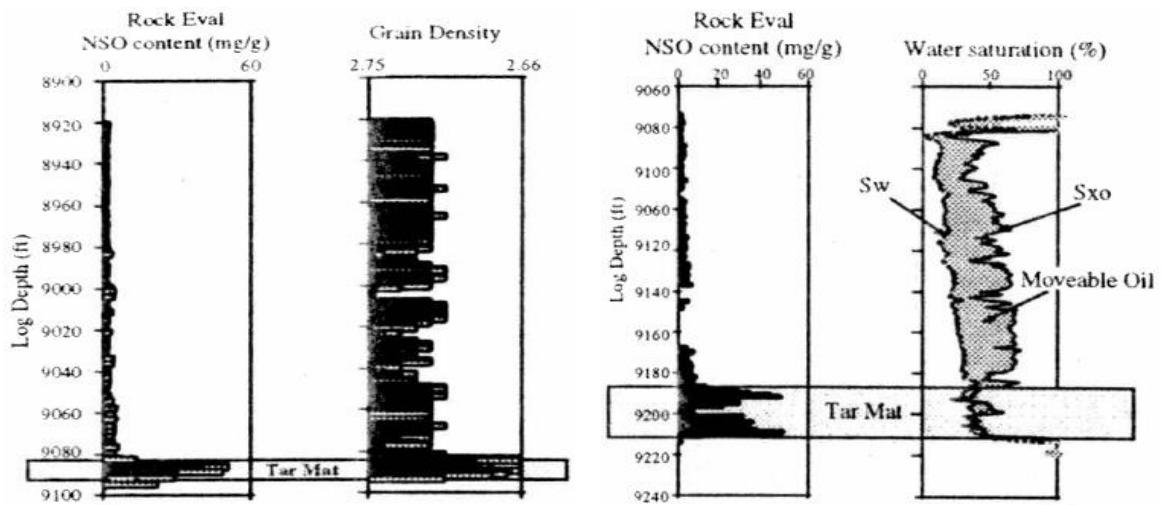


Figure 5.6. Different well logs from two different wells identifying the tar mat in field A.

5.5.1 Tar Mat Analysis

The H field asphaltene compositional grading curve, when extended to deeper depths using PC-SAFT, does not show any kink in the curve; indicating no presence of a tar mat (Figure 5.7) corroborated by the field operations. But the A field showed a sharp asphaltene compositional variation correlating to a tar mat. Recently Zuo et al. reported observing large asphaltene gradients even without destabilized asphaltene for a field in Middle East [146]. Thus a general analysis on when asphaltene show large compositional contrasts is needed.

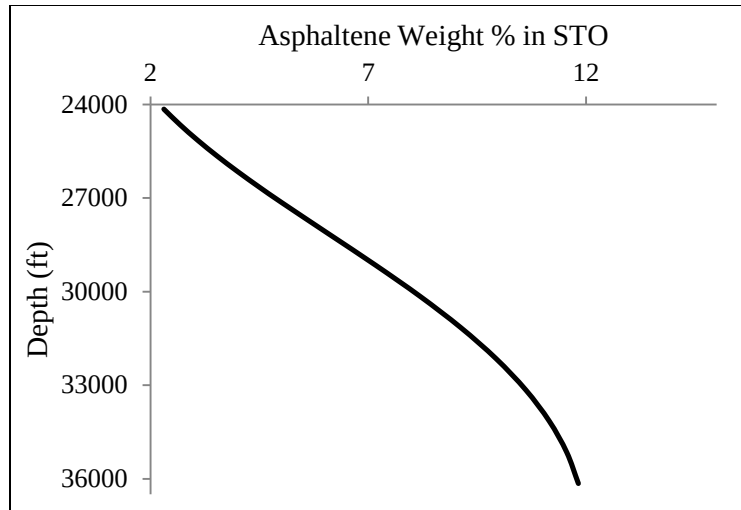


Figure 5.7. Asphaltene compositional variation with depth in the H field generated by PC-SAFT indicates no tar mat.

In the field A, PC-SAFT asphaltene compositional grading plots generated with different starting pressures at the reference depth, 8000 ft are plotted together in Figure 5.8. The sharp compositional contract represents tar mat formation depth where the crude oil is phase splitting into two liquid phases (asphaltene lean and rich phases) existing at equilibrium. The boundaries of these liquid-liquid phase separations when joined using the discontinuous black line represents the phase boundary and is analogues to pressure-vapor isotherms. Observed from Figure 5.8, as one approaches the critical point region on this composition-depth phase diagram, there exists sharp asphaltene compositional gradients even without phase transitions. Thus it is can be concluded that, there need not be phase separation to have large compositional gradients and, based on the system's instability to asphaltene the tar mat formation depth and the asphaltene content in a tar mat vary.

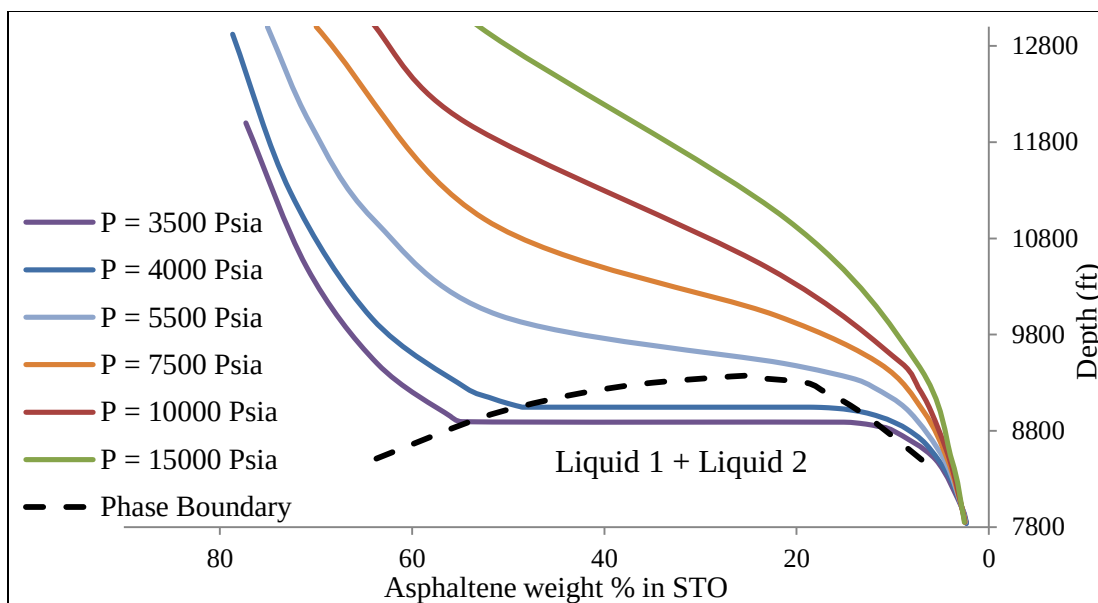


Figure 5.8. Asphaltene compositional grading isotherms with different starting pressures at the reference depth of 8000 ft. (Liquid 1: asphaltene lean phase, Liquid 2: asphaltene rich phase).

5.6 Chapter Summary

After the incorporation of asphaltene as one of the characterized crude oil components, isothermal asphaltene compositional grading is analyzed with the help of the successful algorithm presented in this chapter. A simple analytical model based on solution thermodynamics is also presented under valid assumed conditions. For both the reservoirs A and H, PC-SAFT-generated asphaltene compositional grading shows a close agreement with the field data and evaluated the compartmentalization of the reservoirs. The analytical solution is successfully applied to predict the asphaltene compositional grading in the H field.

A novel representation of the tar mat formation produced by asphaltene compositional grading is presented in the form of a composition–depth phase diagram.

This work successfully predicted the tar mat occurrence depth from just knowing the pressure, temperature, and reservoir oil composition in the upper parts of a formation. The transition depth from oil leg to tar mat was sudden because of asphaltene phase separation and is analogous to gas-oil contact depths. The tar mat formation depth and the asphaltene content in a tar mat vary based on the extent of asphaltene's instability in a crude oil.

Chapter 6. Asphaltene Deposition Experiments

Among the asphaltene flow assurance issues, the major concern because of asphaltene is its potential to deposit in reservoir, well tubing, flow lines, separators, and other systems along production lines causing significant production losses. Hence, the focus of this chapter is to understand the depositional tendency of asphaltene using a quartz crystal microbalance with dissipation measurements (QCM-D). The depositing environment is varied by changing system temperature, asphaltene polydispersity, solvent (asphaltene stability), depositing surface and flow rate.

6.1 Introduction

Knowledge on the deposition mechanism of asphaltene and the factors influencing it are important in many different domains of oil industry. Example, alteration of reservoir rock wettability due to adsorption of asphaltene [147], plugging of flow lines because of asphaltene deposit buildup [148], and refinery catalyst deactivation because of asphaltene adsorption at active sites [149]. Accordingly, appropriate mitigation techniques such as a suitable surfactant, coating material for surfaces exposed to asphaltene or operating conditions can be identified.

QCM-D experiments are performed in this chapter to study different depositional aspects of asphaltene from model oil systems. The quartz crystal microbalance is a highly sensitive equipment for detecting and quantifying the adsorption of a species and is been extensively used in the field of biomaterials, cell and molecular biology, cellulose, polymers, lipids, pharmaceutical, proteins, environmental and nanoparticles [150-158]. Few researchers have also used quartz crystal microbalance for investigating asphaltene adsorption kinetics.

Ekholm et al. used QCM-D to investigate the adsorption of asphaltene and resin on gold surface [159]. Their results showed that unlike resin, asphaltene are irreversibly adsorbed in multilayers from toluene and heptol (50/50 n-heptane in toluene) solutions. Xie and Karan studied kinetics and thermodynamics of asphaltene adsorption from toluene-heptane and toluene-pentane solutions on gold surface using a quartz crystal microbalance in a flow-cell arrangement [160]. The asymptotic analyses indicate an initial adsorption process controlled by the diffusion of asphaltene from bulk solution to adsorption surface. The thermodynamic free energy predictions by Xie and Karan suggested that asphaltene would adsorb preferentially in the order of gold > stainless steel > aluminum surfaces. More recently, Rudrake et al. used a combined quartz crystal microbalance and X-ray photoelectron spectroscopy to investigate asphaltene-metal interactions [34]. The fractional coverage data for Cold Lake asphaltene on gold surface followed Langmuir (type-I) isotherm. Farooq et al. performed a study for the desorption of asphaltene into low saline aqueous solutions from a saturated silica surface [161].

Although previous researchers have investigated asphaltene adsorption on metal surfaces, there is no data on the effect of temperature on the kinetics of asphaltene adsorption. Also, the effect of flow rate has not been fully understood. Many of the researchers just reported the maximum amount of mass adsorbed within the experimental time scale. Some of them failed to incorporate the viscoelastic behavior of the asphaltene deposit.

The objective of this chapter is to provide information on the deposition tendency of asphaltene from model oil systems in different depositing environments. To investigate the effect of temperature, experiments at 20, 40, 60 and 80 °C are done using a

temperature controlled chamber. To study the effect of asphaltene polydispersity, both n-pentane and n-heptane extracted asphaltene are used for adsorption. To observe the impact of asphaltene stability on its deposition, heptol solutions with varying heptane to toluene ratios are used as solvents. To understand the interactions between asphaltene and various surfaces, quartz crystals coated with gold, carbon steel and iron oxide are used. Flow rate is varied by 100 orders of magnitude to check the effect of convective transfer on the asphaltene adsorption process. A novel method proposed by Vargas for the detection of asphaltene precipitation onset is used here [162].

6.2 Experimental Procedures

This section describes the methods for asphaltene extraction, asphaltene model oil solution preparation, asphaltene adsorption experiments using QCM-D, atomic force microscopy and determination of asphaltene precipitation onset. All the reagents used are HPLC grade procured from Sigma-Aldrich.

6.2.1 Sample Preparation

6.2.1.1 Asphaltene Extraction

The crude oil A with a long history of asphaltene depositional problems during oil production is used for asphaltene samples extraction. The following asphaltene extraction procedure is employed for all the asphaltene precipitating agents used in this chapter.

The oil sample is added to n-alkane in 1:40 vol/vol of crude oil to asphaltene precipitating agent. The mixture is prepared in a dark beaker and sonicated for 45 minutes using VWR Branson Sonifier. Temperature is maintained constant during the

sonification process in order to maintain the n-alkane diluted crude oil equilibrium. The mixture is allowed to age for two days in a dark and cool corner of the laboratory with a 45 minute sonification each day. After aging, the solution is vacuum filtered using a 0.2 μm nylon membrane filter. The filter cake is installed in a soxhlet apparatus. The solvent used in the round bottomed flask of the soxhlet apparatus is the same as the asphaltene precipitating agent, which was added to the oil sample in the first stage of extraction. The system is run at solvent boiling temperature until the run down effluent is colorless. The soxhlet apparatus is allowed to cool, and then run with toluene as the solvent to dissolve the now impurity free asphaltene remaining in the filter cake. The system is continued running till the run down effluent is colorless.

