

Modeling of Asphaltene Systems with Association Models

PhD Thesis

Alay Arya (Dec 2016)

Center for Energy Resources Engineering Department of Chemical and Biochemical Engineering Technical University of Denmark DK-2800 Kgs. Lyngby, Denmark

Preface

This thesis is submitted to fulfill the partial requirements for the degree of Doctor of Philosophy at the Technical University of Denmark (DTU). The work has been carried out at the Department of Chemical and Biochemical Engineering and Center for Energy Resources Engineering (CERE), from January 2014 to December 2016, under the supervision of Professor Georgios M. Kontogeorgis and Associate Professor Nicolas von Solms. The project was funded by the CHIGP (Chemical in Gas Processing) consortium (2/3) and partly by the Department of Chemical and Biochemical Engineering, Technical University of Denmark (1/3).

First and foremost, I would like to express my most sincere gratitude to my supervisors for offering this interesting research project on a current industrial problem. I would like to appreciate the flexibility given of doing independent research, keeping faith in me and their full support throughout the project. I have really enjoyed and been stress free working with my supervisors for last three years stint. I am highly indebted to them for the professional development of myself by giving me several opportunities of collaboration, presentations, software activities and teaching assistantships.

A special thanks to my colleagues Xiaodong Liang and Bjørn Maribo-Mogensen for creating PC-SAFT and CPA tools in MATLAB. Without these tools, I would not have achieved a significant part of my work. I would like to thank my BP colleagues (Diamantonis Nicolaos, Leslie Bolton and Susan Little) for reviewing my work and giving constructive feedbacks.

I would like to thank my department for organizing different social events and my colleagues for supporting me. Doing a PhD at DTU would be my cherished lifetime memory.

Last but not least, I would like to recognize and acknowledge the immense love and understanding of my family members. I am extremely grateful to my wife (Niti) and son (Advik) for making my life easy during the project.

Lyngby, Denmark, December-2016

Alay Arya

Dedicated to

My parents, brothers, sisters, wife, son, friends and supervisors

Summary

Asphaltenes are normally present in the reservoir oil and for industry they are analogous to "cholesterol" since their precipitation stops the entire production and causes the loss of millions of dollars. Asphaltenes consist of "ill defined" components of high molecular weight (around 500-4000 gm/mol) and are considered most polar in the oil compared to the other components. This polar nature of asphaltenes is imparted by heteroatoms (O, S, N, vanadium, nickel) present in their structure. Asphaltenes molecules associate with each other and precipitate at certain temperature, pressure and composition. Asphaltenes can easily precipitate as pressure is reduced but also if the oil is diluted by light hydrocarbons eg. A gas such as methane, CO₂ or nitrogen. Ever since the introduction of enhanced oil recovery (EOR) method with gas, the asphaltene precipitation problem has become even worse. In addition, at refinery inlet, more than two crudes (degassed oil) are generally mixed to upgrade or downgrade the feedstock. This blending of different crudes may also cause asphaltene precipitation. However, prediction of these conditions, where asphaltenes precipitate out, is quite uncertain and detailed thermodynamic model and appropriate oil characterization is required.

There have been several attempts to model asphaltene precipitation using various equations of state (EoS) and empirical models. In the past few years, the association models based on the Cubic Plus Association (CPA) and Statistical Associating Fluid Theory (SAFT) EoS are found to be promising models for the asphaltene precipitation study. However, there are different opinions in the literature and it is still unclear whether we can successfully model asphaltene precipitation. Therefore, a systematic study is important to model asphaltene precipitation and show what we can achieve with these models.

In this PhD project, a modeling approach using the CPA and PC-SAFT EoS is developed to model asphaltene precipitation from reservoir oil and degassed crude considering asphaltenes as associating component/s. Several reservoir oils are studied in order to show that the developed approach can be used to predict gas injection and reservoir depressurization effect after calculating the model parameters from the required experimental data. The developed approach with Soave-Redlich-Kwong (SRK) with classical mixing rule and SRK with Huron Vidal mixing rule is also studied considering asphaltenes as non-associating component/s. The well known approach from the literature based on the PC-SAFT EoS, where asphaltenes are considered non-associating component, is also been studied and found that it needs temperature dependency like the developed approach in this work to correlate asphaltenes onset conditions at different temperatures. In addition, asphaltene yield from crude oil during the addition of *n*-paraffin is also studied and concluded that the models cannot predict it but can only correlate the data. The CPA and PC-SAFT models are also studied to predict asphaltene onset conditions when more than two crudes are mixed. A MATLAB tool is also developed in order to use these models to study asphaltene phase envelope with or without gas injection.