The solution of toluene with asphaltene is transferred to a beaker with a wide opening and a known weight. The beaker is then left open in an oven at 80 °C for one day to evaporate toluene. The amount of pure asphaltene can be obtained by knowing the weight of beaker plus asphaltene. Asphaltene extracted using n-pentane as the asphaltene precipitating agent is termed as n-C₅ asphaltene. Similarly, n-C₇ asphaltene is defined.

6.2.1.2 Asphaltene Solution Preparation

To prepare the base asphaltene solution, 100 mL of toluene is added to the extracted asphaltene in the beaker. The mixture is stirred with a glass rod, and then sonicated using Fisher Scientific Sonication Bath (FS60) for 20 min. The mixture is allowed to equilibrate for one day, and then filtered using a 0.2 μm Nylon filter paper to remove the undissolved asphaltene particles. After filtration, the filter paper is dried and weighed to calculate the actual mass of asphaltene in the solution. The filtered solution is transferred into a volumetric flask and a required amount of toluene is added to make a

base solution of known concentration. The base solution is stored in a dark and cool place for future use. Each time before starting the QCM-D experiment, a portion of the base solution is diluted to the required concentration for the experiment. The prepared experimental sample is sonicated for 20 minutes using the sonication bath, and then equilibrated for 10 minutes before injecting into the QCM-D setup.

6.2.2 Asphaltene Adsorption Experiments

6.2.2.1 Quartz Crystal Microbalance Setup

The QHTC extreme temperature chamber 101 (Q-sense AB, Sweden) with a working temperature of 4 to 150 °C is used in this study. The chamber includes a Flow Module 401 made of Titanium. AT-cut sensor crystal (5 MHz) with a diameter of 14 mm is used inside the flow module. Flow lines and pump tubing are made of Teflon. Temperature and solvent resistant o-rings and sealing gaskets are used in the experiments. The instrument monitors in real time the series resonant frequency and dissipation of the freely oscillating crystal by numerically curve fitting the decay voltage to an exponentially damped sinusoidal when the power is disconnected.

6.2.2.2 Procedure

The system is assembled with a clean sensor crystal mounted inside the flow module. The absolute dissipation values are checked in air to make sure that the sensor crystal is rightly mounted and is not damaged. Then the asphaltene free solvent is injected into the system using a peristaltic pump. Liquid is introduced through tubing with 0.75 mm internal diameter. Residence time is around 7 minutes for the liquid before reaching the sensor crystal. The system is left to stabilize in the solvent to establish a

baseline of the measurement. The system is considered stable if the changes in the frequencies are less than 1 Hz in 20 min. Then the main solution, asphaltene plus solvent, is injected at a constant flow rate. To ensure homogenous oil-asphaltene slurry system, samples beyond the onset of asphaltene precipitation are continuously sonicated prior to injection. The instrument records frequencies and dissipations at different harmonics for the sensor crystal. Then, the data are processed with Q-tools software from Q-sense.

In this chapter, a solution of asphaltene in toluene or n-heptane + toluene (heptol) is used as the model oil system. A constant asphaltene concentration of 100 ppm is used for all the experiments, because the effect of this parameter has been widely investigated by others [159, 160]. Each experiment is repeated three times, and the average results are presented in this chapter.

6.2.2.3 Cleaning Procedure

A chemical treatment procedure is used to remove the asphaltene particles from gold crystal surface. After the experiment, the sensor crystal is placed in a crystal holder and sonicated in toluene using a sonication bath for 20 min. Then, it is left in hot toluene for half an hour. After that, the sensor crystal is dried with nitrogen and put through UV light ozone chamber for 1 hour. After UV light, it is placed in a crystal holder and immersed in a heated cleaning solution for 20 minutes. The cleaning solution consists of a 5:1:1 volume ratio mixture of deionized water, ammonium hydroxide and hydrogen peroxide heated to a temperature of 75 °C. After 20 minutes, the sensor crystal is rinsed with deionized water 3 times, and then dried with nitrogen gas. The dried sensor crystal is placed once again under the UV lamp for ultra violet ozone treatment for 1 hour. In this procedure the duration of each step is increased in comparison to the cleaning procedure

used by other researchers [34, 163], because the asphaltene particles used in the current study are very sticky and could not be easily removed using the standard procedure for gold crystal surface cleaning.

For carbon steel sensor, UV ozone treatment could not be used because it would break the carbon bond to the crystal surface. So, after sonicating the crystal in toluene for 20 min and drying under nitrogen, a 2 wt% Hellmanex® III solution for 40 min at 35 °C is used. Then, the sensor crystal is rinsed with deionized water 3 times and dried under nitrogen gas. The same cleaning procedure used for carbon steel crystal is also applied for iron oxide sensor crystal. All sensor crystals are provided by Q-sense.

To make sure that the sensor crystal surface is clean using the above procedures, response of the sensor to 1 wt% of sodium dodecyl sulfate in deionized water is measured before first use and after cleaning procedure (after experiment). Using the proposed procedures, responses of the sensor to sodium dodecyl sulfate solution are very close before and after surface cleaning. The life span of each sensor crystal is 4 to 5 experimental runs.

The flow module is also cleaned after each test. The module is flushed with toluene, dried in air, and then cleaned with 1 wt% sodium dodecyl sulfate in deionized water. Finally the module is rinsed with deionized water and dried with nitrogen gas.

6.2.3 Sample Analysis

6.2.3.1 Asphaltene Precipitation Onset Measurement

The establishment and details of the procedure can be found elsewhere [164]. The working mechanism is only briefly reviewed here for my specific case of n-

heptane/toluene-asphaltene mixtures. Test tubes containing asphaltene model oils with different ratios of n-heptane and toluene are prepared, starting from pure toluene, 1:9 (10 vol% heptane), 2:8, etc. The test tubes are shaken vigorously by hand, and allowed to stand undisturbed for 1 hour. Then the test tubes are centrifuged at 5,000 rpm for 10 minutes in Eppendorf centrifuge 5804. 1 mL of the supernatant liquid is taken and diluted with 4 mL of toluene. Then the absorbance at UV-Vis wavelength of 500 nm is measured, using toluene as the blank. Finally, the values of absorbance as a function of the volume fraction of n-heptane are plotted. The sudden deviation in the data points corresponds to the volume fraction of n-heptane at the precipitation onset.

The working principle behind the procedure is that when asphaltene are unstable even to the slightest extent in the oil, they are removed by centrifugation and the optical properties of the remaining fluid changes. Thus, precipitation independent of aggregation is measured in the current asphaltene onset determination procedure. Previous researchers used direct methods such as gravimetric technique, filtration experiments, microscopy, and near infrared to determine the asphaltene precipitation onset. Such methods require a minimum asphaltene particle size to be detected. Thus precipitation followed by aggregation is involved, and one can find various precipitation onsets at different aging times in direct methods.

Based on the results obtained from the current indirect method, it is observed that changing the aging time has no effect on the final result for precipitation onset. In other words, pure onset of asphaltene precipitation is obtained without considering aggregation effects. Figures 6.1 and 6.2 show the results of onset determined at 500 nm wavelength and at aging time of 1 hour and 24 hours, respectively. The sample consists of 10 volume

percent of crude oil A and 90 volume percent of heptol. For this system the determined precipitation onset is 71.03 and 70.98 volume percent of n-heptane for aging time of 1 hour and 24 hours, respectively, which shows the independency of asphaltene precipitation onset to the aging time.

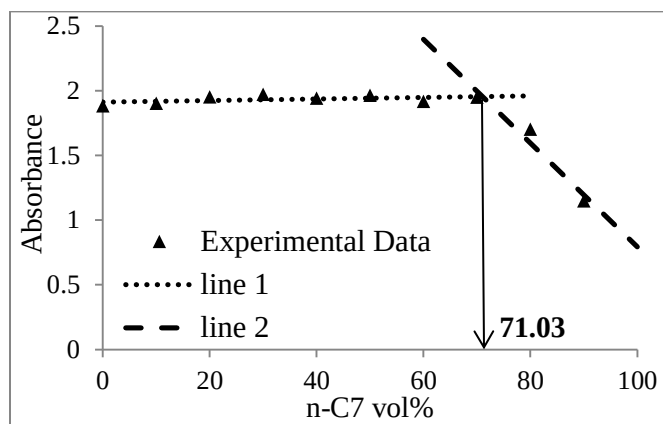


Figure 6.1. Precipitation onset measurement at 500 nm UV-Vis wavelength and after 1 hr.

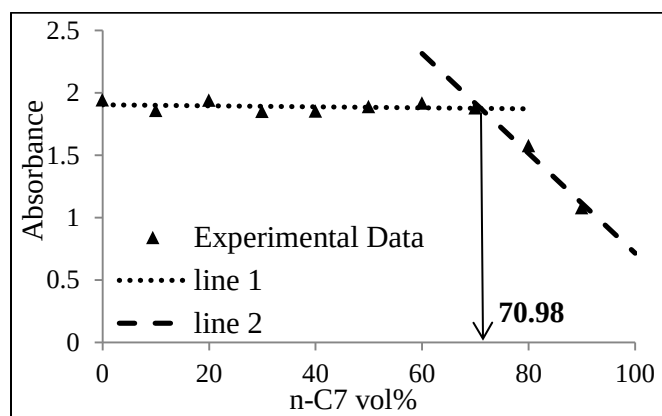


Figure 6.2. Precipitation onset measurement at 500 nm UV-Vis wavelength and after 24 hrs.

6.2.3.2 Atomic Force Microscopy

Images of the asphaltene deposited sensor crystal are captured using a NanoScope IIIA atomic force microscope (AFM). Imaging is performed in air at room temperature using tapping mode. The images are scanned at $5 \times 5 \mu\text{m}^2$. Diameter of the adsorbed species is analyzed using the NanoScope Analysis software.

6.3 Frequency and Dissipation Changes

There can be three main contributions to the frequency and dissipation of the sensor crystals because of the adsorbed film. (a) mass loading, (b) liquid loading and (c) liquid trapping. The equations describing each contribution are.

Mass loading [165]:
$$\Delta f_{\text{adsorption}} - \frac{2nf_0^2}{\rho_q v_q} \frac{\Delta m}{A} = -\frac{n\Delta\Gamma}{C} \quad (6.1)$$

Liquid loading [166]:
$$\Delta f_{\text{liquid loading}} = -\sqrt{\frac{n}{\pi}} \frac{f_0^{1.5}}{\rho_q v_q} (\sqrt{\rho_l \eta_l} - \sqrt{\rho_s \eta_s}) \quad (6.2)$$

$$\Delta D_{\text{liquid loading}} = -\frac{1}{\sqrt{n\pi}} \frac{2f_0^{0.5}}{\rho_q v_q} (\sqrt{\rho_l \eta_l} - \sqrt{\rho_s \eta_s}) \quad (6.3)$$

Liquid trapping [167]:
$$\Delta f_{\text{liquid loading}} = -\frac{2f_0^2}{\rho_q v_q} h_l (\rho_l - \rho_s) \quad (6.4)$$

Where f_0 is the fundamental resonant frequency ($f_0 = 5 \times 10^6 \text{ Hz}$), n is the overtone number ($n = f_n/f_0 = 1, 3, 5, 7, 9, 11$ and 13), Δm is the adsorbed mass, $\Delta\Gamma$ is the adsorbed mass density, A is the active area of the sensor crystal (0.785 cm^2), ρ_q is the specific density of quartz (2650 kg/m^3), v_q is the shear wave velocity in quartz (3340 m/s), $v_q = \sqrt{\mu_q/\rho_q} = 2f_0 h_q$, μ_q is the shear modulus of quartz ($2.947 \times 10^{10} \text{ Pa}$), h_q is the thickness of the quartz crystal ($3.37 \times 10^{-4} \text{ m}$), h_l is the thickness of trapped liquid, and C is the constant of the quartz crystal ($17.7 \text{ ngHz}^{-1} \text{ cm}^{-2}$ for a 5 MHz crystal). ρ is density, η is viscosity, and subscripts s and l refer to the solvent and liquid mixtures, respectively.

When asphaltene particles are adsorbed onto the sensor crystal, it can be treated as an equivalent mass change of the crystal itself. An increase in mass, Δm induces a proportional shift in frequency, Δf . This linear relationship between Δm and Δf was first

demonstrated by Sauerbrey in equation 6.1. The relationship is valid when the following conditions are fulfilled.

- The adsorbed mass is distributed evenly over the sensor crystal.
- Δm is much smaller than the mass of the sensor crystal itself ($< 1\%$).
- The adsorbed mass is rigidly attached, with no slip or inelastic deformation in the added mass due to the oscillatory motion.

The last condition is valid when the frequency decreases in proportion to the true mass of the adsorbate with no change in energy dissipation, ΔD . The characteristics for a rigid film are.

- All harmonics overlay in Δf responses.
- ΔD is small (more specifically: $\Delta D/\Delta f \ll 0.4 \times 10^{-6} \text{ Hz}^{-1}$) [168].

When a sensor crystal is operated in Newtonian liquid phase (eg. crude oil in heptol), the liquid becomes coupled to the crystal oscillation and the increase in density and/or viscosity of the medium leads to a rise in both frequency and dissipation factors termed as liquid loading [169]. Additional shifts may arise with surface roughness because of liquid trapping by interfacial cavities and pores [170, 171]. This contribution is usually small, and liquid trapping can be eliminated by using smooth surfaces [163]. Both liquid loading and liquid trapping are made insignificant for the current study by using model oil (asphaltene in heptol) and smooth sensor crystal surface respectively.

In some cases, the adsorbed film does not show a rigid behavior and the following characteristics can be seen.

- Spreading of the overtones in Δf responses.
- ΔD is high (more specifically: $\Delta D/\Delta f$ comparable to $0.4 \times 10^{-6} \text{ Hz}^{-1}$).

These characteristics show a viscoelastic (soft) film. In this case, viscoelastic behavior can be characterized by measuring the resonance curves at multiple frequencies according to the Voigt model [172]. In the current asphaltene study, all experiments showed viscoelastic behavior for the adsorbed layer from the model oil system onto the sensor crystal surface. Figure 6.3 presents frequency and dissipation changes versus time for the adsorption of n-C₅ asphaltene from asphaltene + toluene system onto a gold coated quartz crystal surface. In Figure 6.3, Δf and ΔD represent an adsorbed viscoelastic film.

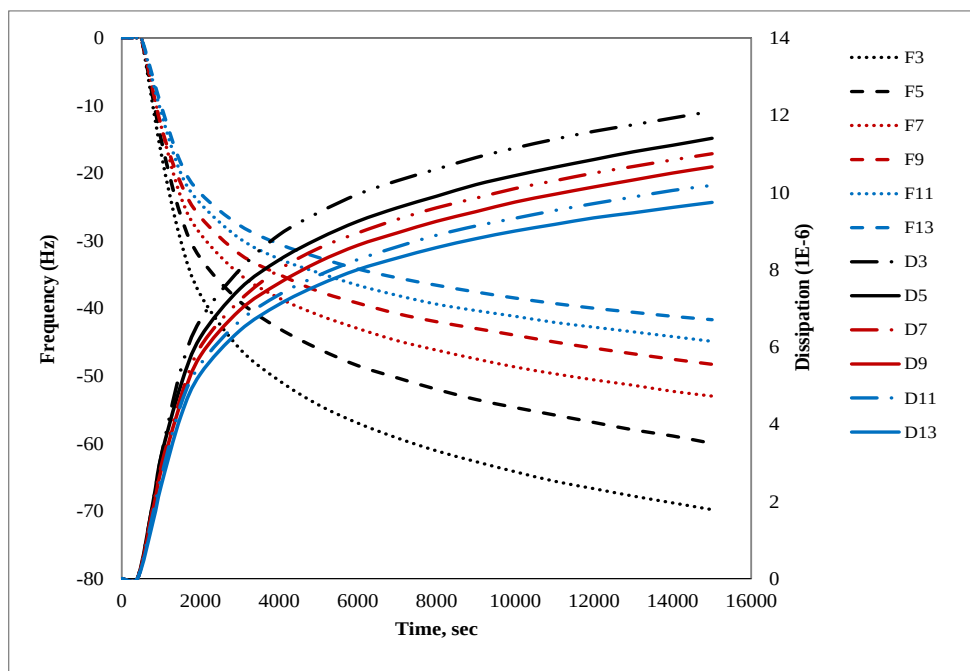


Figure 6.3. Frequency and dissipation changes versus time for the adsorption of n-C₅ asphaltene from asphaltene + toluene system onto a gold coated quartz crystal surface.

Voinova et al. derived the general solution of a wave equation describing the dynamics of two-layer viscoelastic polymer materials of arbitrary thickness deposited on

quartz surfaces in a fluid environment. Within the Voigt model of viscoelastic element, Voinova et al. calculated the acoustic response of the system to an applied shear stress. The Voigt model assumptions are.

- A laterally homogeneous and evenly distributed film.
- The bulk fluid is Newtonian.
- The adsorbed layer couples perfectly to the sensor (no slip).
- The observed signal is only due to the film.

The necessary input parameters for using Voigt model are.

- Δf and ΔD from different overtones.
- Deposit layer density.
- Solvent density and viscosity (pure solvent without the solute used for adsorption).

The Voigt model, available in the Q-tools software from Q-sense, is used in this chapter for viscoelastic modeling of frequency and dissipation changes. The resultant mass and viscosity are treated as experimental data like all other QCM-D experiments in literature.

6.4 Accuracy of Voigt Viscoelastic Modeling

To verify the accuracy of viscoelastic modeling results, atomic force microscopy is applied to find the thickness of the adsorbed layer on the sensor crystal surface after the experiment. For the same experiment, Figures 6.4 A and B show the viscoelastic modeling result for the thickness of the adsorbed asphaltene layer, and AFM image for

the asphaltene deposited surface of gold coated quartz crystal respectively. This QCM-D experiment was run with n-C₅ asphaltene in toluene at 80 °C and 80 µL/min flow rate. Comparison of Figures 6.4 A and B show that viscoelastic modeling result is in reasonable agreement with AFM result for the adsorbed layer thickness. It can also be seen from Figure 6.4B that the adsorbed mass is distributed uniformly on the surface of the sensor crystal except for a few locations. High thickness at these few locations is because of the dust particles depositing on the gold crystal surface during the transfer of sensor crystal from QCM-D setup to AFM apparatus.

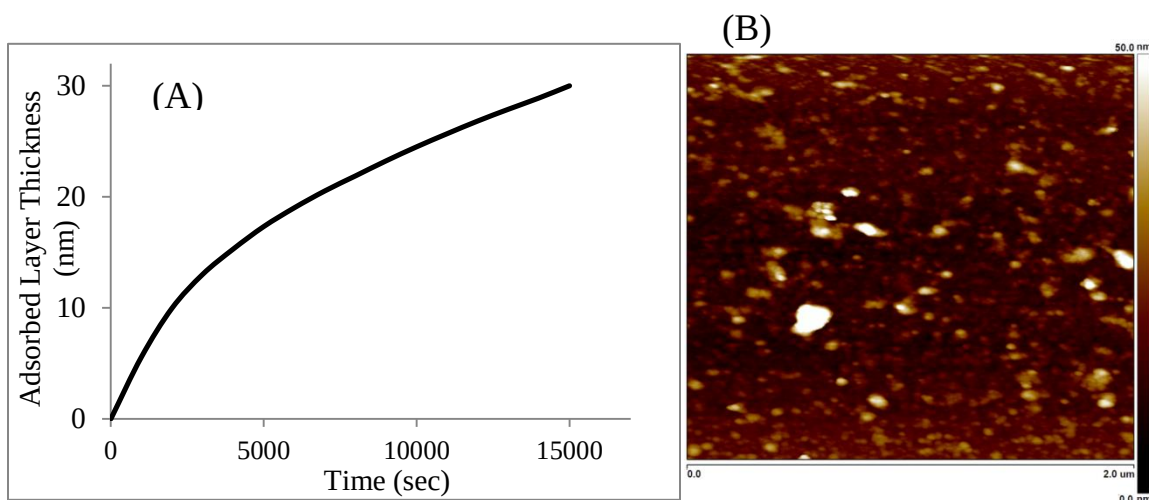


Figure 6.4. Thickness of the adsorbed layer from n-C₅ asphaltene + toluene system onto a gold crystal surface versus time at 80 °C and 80 µL/min flow rate using (A) Q-tools (B) AFM.

6.5 Temperature

Figure 6.5 presents the effect of temperature on the amount of adsorbed mass from n-C₅ asphaltene in toluene onto a gold crystal surface versus time at a constant flow rate of 80 µL/min. The asphaltene at all the four temperature is stable in the solution. It can be seen from Figure 6.5 that the maximum adsorbed mass after 4 hours is increasing

when the temperature increases from 20 to 80 °C. As temperature increases the solution viscosity decreases, and so both temperature increase and viscosity decrease will result in a higher diffusion coefficient of the asphaltene particles in model oil. A higher diffusion coefficient will cause a higher amount for mass adsorbed, because the adsorption is mainly controlled by diffusion at long times as discussed by Tavakkoli et al. [173].

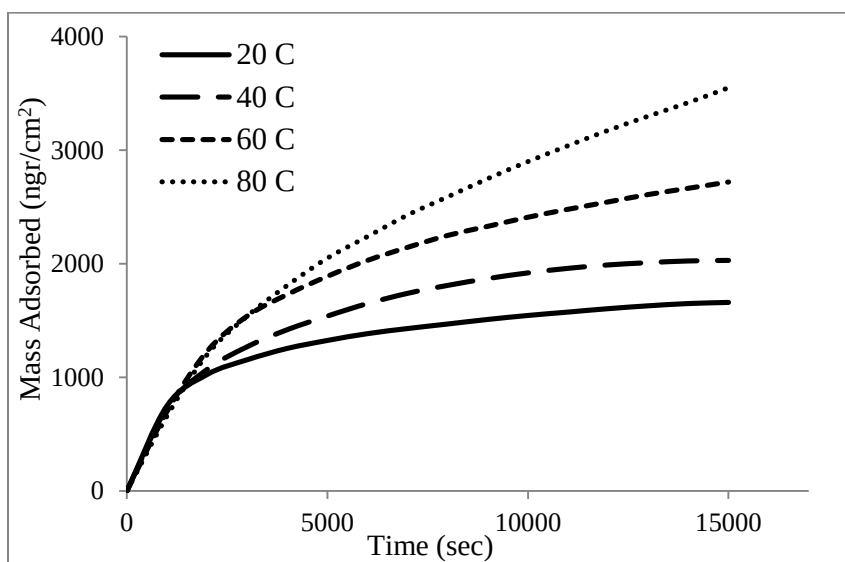


Figure 6.5. Effect of temperature on the amount of adsorbed mass from n-C₅ asphaltene + toluene system onto a gold crystal surface versus time at 80 μ L/min flow rate.

An interesting observation in Figure 6.5 is that for the temperatures of 20 and 40 °C the mass adsorbed reaches equilibrium within the experimental time scale. But, for 60 and 80 °C, saturation plateaus are not observed in the same time scale. Figure 6.6 shows the effect of temperature on viscosity of adsorbed mass from n-C₅ asphaltene in toluene onto a gold crystal surface versus time at a constant flow rate of 80 μ L/min. As expected, the viscosity of the deposit is decreasing when temperature increases from 20 to 80 °C, but is always less than 1 cP. The viscosity value is small, because the adsorbed mass consists of asphaltene molecules and not bulk asphaltene. Viscosity of the adsorbed layer

at 60 and 80 °C does not reach an equilibrium value because the total mass adsorbed at 60 and 80 °C does not reach equilibrium within the experimental time scale of 4 hours.

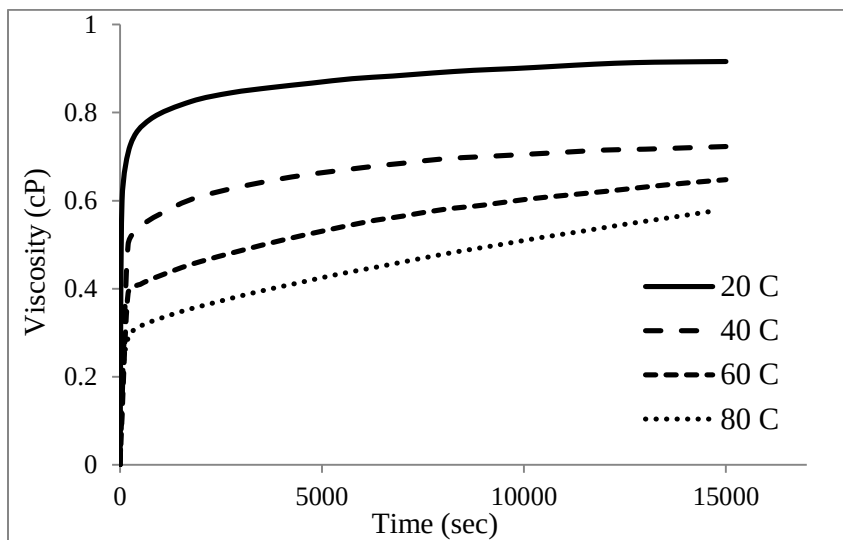


Figure 6.6. Effect of temperature on the viscosity of adsorbed mass from n-C₅ asphaltene + toluene system onto a gold crystal surface versus time at 80 µL/min flow rate.