Resumé

Asfaltener er normalt til stede i reservoir olie, og for industrien virker de lige som "kolesetrol", da udfældning af dem kan stoppe hele produktionen, med tab af millioner af dollars som følge. Asfaltener består af "ikke fuldt definerede" komponenter med høj molekylvægt (omkring 500-4000 g/mol), og er samtidig anset som de mest polære komponenter i olien. Denne polære natur af asfaltener skabes af tilstedeværelsen af heteroatomer (O, S, N, Vanadium and Nickel). Asfalten molekyler associerer med hinanden, og vil udfælde ved bestemte temperaturer, tryk og sammensætning. Asfaltener vil nemt udfælde når trykket falder, men også hvis olien er fortyndet med lette carbonhydrider for eksempel en gas som CO₂ eller nitrogen. Siden introduktionen af forbedret olieudvinding (EOR) med gas er problemet med udfældning af asfaltener kun blevet større. Derudover vil mere end to råolier (afgasset) ofstest bliver blandet ved indløbet til et rafinaderi for at op- eller nedgradere råmaterialet. Denne blanding af forskellige råolier kan også inducere asfalten udfældning. Forudsigelsen af de forhold hvor asfaltener vil udfælde er i midlertid tæmmelig usikker, og en detaljeret termodynamisk model og passende olie karakterisering er nødvendig.

Der har været flere forsøg på at modellere asfalten udfældning med flere forskellige tilstandsligninger (EoS) og empiriske modeller. I de sidste par år har associations modeller som Cubic Plus Association (CPA) og Statistical Associating Fluid Theory (SAFT) vist sig som lovende for undersøgelser af asfalten udfældning. Der er imidlertid forskellige meninger i litteraturen og det er stadig uklart om vi succesfuldt kan modeller asfalten udfældning. Derfor er et systematisk studie i modellering af asfalten udfældning vigtig og vil vise hvad vi kan opnå med disse modeller.

I dette PhD projekt er en modellerings tilgang for modellering af asfalten udfældning fra reservoir olie og afgasset råolie, hvor asfaltenerne er betragtet som associerende, udviklet. Flere reservoir olier er studeret for at vise at den udviklede tilgang kan bruges til at forudsige effekten af gas injektion og tryk reduktionen i reservoirer, eftter at model parametrene er beregnet fra det nødvendige eksperimentielle data. Den udviklede tilgang er også studeret med Soave-Redlich-Kwong (SRK) med klassisk blandingsregel og SRK med Huron Vidal blandingsregel, hvor asfaltenerene er betragtet som ikke associerende. Den velkendte tilgang fra literaturen for PC-SAFT, hvor asfaltener er betragtet som ikke associerende er også studeret og det er fundet at der er et behov for en temperaturafhængighed for at korrolere asfaltenernes udfældningspunkt ved forskellige temperature, i lighed med tilgangen udviklet i dette studie. Udover dette, er asfalten udbyttet fra råolie ved tilsætning af n-paraffin også studeret og det konkluderes at modellen ikke kan forudsige dette, men kun korrelere dataen. Forudsigelse af asfaltenernes udfældningsbetingelser når mere end to råolier er blandet er også studeret med CPA og PC-SAFT modelleren. Et MATLAB værktøj er også udviklet således at man kan bruge de nævnte modeller til at studere asfaltens "phase envelope" med og uden gas injektion.