6.6 Asphaltene Polydispersity

To investigate the effect of asphaltene polydispersity, model oil solutions with n-C₅ asphaltene and n-C₇ asphaltene, each at 100 ppm in toluene are used for adsorption at 80 µL/min flow rate onto a gold coated quartz crystal at 20 °C. Figures 6.7 and 6.8 present the effect of asphaltene polydispersity on the amount of adsorbed mass and viscosity of the adsorbed layer, respectively, from the two model oil systems. From Figure 6.7 it is observed that the maximum amount of mass adsorbed at equilibrium for n-C₅ asphaltene is much more than n-C₇ asphaltene, and the n-C₇ asphaltene mass adsorbed reaches equilibrium much sooner than n-C₅ asphaltene. This shows that C₅₋₇ asphaltene fraction plays an important role in the adsorption of asphaltene onto a gold surface. From Figure 6.8, it can be observed that the adsorbed n-C₇ asphaltene viscosity

is higher than n-C₅ asphaltene viscosity which is in line with the fact that n-C₇ asphaltene are heavier with higher molecular weight than n-C₅ asphaltene.

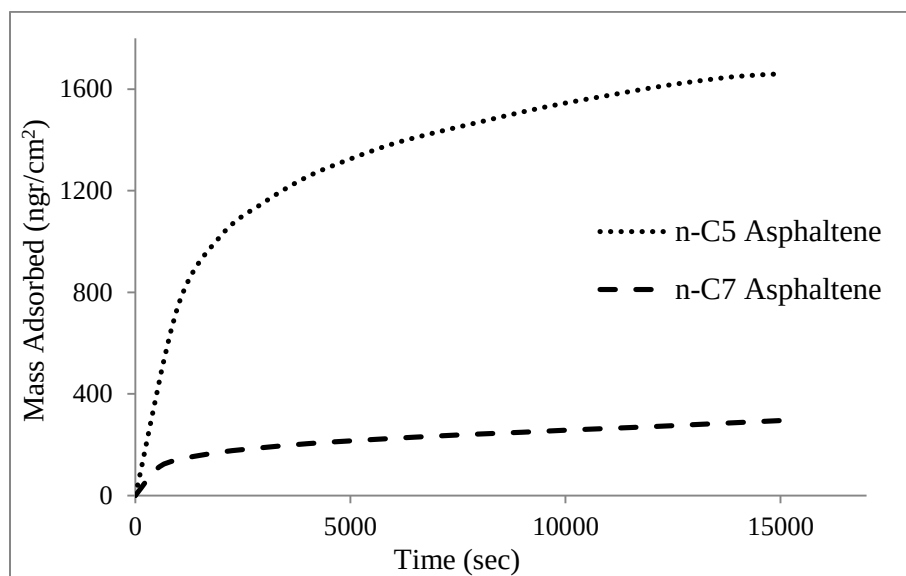


Figure 6.7. Amount of adsorbed mass from model oil system onto a gold crystal surface versus time at 20 °C and 80 $\mu\text{L}/\text{min}$ flow rate.

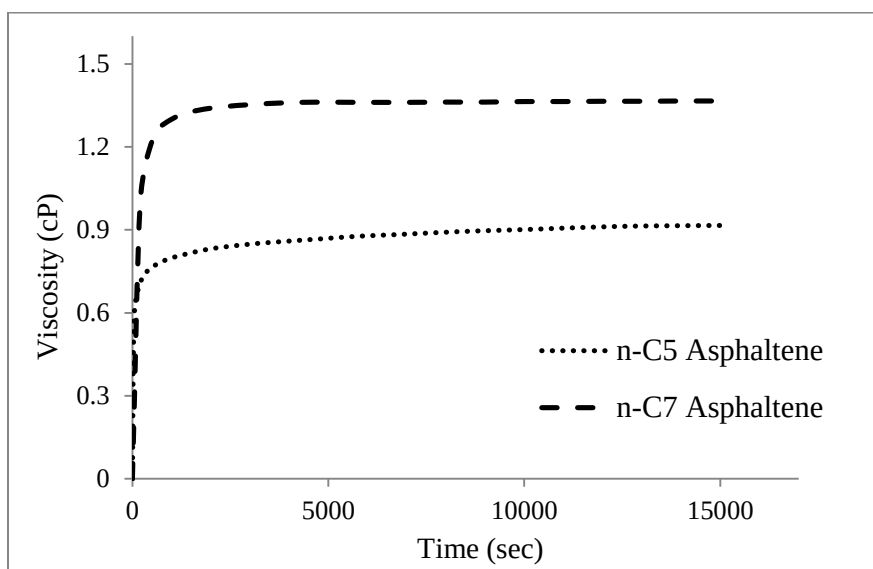


Figure 6.8. Viscosity of the deposited mass from model oil system onto a gold crystal surface versus time at 20 °C and 80 $\mu\text{L}/\text{min}$ flow rate.

6.7 Solvent (Asphaltene Stability)

To understand the effect of solvent on the amount of adsorbed mass, heptol model oil systems with a constant asphaltene concentration of 100 ppm are used. To find the onset of precipitation, the procedure described in *Asphaltene Precipitation Onset Measurement* section is applied. Figure 6.9 presents the absorbance as a function of heptane volume percent for UV-Vis wavelength of 500 nm, and using toluene as the blank. The intersection of two straight lines which pass through the data points shows the volume percent of n-heptane at precipitation onset. For the model oil used in this chapter (100 ppm of n-C₇ asphaltene in heptol), the precipitation onset happens near 53.32 volume % of n-heptane based on the results obtained from Figure 6.9.

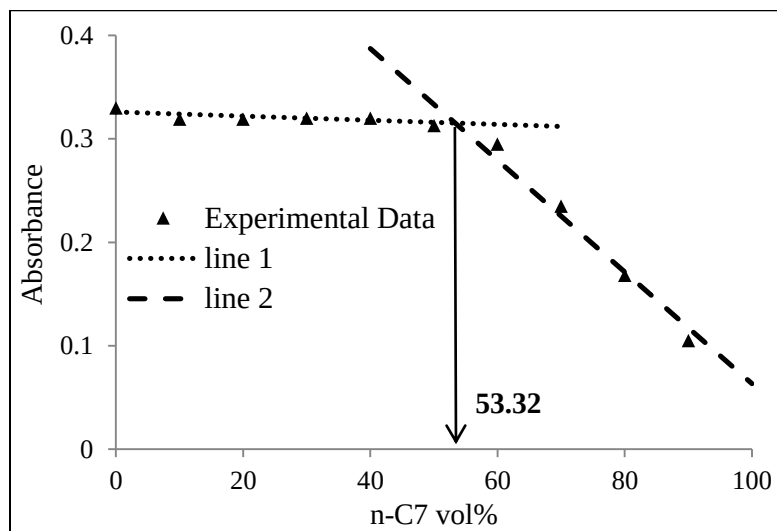


Figure 6.9. Precipitation onset measurement at 500 nm UV-Vis wavelength.

Using different UV-Vis wavelengths produced almost same result for the volume percent of n-heptane at precipitation onset. Figures 6.10 and 6.11 present the absorbance at UV-Vis wavelengths of 300 and 700 nm, respectively, as a function of heptane volume percent. Based on the results obtained from Figures 6.10 and 6.11, the precipitation onset

happens around 52.43 and 52.53 volume percent of n-heptane, respectively, which are very close to the value obtained at UV-Vis wavelength of 500 nm.

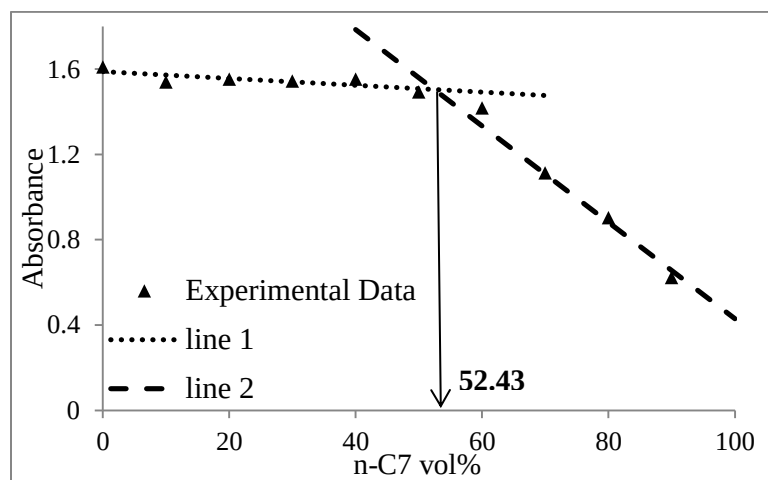


Figure 6.10. Precipitation onset measurement at 300 nm UV-Vis wavelength.

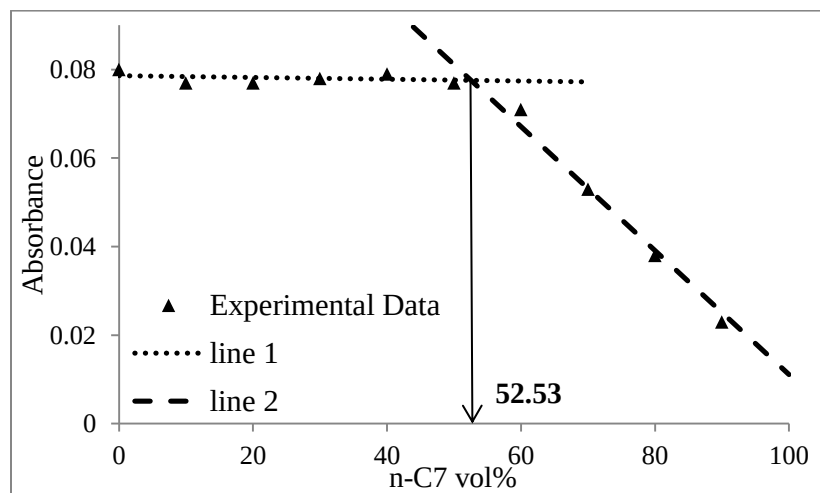


Figure 6.11. Precipitation onset measurement at 700 nm UV-Vis wavelength.

Figure 6.12 shows the adsorption of 100 ppm n-C₇ asphaltene from heptol solutions with different volume fractions of heptane and toluene. No saturation plateau is observed for heptol 50:50 and 75:25 within the experimental time scale. Based on the experimental results, when the ratio of heptane to toluene increases, the amount of

corresponding mass adsorbed increase up to a certain ratio and decrease beyond that. This maximum amount of asphaltene adsorption is occurring for a heptol solution with equal amounts of heptane and toluene, and is near the asphaltene precipitation onset for our model oil system. After precipitation onset, asphaltene aggregate forming larger particles which can pass through the sensor crystal surface without depositing because of convective transfer.

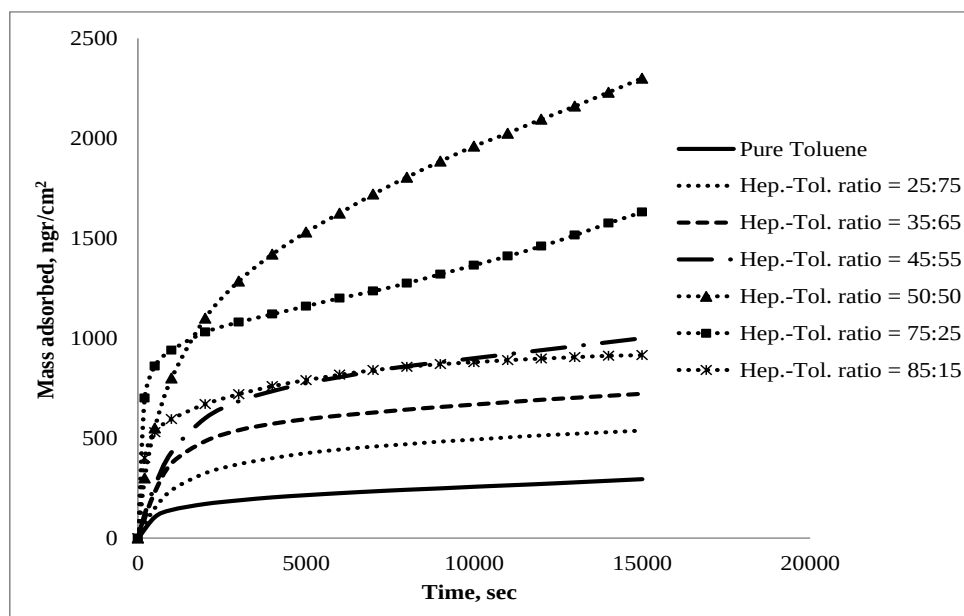


Figure 6.12. Effect of solvent on the amount of adsorbed mass from n-C₇ asphaltene + heptol systems onto a gold crystal surface versus time at 20 °C and 80 μ L/min flow rate.

6.8 Depositing Surface

To investigate the interaction between asphaltene and pipeline material, carbon steel and iron oxide sensor crystals are used. Many pipelines used for crude oil transport are made of carbon steel. Iron oxide presents the case of rust, and can provide an insight on the change in asphaltene deposition behavior because of a rusted pipeline compared to a new steel pipeline.

Figure 6.13 shows the amount of adsorbed mass from n-C₅ asphaltene + toluene system onto gold, iron oxide and carbon steel crystals versus time at 20 °C and 80 µL/min flow rate. It can be observed from Figure 6.13 that when a steel pipeline is rusted the mass adsorbed during initial stages increases, but it shows a decrease in long run. Both carbon steel and iron oxide surfaces represent more mass adsorbed in comparison to gold surface.

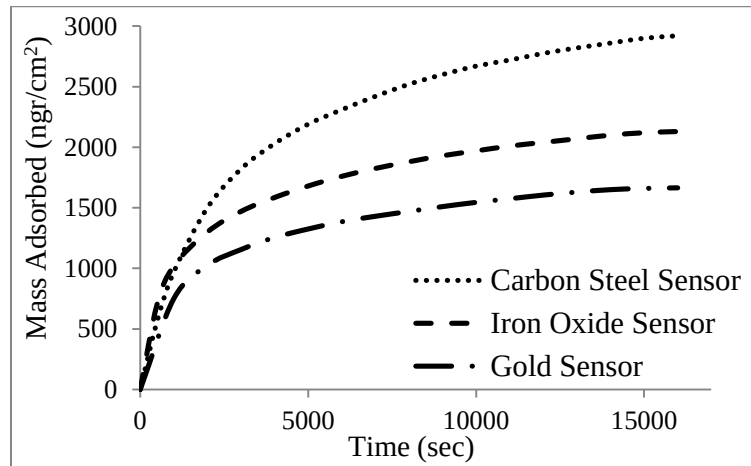


Figure 6.13. Adsorbed mass amount from n-C₅ asphaltene + toluene system onto different surfaces versus time at 20 °C and 80 µL/min flow rate.

6.9 Flow Rate

QCM-D experiments are performed at various flow rates to check the effect of convective transfer on asphaltene adsorption process. The results are plotted in Figure 6.14. It can be observed from Figure 6.14 that at long times, increase of flow rate cause more adsorbed mass on the sensor crystal. Increase in flow rate increases the wall shear rate which is against the particle deposition on the sensor crystal. But at the same time, the sensor crystal is provided with more amounts of asphaltene and the net result of these two effects causes more mass adsorbed on the sensor crystal. In a wellbore/pipeline with

high concentration of asphaltene in the bulk, the deposition is not limited by the availability of asphaltene and only the effect of shear rate is dominant with changes in flow rate. In such cases, an increase in flow rate decreases the amount of asphaltene deposited.

Also observed from Figure 6.14, at higher flow rates the adsorption curve reaches equilibrium sooner than at lower flow rates. At very long times and at high enough flow rates, the rate of adsorption is independent of the flow rate. At very high flow rates (flow rates higher than 2.6 ml/min) the adsorption curves almost overlap, which means there is no dependency to flow rate for all times starting from initial time scale.

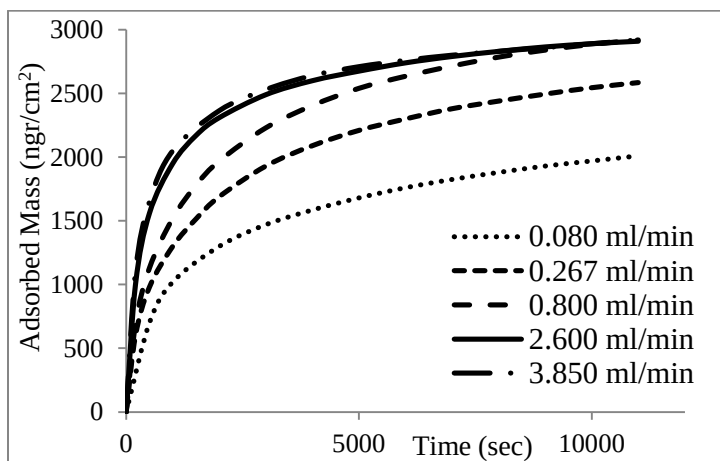


Figure 6.14. Effect of flow rate on the amount of adsorbed mass from n-C₅ asphaltene + toluene system onto an iron oxide crystal surface versus time at 20 °C and at different flow rates.

6.10 Chapter Summary

In this chapter QCM-D experiments are performed to study different depositional aspects of asphaltene from model oil systems. The frequency and dissipation changes because of the adsorbed asphaltene layer show a viscoelastic behavior of the deposit. The

accuracy of frequency and dissipation interpretation into amount of mass adsorbed (Voigt viscoelastic model) is ensured by comparing with AFM result for the adsorbed layer thickness. The following conclusions can be drawn from this study by varying the depositing environment of a model oil system.

- For long times the diffusion coefficient is increasing with temperature which results in more amount of adsorbed mass at higher temperatures in the long run.
- Viscosity of the adsorbed layer decreases with increase in temperature. The viscosity value is small because the adsorbed mass consists of asphaltene molecules and not bulk asphaltene.
- Polydispersity of asphaltene plays an important role in the deposition of asphaltene onto a gold surface, and in the properties of the deposit.
- When the ratio of heptane to toluene increases, the amount of asphaltene mass adsorbed from the corresponding heptol solution increases up to the precipitation onset, and decrease beyond that. After precipitation onset, asphaltene aggregate forming larger particles which can pass through the sensor crystal surface without depositing because of convective transfer.
- Investigating different surface types showed that when steel rusts, the asphaltene mass adsorbed during initial time increases, but in long run shows a decrease.
- The asphaltene adsorption curve reaches equilibrium sooner at higher flow rates. At very long times and at high enough flow rates, the rate of adsorption is independent of the flow rate. At very high flow rate the asphaltene adsorption curves have no dependency on flow rate and overlaps for all times.

Chapter 7. Asphaltene Deposition Simulator

The possibility of simulating asphaltene deposition in a well-bore is discussed by modeling the capillary data. The observations from asphaltene deposition experiments are incorporated while proposing the deposition mechanism. The mechanism includes different phenomena, such as precipitation, aggregation, diffusion, advection and deposition. The very limited data on the kinetics of each phenomena resulted in first order rate kinetics with three parameters to be estimated for the computer code. Results obtained with this simulation tool were encouraging to further validate with field observations by scaling up the parameters for field conditions.

7.1 Introduction

The flow behavior of petroleum fluids containing asphaltene is important in many different domains of oil industry. In exploration, the modeling of petroleum migration (often rich in resin and asphaltene) from source rocks to reservoir rocks is based on the extended Darcy's law [174]. Understanding how asphaltene impart high viscosity in heavy oils and bitumen can help to find more effective and economical methods for reduction of the viscosity of heavy and extra heavy oils, thus necessary to facilitate their production and transport [175]. Flow of slurries containing high asphaltene content is important in the field of refining processes. Rheological properties of vacuum residue are of considerable technical interest in asphalt manufacture [176].

The current chapter is focused on predicting asphaltene deposition in a well-bore or pipeline during crude oil production. Insufficient understandings of asphaltene deposition mechanism lead to only a few studies being published in literature. Ramirez et

al. described the usage of a molecular diffusion model to represent the asphaltene deposition assuming that the particle concentration gradient is caused by the temperature gradient at the wall [177]. But, the asphaltene deposition rate is not affected by the temperature gradient [178]. Jamialahmadi et al. developed an experimental setup to measure the thickness of asphaltene deposit based on change in resistivity of the boundary layer [179]. Their mechanistic model for asphaltene deposition failed to take into account the aggregation process. Hongjun et al. performed three phase computational fluid dynamic calculations for determining the asphaltene deposition and concluded that deposition in bend and sudden changed pipelines is greater than that in straight ones [180].

Sileri et al. focused on modeling of asphaltene deposition in crude preheat train [181]. This is the only work which incorporated aging phenomena of asphaltene (even though empirical). Nevertheless, their focus was on displacement and removal of an initial uniformly distributed layer of deposit at the walls. Recently, Eskin et al. used particle flux mass transfer expressions for turbulent flows to model the deposition process [182]. The required model parameters are obtained by fitting the model predictions to the deposition results obtained from their coquette flow device. Vargas et al. proposed a deposition simulator based on species conservation coupled with thermodynamic modeling of oil with PC-SAFT [183].

7.2 Capillary Asphaltene Deposition Setup

Figure 7.1 shows the capillary asphaltene deposition setup from New Mexico Institute of Mining and Technology used for obtaining the capillary scale data. The

capillary thickness is 200 μm – 500 μm and ~ 30 m long. Two high pressure syringe pumps are used to inject fluids at constant flow rates. A pressure transducer connected to a computer, is used to measure the pressure drop continuously across the capillary tubing. The capillary tube is immersed in a water bath to maintain isothermal conditions.

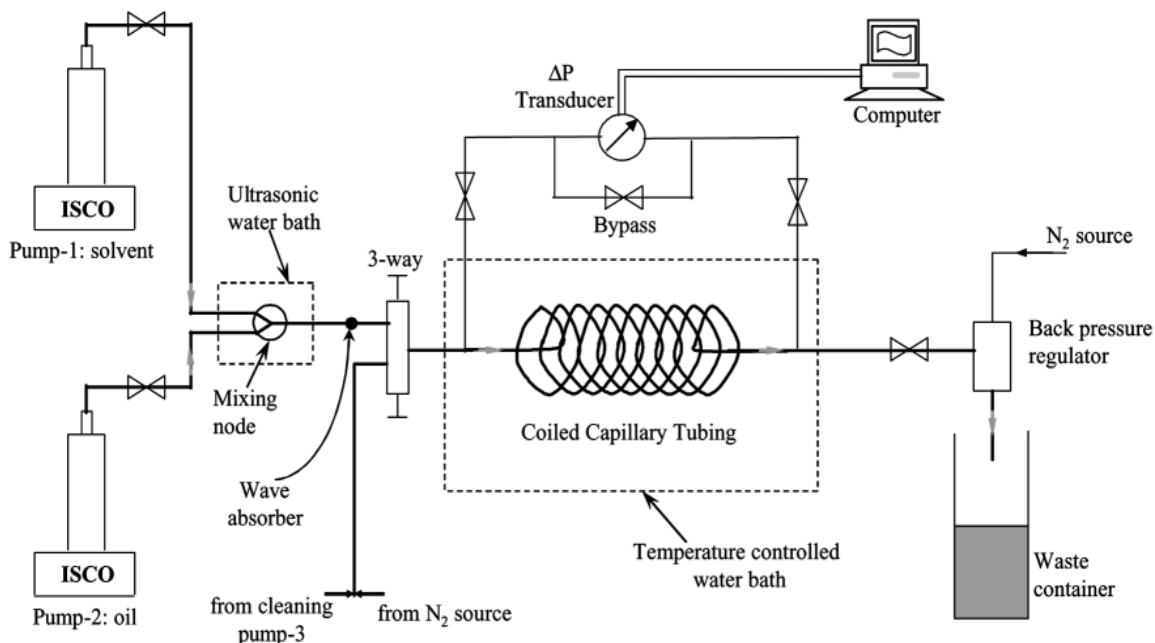


Figure 7.1. Schematic view of capillary deposition test apparatus [184].

For a typical experimental run, to study the asphaltene deposition in the capillary, the oil stream from pump 2 is mixed with precipitant from pump 1 by flowing through a mixing node within an ultrasonic bath to ensure complete mixing. The total flow rate is maintained within laminar flow regime. Toluene is pumped through the capillary to measure its actual radius prior to each test. At the end of each experimental run, nitrogen is passed through the capillary using a constant pressure source connected to the capillary inlet. The remaining liquid inside capillary is gradually displaced out from the outlet and weighed by an electronic balance. The recorded weight of effluent as a function of time is then used to calculate in-situ deposition thickness. Alternatively, an oil immiscible,

viscous fluid such as glycerin can be injected from one end of capillary under constant flow rate after the remaining oil-precipitant mixture has been flushed out by nitrogen. Pressure buildup at injection port is continuously recorded with a pressure transducer connected to a computer, while the capillary outlet is opened to atmosphere. Under constant flow rate, the variation of pressure drop determines the local effective diameter of capillary, and is used to retrieve in-situ deposition thickness.