Table of Contents

Preface	iii
Summary	v
Resumé	vi
Table of Contents	vii
Chapter 1. Introduction	
1.1 Asphalenes: A Flow Assurance Problem	10
1.2 Quantification of Asphaltenes by SARA analysis	10
1.3 Asphaltene Structure and Properties	12
1.4 Asphaltene phase envelope	
1.5 Literature Survey on Thermodynamic Models for Asphaltene precipitation	13
1.5.1 Ashpaltenes as True Components	14
1.5.2 Ashpaltenes as Colloids	15
1.6 Scope of Research	19
1.7 Objectives of Thesis	19
1.8 Organization of Thesis	
Chapter 2. Equations of State	
2.1 Cubic Plus Association	
2.2 Perturbed-Chain-Statistical-Associating-Fluid-Theory	
2.3 Soave-Redlich-Kwong with Classical Mixing Rule	
2.4 Soave-Redlich-Kwong with Huron-Vidal Mixing Rule	
Chapter 3. Modeling of Asphaltene Onset Condition using the CPA Equation of State	
3.1 Introduction	
3.2 Modeling Approach	
3.3 Results and Discussion	
3.4 Conclusions	
Chapter 4. Study of Gas Injection Effect and Sensitivity of the CPA Model	
4.1 Introduction	

4.2 Hypothesis behind Modeling Approach	
4.3 Results and Discussion	60
4.4 Conclusions	75
4.5 Supplementary Information	76
Chapter 5. Modeling of Asphaltene Onset Condition using the CPA and PC-SAFT Equa	ations of State
5.1 Introduction	
5.2 Modeling Approach with CPA & PC-SAFT (WA)	
5.3 Modeling Approach with PC-SAFT (WOA)	
5.4 Results and Discussion	91
5.5 Conclusions	
5.6 Supplementary Information	107
Chapter 6. Modeling of Asphaltene Onset Condition using the CPA, SRK, and SRK+ of State	HV Equations
6.1 Introduction	114
6.2 Modeling Approach	116
6.3 Results and Discussion	
6.4 Conclusions	
6.5 Supplementary Information	
Chapter 7. Modeling of Asphaltene Precipitation from Crude (Degassed) Oil	
7.1 Introduction	
7.2 Modeling Approaches	141
7.3 Results and Discussion	146
7.4 Conclusions	160
Chapter 8. Conclusions and Recommendations	
8.1 Conclusions	
8.2 Recommendations	164
List of Symbols	166
List of Figures	170
List of Tables	177
APPENDICES	

Appendix A. Academic activities	
Peer reviewed journal articles	
Conference presentations	
Teaching Assistance	

Chapter 1. Introduction

1.1 Asphalenes: A Flow Assurance Problem

Generally, oil contains hundreds to thousands of components. Among these components, lower molecular weight components (lighter components) can be separated out and defined in terms of its properties like vapor pressure, liquid density, critical temperature and pressure. The components with higher molecular weight (heavier components) cannot be separated out and defined. However, there is a way to define different fractions of these heavier components based on their solubility in different solvents. The fraction, which is not soluble in n-pentane/n-heptane, is known as asphaltenes and is the heaviest fraction in the reservoir oil. It is an "ill defined" component of high molecular weight (around 500-4000 Da) and is considered most polar part in the oil compared to the other components [1]. This polar nature of asphaltenes is believed to be imparted by heteroatoms (O, S, N, vanadium, nickel) present in its structure. Asphaltenes molecules associate with each other and precipitate at certain temperature, pressure and composition. However, prediction of these conditions, where asphaltenes precipitate, is quite uncertain and detailed thermodynamic model together with appropriate oil characterization is required. Asphaltenes can easily precipitate as pressure is reduced but also if the oil is diluted by light hydrocarbons or gas eg. methane, CO_2 or N_2 . Ever since the introduction of enhanced oil recovery (EOR) method with gas injection, this problem has become even worse. Moreover, when more than one crude oils are mixed in refineries, there may be possibility of asphaltene precipitation. For industry, asphaltenes are analogous to "cholesterol" since their precipitation stops the oil production and causes loss of millions of dollars. Asphaltenes constituents are generally soluble in liquids with a surface tension above 25 dyne/cm, for example pyridine, carbon disulfide, carbon tetrachloride and benzene [1] and therefore they can be used as inhibitors or to remove any asphaltene precipitation. The cost of installing and maintaining asphaltene mitigation equipment and chemicals is in the millions of dollars per year, but failure to anticipate asphaltene deposition can cost the operator even more in terms of remediation and production loss. Therefore, the ability to predict the occurrence and the magnitude of asphaltene deposition in wellbores and flow lines is the key in the flow assurance effort [2].