7.3 Capillary Asphaltene Deposition Simulator

The following mechanism is assumed for asphaltene deposition from oil. Transport of asphaltene in a pipe is pictorially summarized in Figure 7.2 which involves multistep process of precipitation, aggregation, diffusion, advection and deposition. In the deposition experiment, asphaltene is unstable in the oil and begins to precipitate at a certain rate forming the primary particles, represented in Figure 7.2 as small black circles. These primary particles, can further aggregate forming secondary particles or diffuse to the surface of the tubing, where they stick and build up a deposit. Additionally, both primary and secondary particles can be transported by advection.

All these phenomena can be incorporated into a mathematical model that tracks the transport of asphaltene primary particles. The material balance in transient state for these asphaltene primary particles is represented by the following equation.

$$\text{Accumulation} = \text{Advection} + \text{Diffusion} + \text{Aggregation} + \text{Precipitation} \quad (7.1)$$

Assuming all rates to be first order, the following are the terms in detail.

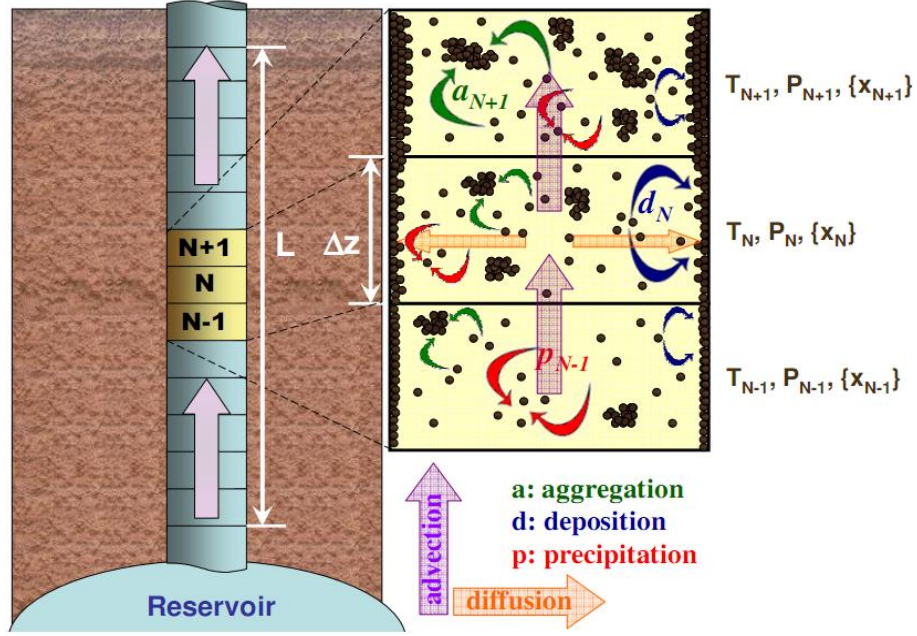


Figure 7.2. Asphaltene transport mechanism [183].

7.3.1 Precipitation Kinetics

Asphaltene and oil are considered as a single phase fluid out of which asphaltene precipitate out if exceeds the equilibrium concentration (C_A^{eq}). If C_A' is the concentration of asphaltene in oil, and K_p is the rate constant of precipitation, the rate of asphaltene precipitating out of oil (r_p) is given by equation 7.2.

$$r_p = \frac{dC_A'}{dt} = -K_p(C_A' - C_A^{eq}) \quad (7.2)$$

If C_o is the initial concentration of asphaltene in the oil, the rate of asphaltene precipitating out of oil can be rewritten as equation 7.3.

$$r_p = -K_p(C_o - C_A^{eq})\exp(-K_p t) \quad (7.3)$$

This rate of asphaltene precipitation out of oil is the rate of asphaltene primary particles generation. Redissolution of precipitated asphaltene is feasible, and rates of generation and redissolution are considered equal for the asphaltene primary particles.

7.3.2 Aggregation Kinetics

The precipitated primary particles can stick to one another undergoing an aggregation process, forming bigger secondary particles. For C_A concentration of asphaltene primary particles, and with a first order rate constant K_A , the aggregation rate of asphaltene primary particles is described in equation 7.4.

$$r_A = -K_A C_A \quad (7.4)$$

As discussed in the *Aggregation* section of *Asphaltene Properties* chapter, the redissolution kinetics of secondary asphaltene particles are neglected in the time scale of well-bore travel.

7.3.3 Deposition Kinetics

The flux of asphaltene primary particles at the wall due to diffusion (D) is consumed as deposition on the wall. Equation 7.5 is the governing equation with K_D as the rate constant of deposition.

$$r_D = D \frac{\partial C_A}{\partial r} = -K_D C_A \quad (7.5)$$

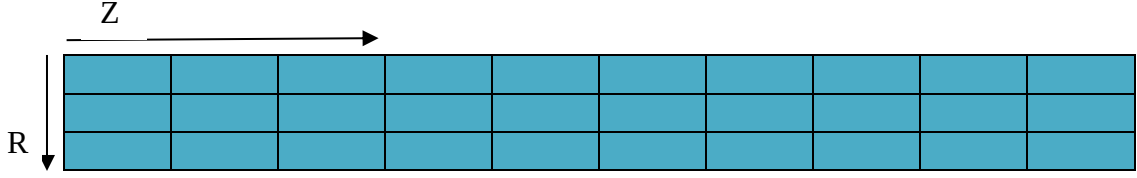
7.3.4 Overall Governing Equations

The calculated Peclet number for the capillary setup is in the order of 10^9 . With convection dominating in the axial direction, the overall material balance for asphaltene primary particles assuming an incompressible flow at constant operating conditions is,

$$\frac{\partial C_A}{\partial t} = -u_z \frac{\partial C_A}{\partial z} + \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) - K_A C_A + K_P (C_o - C_A^{eq}) \exp(-K_P t) \quad (7.6)$$

With the following boundary conditions for a capillary setup,

- $C_A = 0$ at $t = 0$ (no asphaltene primary particles before the start of experiment)
- $\frac{\partial C_A}{\partial r} = 0$ at $r = 0$ (from symmetry)
- $C_A = 0$ at $z = 0$ (no asphaltene primary particles exist before entering the system)
- $D \frac{\partial C_A}{\partial r} = -K_D C_A$ at $r = R$ (deposition on the inner wall of capillary)



The experimental data is measured after operating the setup at constant conditions for a specific period of time. Also, the asphaltene deposit buildup rate is small to safely consider a constant inner radius over the span of the experiment. Therefore, the system can be assumed to be at steady state. Reynolds number for the current set of capillary experiments is in the order of 1. In a laminar flow, the axial velocity, u_z can be expressed as a function of average velocity, $\langle u_z \rangle$ and radius, r given by expression 7.7.

$$u_z = 2 \langle u_z \rangle \left(1 - \left(\frac{r}{R} \right)^2 \right) \quad (7.7)$$

With the above assumptions, the overall material balance for asphaltene primary particles becomes equation 7.8 with the same boundary conditions as before except for the initial condition.

$$2 \langle u_z \rangle \left(1 - \left(\frac{r}{R} \right)^2 \right) \frac{\partial C_A}{\partial z} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) - K_A C_A + K_P (C_o - C_A^{eq}) \exp \left(- \frac{K_P z}{\langle u_z \rangle} \right) \quad (7.8)$$

The above partial differential equation in dimensionless form yields Peclet and Damkohler numbers in the expression 7.9.

$$2(1-r^*) \frac{\partial C}{\partial z^*} = \frac{L}{R} \frac{1}{Pe} \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C}{\partial r^*} \right) - Da_A C + Da_p (1 - C^{eq}) \exp(-Da_p z^*) \quad (7.9)$$

Where,

$$C = \frac{C_A}{C_O}; C^{eq} = \frac{C_A^{eq}}{C_O}; r^* = \frac{r}{R}; z^* = \frac{z}{L}; Pe = \frac{R \langle u_z \rangle}{D}; Da_A = \frac{K_A L}{\langle u_z \rangle}; Da_p = \frac{K_p L}{\langle u_z \rangle}$$

and $Da_D = \frac{K_D R}{D}$ (K_D is defined accordingly)

With boundary conditions

- $\frac{\partial C}{\partial r^*} = 0$ at $r^* = 0$
- $C = 0$ at $z^* = 0$
- $\frac{\partial C}{\partial r^*} = -Da_D C$ at $r^* = 1$

Thus the capillary scale deposition simulator is a two dimensional model, and the transport of asphaltene primary particles in both radial as well as axial directions is taken into consideration. The diffusion of particles in radial direction is considered while in axial direction is neglected. A MATLAB code using finite central difference method is written to solve the above set of equations. The discretization is made only in radial direction, and solved as an ordinary differential equation in axial direction using Gear's method.

The asphaltene deposition study is conducted at NMIMT using a stainless steel capillary pipe with crude oil I and pentadecane as the asphaltene precipitant according to the procedure described earlier. The operating conditions for Test 1 are reported in Table

7.1. With the estimated parameters as shown in Table 7.2, the model was able to match peak magnitude and shape of deposition profile of Test 1 observed from Figure 7.3.

Table 7.1. Experimental data for asphaltene capillary Test 1.

Capillary Material	Stainless steel 316	
Length	3193	cm
Radius	385	μm
Oil : Precipitant	76:24	v/v
Temperature	70	$^{\circ}\text{C}$
$\rho_{\text{precipitant}}$	0.737	g/ml
ρ_{oil}	0.845	g/ml
ρ_{mixture}	0.819	g/ml
μ_{mixture}	3.95	mPa.s
Flow rate	11.68	ml/hr
Flow time	35.9	hrs

Table 7.2. Kinetic parameters used for the prediction of asphaltene deposition profile in capillary deposition Test 1.

$K_p (\text{sec}^{-1})$	9.96×10^{-4}
$K_a (\text{sec}^{-1})$	1.8×10^{-4}
$K_d (\text{cm/sec})$	8.7×10^{-3}

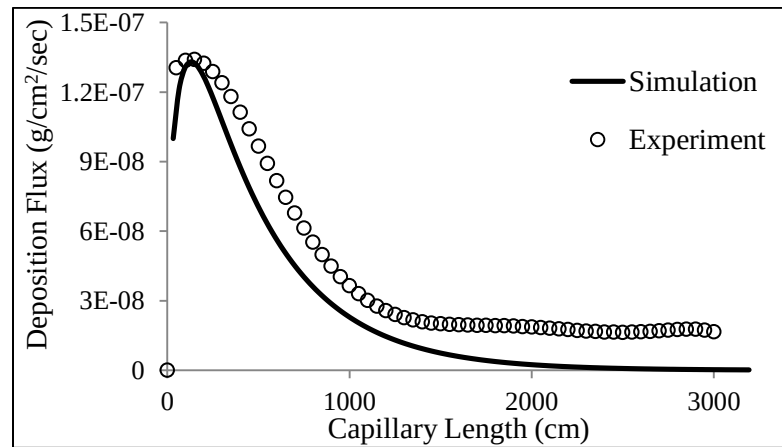


Figure 7.3. Comparison of experimentally observed asphaltene deposition flux against simulator prediction for Test 1.

As per the experiment, maximum asphaltene deposition is at the entrance of the pipe and decreases along the axial length of the capillary. The model is able to capture this phenomenon, because the kinetics of precipitation is proportional to the difference between the asphaltene concentration in the mixture and the maximum solubility of asphaltene in the oil. The highest driving force is at the entrance and decreases as the super saturation of asphaltene gets exhausted from the mixture.

Another capillary test (Test 2) is also conducted with the crude oil I – pentadecane mixture at same temperature, but with different operating conditions reported in Table 7.3. With only the flow properties changing, kinetic parameters of Test 1 are used to predict the asphaltene deposition profile and compared with experimental observation in Figure 7.4. The predictions match well with the experimental observations for Test 2.

Comparing the deposition profiles from the two experiments, it can be concluded that for a larger diameter pipe and when operating at a higher flow rate, a higher amount of asphaltene deposition flux is observed. This is because, a larger pipe diameter and higher flow rate result in higher amount of asphaltene mass flux into the pipe allowing more asphaltene to be precipitated and available for deposition. Comparing the shape of the deposition flux profile from the two experiments, it can be concluded that Test 1 shows a broader deposition peak which shifts axially more towards the exit of the pipe as against Test 2 with a sharp peak. This is because, at higher flow rate the precipitated asphaltene that is available for deposition is carried away by the flow for longer distances before finally depositing, and making the deposition peak much broader than Test 2.

Table 7.3. Experimental conditions for asphaltene capillary Test 2.

Capillary Material	Stainless steel 316	
Length	3245	cm
Radius	269	μm
Oil: Precipitant	76:24	v/v
Temperature	70	$^{\circ}\text{C}$
$\rho_{\text{precipitant}}$	0.7366	g/ml
ρ_{oil}	0.8454	g/ml
ρ_{mixture}	0.8193	g/ml
μ_{mixture}	3.95	mPa.s
Flow rate	4	ml/hr
Flow time	63.2	hrs

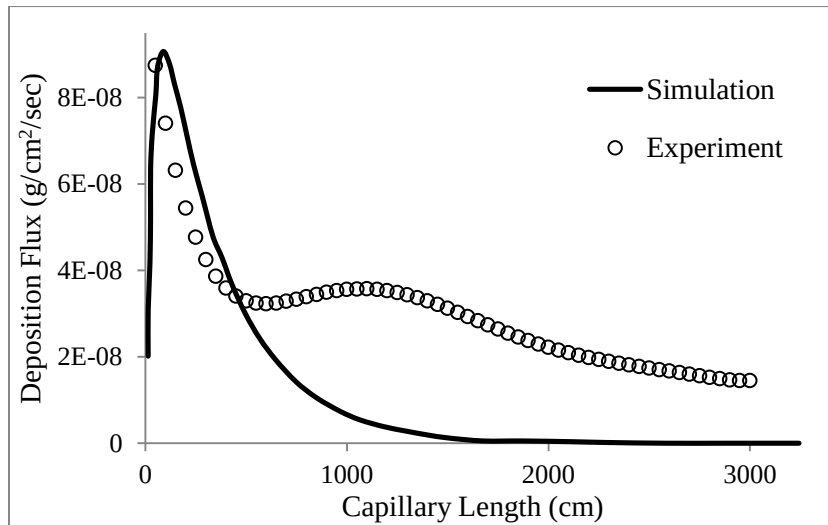


Figure 7.4. Comparison of experimentally observed asphaltene deposition flux against simulator prediction for Test 2.

7.4 Scale-up

The current work on asphaltene capillary deposition is developed into a computationally efficient deposition simulator called asphaltene deposition tool (ADEPT) by Kurup et al., and discussed asphaltene deposition in a few field cases [185]. A methodology to scale-up the deposition constant measured from a small scale capillary

deposition experiment to a large scale flow line is presented by Kurup et al. [186]. The predictions made use of such a scaled deposition constant are in good agreement with field observations like decreasing deposit thickness with increasing flow rates. The asphaltene deposition tool was successfully used in a fully predictive manner to study the asphaltene deposition observed in one of the subsea pipelines in the Gulf of Mexico. More recently, asphaltene deposition tool has also been applied to study asphaltene deposit profile due to changes in gas-to-oil ratio of a reservoir fluid [187].

Kurup et al. also discusses a modified pseudo-transient simulator that is capable of incorporating the effect of deposit buildup on flow velocities and frictional pressure drop, which in turn affects the phase behavior of asphaltene [186]. Simulation results show that incorporating the effect of deposit buildup causes a decrease in deposition rates with time. However, it is also observed that the difference between the predictions of pseudo-transient simulator and ADEPT simulator (which does not recalculate the changed transport and thermodynamics because of the deposit restriction) is not very significant for smaller deposit thicknesses.

7.5 Chapter Summary

A mechanism is presented in this chapter for the transport and deposition of asphaltene in production tubing. A complex multi-step process that includes precipitation, aggregation, diffusion, advection and deposition of asphaltene has been coded in a simulation tool, and the results obtained are validated with capillary experimental data.

The model discussed in this chapter is first bench marked against capillary asphaltene deposition Test 1, and then used to predict the change in capillary deposition

profile when the experiment (Test 2) is conducted at a different operating condition for the same oil-precipitant mixture. The model predictions are in good agreement capturing the shape and peak of the asphaltene deposition profile. Between capillary asphaltene deposition Tests 1 and 2, mass and volumetric flow rates are the deciding factors on the shape of the curve. Higher the mass flow rate, higher the deposition flux. Increasing the volumetric flow rate widens the shape of asphaltene deposit profile because of increased carryover of the asphaltene primary particles available for deposition.

The capillary asphaltene deposition model presented in this chapter has been successfully developed by others into a computationally efficient deposition simulator, along with scale-up of parameters from laboratory data to field conditions. This asphaltene deposition tool is successfully applied for asphaltene deposit predictions in different well-bores and pipelines.

Chapter 8. Conclusion and Recommendation

8.1 Conclusion

Important progress is made for understanding thermodynamic and transport behavior of asphaltene in crude oil systems. This research is motivated by four main objectives, which are successfully addressed according to the developments and results described below.

8.1.1 Properties

I have developed semitheoretically based expressions for determining the electronic polarizability, dielectric constant, critical temperature, critical pressure, and surface tension of nonolar hydrocarbons. The work as discussed in the *Predicted Asphaltene Properties* section in Chapter 3 can be applied to predict the properties of asphaltene. Knowledge of the chemical structure is not needed in these methods, and the only input parameters are normal boiling point, mass density, and molar mass. After looking into different chemical and physical properties of asphaltene, solubility model with liquid-liquid equilibrium using a SAFT based equation of state is chosen as the most appropriate theory for modeling asphaltene phase behavior.

8.1.2 Precipitation

I have proposed a PC-SAFT characterization methodology for crude oils with asphaltene as one of the components. Asphaltene phase behavior calculations are performed for different crude oils in the presence of different amounts of injected gas. The results are better compared to similar calculations performed with a cubic equation

of state. The amount of precipitated asphaltene which are needed for asphaltene deposition simulator and solvent deasphalters are also computed. This thesis also discusses about aging which can result in the enrichment of asphaltene in the deposit. The work as discussed in the *Routine and EOR PVT* section is not limited for asphaltene study, but can also be utilized to compute different thermodynamic data.

8.1.3 Segregation

Segregation refers to asphaltene compositional grading to an extent of phase separation. After the incorporation of asphaltene as one of the characterized crude oil components, isothermal asphaltene compositional grading is analyzed with the help of an algorithm presented in this thesis. A simple analytical model based on solution thermodynamics is also presented under valid conditions. The results show a close agreement with the field data, and are used to evaluate the compartmentalization of reservoirs and connectivity of wells. The compositional grading when extended to further depths may present asphaltene phase splitting corresponding to tar mat formation. The tar mat formation depth and the asphaltene content in a tar mat vary based on the extent of asphaltene's instability in a crude oil. This thesis successfully predicted the tar mat occurrence depth from just knowing the pressure, temperature, and reservoir oil composition in the upper parts of a formation.

8.1.4 Deposition

In this thesis quartz crystal microbalance experiments are performed to study different depositional aspects of asphaltene from model oil systems. The factors changed while investigating the deposition of asphaltene are temperature, polydispersity, stability

of asphaltene, depositing surface and flow rate. It is observed that with increasing temperature the amount of mass adsorbed increases because of a higher diffusion coefficient. It is demonstrated that different asphaltene fractions deposit in different amounts even when under same conditions. It is experimentally observed that beyond asphaltene precipitation onset, the amount of mass adsorbed decreases due to formation of asphaltene aggregates which can pass through the surface without depositing because of convective transfer. To represent the pipeline material, carbon steel and iron oxide are used as the different depositing surfaces. The asphaltene adsorption curve reaches equilibrium sooner at higher flow rates. At very long times and at high enough flow rates, the rate of adsorption is independent of the flow rate. At very high flow rate the asphaltene adsorption curves have no dependency on flow rate and overlaps for all times.

Based on the asphaltene aggregation effect on deposition, a mechanism is presented in this thesis for the transport and deposition of asphaltene in production tubing. The complex multi-step process which includes precipitation, aggregation, diffusion, advection and deposition of asphaltene is coded, and the results obtained are validated with capillary experimental data. The model predictions are in good agreement capturing the shape and peak of the asphaltene deposition profile. The capillary asphaltene deposition model presented here has been successfully developed by others into a computationally efficient deposition simulator, along with scale-up of parameters from laboratory data to field conditions. This asphaltene deposition tool is successfully applied for asphaltene deposit predictions in different well-bores and pipelines.

8.2 Recommendations

The results presented in this thesis are encouraging and lead to the following recommendations for future work.

8.2.1 *Asphaltene Phase Behavior*

The characterization procedure can be automated for the selection of PC-SAFT parameters by employing a global error minimization algorithm. This will be very much for the liking of commercial simulators who can incorporate the proposed characterization procedure to plot asphaltene phase behavior, or can be used for in general thermodynamic calculations of crude oils.

8.2.2 *Asphaltene Compositional Grading*

The asphaltene compositional grading is calculated for isothermal reservoirs in this thesis. For non-isothermal reservoirs, the driving forces contributing to the variations of composition with depth are chemical energy, gravity and thermal gradient. Calculating the variations is based on the assumption that all components exist in a stationary state. The general equation to be satisfied is [188].

$$\nabla\mu_i = M_i g - S_i \nabla T - F_{Ti} \frac{\nabla T}{T} \quad (8.1)$$

Simplified assumptions will lead to the following conditions.

- Isothermal gravity or chemical equilibrium ($dT = 0$)
- Passive thermal diffusion ($F_{Ti} = 0, dT \neq 0$)
- Soret effect ($F_{Gi} = 0$)

It will be interesting to observe the opposing effects of Soret and thermal diffusion with respect to isothermal gravity and their magnitudes for asphaltene compositional gradient.

8.2.3 QCM-D Asphaltene Deposition Modeling

A quantitative theory of kinetic-diffusive-convective adsorption in a flow cell was developed by Filippov for different adsorption isotherms [189]. The transient convective diffusion equation governing the transport of adsorbate molecules in the flow cell is given by.

$$\frac{\partial c(x, y, t)}{\partial t} + V_x(y) \frac{\partial c(x, y, t)}{\partial x} = D \frac{\partial^2 c(x, y, t)}{\partial y^2} \quad (8.2)$$

It will be interesting to study the roles of diffusion and deposition kinetics before asphaltene precipitation in a QCM-D experiment. The mechanism of deposition after the asphaltene precipitation onset is different, because of the effects of precipitation and aggregation of the precipitated asphaltene coming into picture after the onset. Hence, the model proposed by Filippov cannot be used after the precipitation has occurred. The mechanism proposed in this study for asphaltene deposition in capillary scale experiments can be utilized for QCM-D experiments to extract the deposition kinetics required for the scale up of asphaltene deposition simulator.

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Appendix A. Data for Property Correlations

Because of the hundreds of components used in the Property Scaling Relations chapter, only the references from which the data is taken are reported here in Appendix A. For detailed values of each property, Panuganti et al., *Ind. Eng. Chem. Res.* (2013) and Panuganti et al., *IEEE Trans. Dielectr. Electr. Insul.* (2013) can be referred.

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Appendix B. Details of Crude Oils

Details of crude oils used in the study are listed below. Table B.1 shows the oils used for both asphaltene and PVT studies. SARA analysis is not necessary for routine and EOR PVT study as discussed before.

Table B.1. Properties of the crude oils used in the thesis.

	Crude Oil A	Crude Oil B	Crude Oil C	Crude Oil D	Crude Oil E	Crude Oil F
GOR (scf/stb)	787	852	1603	798	214	1060
MW of reservoir fluid (g/mol)	97.75	92.78	75.4	96.15	161.96	89.42
MW of flashed gas (g/mol)	29.06	30.24	29.6	28.54	33.27	30.43
MW of STO (g/mol)	192.99	182.02	212.9	191.02	212.38	170.39
STO Density (g/cc)	0.820	0.817	0.846	0.823	0.867	0.815
Saturates (wt %)	66.26	73.42	67.09	75.56	60.82	-
Aromatics (wt %)	25.59	19.32	25.84	20.08	23.11	-
Resins (wt %)	5.35	7.05	6.92	4.14	14.30	-
Asphaltene (wt %)	2.80	0.17	0.15	0.22	1.77	-

	Crude Oil G	Crude Oil H
GOR (scf/stb)	945	510
MW of reservoir fluid (g/mol)	96.07	131.50
MW of flashed gas (g/mol)	29.45	25.83
MW of STO (g/mol)	180.32	243.26
STO Density (g/cc)	0.817	0.880
Saturates (wt %)	-	52.90
Aromatics (wt %)	-	29.70
Resins (wt %)	-	13.20
Asphaltene (wt %)	-	4.00

Appendix C. Characterized Crude Oils with PC-SAFT Parameters

This appendix has all the simulation parameters for the different crude oils studied in the thesis. Tables C1 to C4 discussed the oils used for asphaltene study. Tables C5 to C9 discusses the oils used for routine and EOR PVT study.

Table C.1. Characterized crude oil A for asphaltene study.

	Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
				m	σ (Å)	ε (K)
Gas	N ₂	28.01	0.16	1.21	3.31	90.96
	CO ₂	44.01	1.94	2.07	2.78	169.21
	C ₁	16.04	33.60	1.00	3.70	150.03
	C ₂	30.07	7.56	1.61	3.52	191.42
	C ₃	44.10	6.74	2.00	3.62	208.11
	Heavy gas	65.49	8.20	2.53	3.74	228.51
Liquid	Saturates	167.68	31.74	5.15	3.90	249.69
	Aromatics + Resins ($\gamma = 0.22$)	253.79	9.91	6.41	3.99	285.00
	Asphaltene	1700.00	0.13	33.00	4.20	353.50

Table C.2. Characterized crude oil B for asphaltene study.

	Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
				m	σ (Å)	ε (K)
Gas	N ₂	28.01	0.15	1.21	3.31	90.96
	CO ₂	44.01	1.72	2.07	2.78	169.21
	C ₁	16.04	32.56	1.00	3.70	150.03
	C ₂	30.07	7.89	1.61	3.52	191.42
	C ₃	44.10	7.29	2.00	3.62	208.11
	Heavy gas	66.36	9.31	2.55	3.74	228.95
Liquid	Saturates	169.17	32.63	5.19	3.90	249.81
	Aromatics + Resins ($\gamma = 0.22$)	234.78	8.46	5.57	4.03	319.70
	Asphaltene	1700.00	0.01	35.75	4.48	413.42

Table C.3. Characterized crude oil D for asphaltene study.

	Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
				m	σ (Å)	ε (K)
Gas	N ₂	28.01	0.17	1.21	3.31	90.96
	CO ₂	44.01	2.10	2.07	2.78	169.21
	C ₁	16.04	34.86	1.00	3.70	150.03

Liquid	C ₂	30.07	7.58	1.61	3.52	191.42
	C ₃	44.10	6.04	2.00	3.62	208.11
	Heavy gas	67.12	7.56	2.57	3.75	229.32
	Saturates	176.08	34.15	5.37	3.91	250.36
	Aromatics + Resins ($\gamma = 0.05$)	256.14	7.53	6.36	4.00	293.30
	Asphaltene	1700.00	0.01	37.22	4.49	413.54

Table C.4. Characterized crude oil H for asphaltene compositional grading study.

	Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
				m	σ (Å)	ε (K)
Gas	N ₂	28.01	0.03	1.21	3.31	90.96
	CO ₂	44.01	0.08	2.07	2.78	169.21
	C ₁	16.04	36.06	1.00	3.70	150.03
	C ₂	30.07	4.42	1.61	3.52	191.42
	C ₃	44.10	4.96	2.00	3.62	208.11
	Heavy gas	67.13	5.84	2.57	3.75	229.32
Liquid	Saturates	207.77	30.14	6.18	3.92	252.44
	Aromatics + Resins ($\gamma = 0.05$)	280.20	18.19	6.27	4.09	337.00
	Asphaltene	1700.00	0.28	39.00	4.28	349.00

Table C.5. Characterized crude oil B for PVT study.

Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
			m	σ (Å)	ε (K)
N ₂	28.01	0.17	1.21	3.31	90.96
CO ₂	44.01	1.68	2.07	2.78	169.21
H ₂ S	34.08	0.00	1.65	3.07	227.34
C ₁	16.04	32.95	1.00	3.70	150.03
C ₂	30.07	7.92	1.61	3.52	191.42
C ₃	44.10	7.80	2.00	3.62	208.11
Heavy gas	71.93	15.67	2.69	3.76	231.48
Liquids ($\gamma = 0.2$)	193.88	33.81	5.40	3.96	285.52

Table C.6. Characterized crude oil C for PVT study.

Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
			m	σ (Å)	ε (K)
N ₂	28.01	0.09	1.21	3.31	90.96
CO ₂	44.01	3.70	2.07	2.78	169.21
H ₂ S	34.08	5.29	1.65	3.07	227.34
C ₁	16.04	46.06	1.00	3.70	150.03

C ₂	30.07	5.37	1.61	3.52	191.42
C ₃	44.10	4.19	2.00	3.62	208.11
Heavy gas	75.26	10.57	2.78	3.77	232.84
Liquids ($\gamma = 0.223$)	212.90	24.72	5.77	3.98	292.82

Table C.7. Characterized crude oil E for PVT study.

Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
			m	σ (Å)	ε (K)
N ₂	28.01	0.11	1.21	3.31	90.96
CO ₂	44.01	1.09	2.07	2.78	169.21
H ₂ S	34.08	0.00	1.65	3.07	227.34
C ₁	16.04	14.60	1.00	3.70	150.03
C ₂	30.07	5.38	1.61	3.52	191.42
C ₃	44.10	5.97	2.00	3.62	208.11
Heavy gas	65.42	6.00	2.53	3.74	228.45
Liquids ($\gamma = 0.285$)	212.38	66.85	5.61	4.00	303.87

Table C.8. Characterized crude oil F for PVT study.

Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
			m	σ (Å)	ε (K)
N ₂	28.01	0.23	1.21	3.31	90.96
CO ₂	44.01	1.99	2.07	2.78	169.21
H ₂ S	34.08	0.00	1.65	3.07	227.34
C ₁	16.04	31.89	1.00	3.70	150.03
C ₂	30.07	8.57	1.61	3.52	191.42
C ₃	44.10	7.92	2.00	3.62	208.11
Heavy gas	65.43	9.29	2.53	3.74	228.46
Liquids ($\gamma = 0.22$)	170.39	40.10	4.83	3.94	283.52

Table C.9. Characterized crude oil G for PVT study.

Component	MW (g/mol)	Mole %	PC-SAFT Parameters		
			m	σ (Å)	ε (K)
N ₂	28.01	0.16	1.21	3.31	90.96
CO ₂	44.01	1.88	2.07	2.78	169.21
H ₂ S	34.08	0.00	1.65	3.07	227.34
C ₁	16.04	31.54	1.00	3.70	150.03
C ₂	30.07	7.12	1.61	3.52	191.42
C ₃	44.10	6.61	2.00	3.62	208.11
Heavy gas	65.17	8.23	2.52	3.74	228.32
Liquids ($\gamma = 0.175$)	180.32	44.44	5.14	3.94	278.77

Appendix D. Binary Interaction Parameters

Table D1 shows the PC-SAFT binary interaction parameters (k_{ij}) for a crude oil used for asphaltene study including the asphaltene compositional grading. The constant set of PC-SAFT temperature independent binary interaction parameters are established by adjusting the binary vapor–liquid or liquid-liquid equilibrium for the combination of pure components. The references in Table D1 indicate the data used to establish the interaction parameters.

Unlike for cubic equation of state, the values of PC-SAFT binary interaction parameters for crude oil components in routine and EOR PVT study are not well established. Most of the parameters used here are based on Table D1. The injected gases being rich in light ends, the PVT simulation results are sensitive towards the binary interaction parameter between nitrogen to propane – liquids. The constant set of binary interaction parameters used in routine and EOR PVT study are reported in Table D2.

Table D.1. PC-SAFT temperature independent binary interaction parameters used for asphaltene study.

Components	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	Heavy gas	Saturates	Aromatics + Resins	Asphaltene
N ₂	0	0 ¹	0.09 ²	0.03 ³	0.044	0.06	0.075 ⁵	0.14 ⁶	0.158 ⁷	0.16
CO ₂		0	0.0678 ⁸	0.05 ⁹	0.097 ¹⁰	0.1 ¹¹	0.12 ¹²	0.13 ¹³	0.1 ¹⁴	0.1 ¹⁵
H ₂ S			0	0.062 ¹⁶	0.058 ¹⁷	0.053 ¹⁸	0.07 ¹⁹	0.09 ²⁰	0.015 ²¹	0.015
C ₁				0	0 ²²	0 ²³	0.03 ²⁴	0.03 ²⁵	0.029 ²⁶	0.07
C ₂					0	0 ²⁷	0.02	0.012 ²⁸	0.025 ²⁹	0.06
C ₃						0	0.015 ³⁰	0.01	0.01 ³¹	0.01 ¹⁵
Heavy gas							0	0.005 ³²	0.012 ³³	0.01
Saturates								0	0.007 ³¹	-0.004
Aromatics + Resins										0 ¹⁵
Asphaltene										0

Note: The binary interaction parameter between ethane and asphaltene for crude oil H is readjusted to 0.08.

Table D.2. PC-SAFT temperature independent binary interaction parameters used for routine and EOR PVT study.

Component	N ₂	CO ₂	H ₂ S	C ₁	C ₂	C ₃	Heavy gas	Liquids
N ₂	0	0	0.090	0.030	0.040	0.060	0.075	0.100
CO ₂		0	0.0678	0.057	0.097	0.107	0.090	0.100
H ₂ S			0	0.062	0.058	0.053	0.080	0.050
C ₁				0	0	0	0.080	0
C ₂					0	0	0.050	0
C ₃						0	0.030	0
Heavy gas							0	0.067
Liquids								0

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Appendix E. Acronyms

PC-SAFT: Perturbed chain form of the statistical associating fluid theory

PVT: Pressure, vapor and temperature

EOR: Enhanced oil recovery

SAFT: Statistical associating fluid theory

L–L: Lorentz–Lorenz

NTP: Normal temperature and pressure

SARA: Saturates, aromatics, resins and asphaltene

STO: Stock tank oil

AOP: Asphaltene onset pressure

GOR: Gas-to-oil ratio

TLC-FID: Thin layer chromatography with flame ionization detection

HPLC: High pressure liquid chromatography

SRK-P: Soave-Redlich-Kwong with Peneloux correction

QCM-D: Quartz crystal microbalance with dissipation

AFM: Atomic force microscope

ADEPT: Asphaltene deposition tool

Appendix F. Nomenclature

Chapter 2

δ : Solubility parameter

CED : Cohesive energy density

U^{rm} : Residual internal energy

v : Liquid volume

n : Refractive index

c : Concentration of asphaltene flocs

r : Mean radius of aggregates

c_∞ : Final concentration of asphaltene flocs

R_∞ : Final mean radius of aggregates

t : Time of aggregation

τ : Characteristic time

Chapter 3

n : Refractive index

ρ : Density

r : Specific refractivity

mr : Molar refractivity

MW : Molecular weight

j : Ratio of volume actually occupied by the molecules to that apparently occupied by the molecules

N : Number of molecules per unit volume

α : Mean polarizability

N_a : Avogadro Number

v : Molar volume

c : Speed of light in vacuum

v : Speed of light in a medium

E : Permittivity

μ : Magnetic permeability

k : Dielectric constant

ω : frequency

τ : Dielectric relaxation time

A : Helmholtz free energy

E : Internal energy

S : Entropy

T : Temperature

P : Pressure

V : Volume

C_α : Coefficient of thermal expansion

C_β : Isothermal compressibility coefficient

δ = Solubility parameter

a : Van der Waal's parameter which is a measure of the attraction between the particles

T_C : Critical temperature

P_C : Critical pressure

T_B : Normal boiling temperature

σ : Surface tension

h : Planck constant

Chapter 4

m : Number of segments per molecule

σ : Temperature independent diameter of each molecular segment

ε : Segment–segment dispersion energy

γ : Aromaticity

Chapter 5

μ : Chemical potential

P : System pressure

X : Mole fraction

T : System temperature

M : Molecular weight

g : Acceleration due to gravity

h : Depth

R : Universal gas constant

$\hat{f}$: Fugacity in mixture

ρ : Density

Y : Corrected mole fraction

Q : Error

$\bar{V}$: Partial molar volume

dh : Difference in depths

Z : Compressibility factor

$\hat{\phi}$: Fugacity coefficient in the system

$\Delta\rho$: Density difference between asphaltene and crude oil

K : Boltzman constant

n_a : Number of asphaltene molecules per asphaltene particle

γ_a : Average size of asphaltene particle

k : Permeability

Superscript

O : Reference condition

N : Number of components

n : Iteration number

Subscript

i : Component number

v : Vertical

h : Horizontal

Chapter 6

f_0 : Fundamental resonant frequency

n : Overtone number

Δm : Adsorbed mass

$\Delta\Gamma$: Adsorbed mass density

A : Active area

ρ : Density

v : Shear wave velocity

μ : Shear modulus

h : Thickness

C : Constant

η : Viscosity

Δf : Change in frequency

ΔD : Change in energy dissipation

Subscripts

q : Quartz

l : Liquid

s : Solvent

Chapter 7

C_A^{eq} : Equilibrium concentration

C_A' : Concentration of asphaltene in oil

K_P : Precipitation rate constant

r_P : Rate of asphaltene precipitating out of oil

t : Time

C_o : Initial concentration of asphaltene in the oil

C_A : Concentration of asphaltene primary particles

K_A : Aggregation rate constant

D : Diffusion

K_D : Deposition rate constant

r_D : Rate of deposition

u_z : Axial velocity

$\langle u_z \rangle$: Average velocity

r : Radius

z : Axial length

Pe : Peclet number

Da_P : Damkohler number for precipitation

Da_A : Damkohler number for aggregation

Da_D : Damkohler number for deposition

R : Radius of capillary

L : Length of capillary