1.2 Quantification of Asphaltenes by SARA analysis

A reservoir oil (live oil), when reaches earth surface from the well, is flashed in a separator or series of separators. A typical separator unit is shown in Fig. 1.1. Pressures in the separators are optimized to increase the oil gravity and to decrease the gas formation volume factor [ratio of gas (composition y_i) volume at reservoir T & P to gas (composition y_i) volume at standard T & P] and oil formation volume factor [ratio of reservoir oil (composition z_i) volume at reservoir T & P to heavy oil (composition x_i , excluding gas y_i) volume at standard T & P]. In other words, distribution of

intermediate components is very important between gas and liquid phases to increase oil gravity. The gas from the overhead is then measured in terms of volumetric flow rate and composition by flowmeter and gas chromatography respectively. The liquid oil (dead oil) from the separator is usually analyzed at ambient condition by so called SARA (Saturates Aromatics Resins Asphaltenes) analysis to determine quantity of saturates, aromatics, resins and asphaltenes fractions in terms of wt%. The molecular weights of individual fractions are not determined in this analysis. There are different techniques for SARA analysis [3-5]. Comparisons of SARA fraction measurements by different techniques, usually from different laboratories, can show large differences [6]. It should be noted that the composition of the reservoir oil (recombined oil) can be calculated from the information of gas and oil compositions and flowrates.



Fig. 1.1. Oil-Gas Separator System.

Since we are more interested in modeling than experimental techniques, we will not go into details of these different SARA techniques. A typical procedure of SARA analysis [1] is shown in Fig. 1.2. Adding around 40 volumes of *n*-heptane/*n*-pentane into 1 g of heavy oil, insoluble fraction is separated out, which is called as asphaltenes fraction. The fraction, which is soluble in n-heptane/*n*-pentane, is further divided into three subfractions. To do so, mixture of *n*-heptane/*n*-pentane and soluble oil is passed through adsorbent beds of alumina. The polar compounds get adsorbed on alumina. An *n*-heptane/*n*-pentane wash on adsorbent bed verifies that no saturated non-polar components are present on the bed. Knowledge of the mass of used *n*-heptane/*n*-pentane, non-polar fraction, which is called "Saturates", can be quantified. A toluene wash absorbs a fraction of adsorbed polar compounds, known as "Aromatics". A pyridine (more polar than toluene) wash absorbs rest of the adsorbed fraction of polar compounds, known as "Resins".



Fig. 1.2. Typical procedure of SARA analysis. STO=Stock Tank Oil (oil at ambient condition).

1.3 Asphaltene Structure and Properties

There is no specific structure of asphaltene molecules. It is believed that asphaltene molecule consists of a number of aromatic rings, alkyl chains and heteroatoms (eg. N, S, O). Depending upon the asphaltene structure, they create the colloid, oligomer or miscelle [7]. Asphaltene monomer molar mass is also a topic of debate. Different techniques have been employed to measure asphaltene molar mass and are discussed by Strausz et al [8]. Some of the modern techniques show that the asphaltene fraction has a solubility parameter between 19 and $24 MPa^{1/2}$ and density between 1.13 and 1.20 g/ml at room conditions [11-14]. In light crudes, asphaltenes, associated with resins, behave as a liquid phase with a solubility parameter close to that of liquid naphthalene. Purified asphaltenes have a strong tendency to aggregate and behave as a solid phase. The solubility parameter of purified asphaltenes is close to that of pyridine or quinoline [11]. The tendency of asphaltene constituents to vary with the solubility parameter of the hydrocarbon medium is related to the aromaticity and polarity of asphaltene constituents rather than to the molecular size or dimensions of asphaltene constituents [15-18].

1.4 Asphaltene phase envelope

A reservoir oil (live oil) is generally present at moderate temperature (e.g. 320-400 K) and high pressure (e.g. 250-1000 bar). As shown in Fig. 1.3, when oil travels up towards the surface, its pressure and temperature decrease. As oil pressure decreases (Point-A to B), asphaltenes may precipitate out at certain temperature and pressure (Point-B) for a given composition of oil. This temperature and pressure boundary is known as upper onset pressure (UOP) boundary. Below this

boundary, there are oil and asphaltene phases present. If pressure keeps decreasing (from Point-B to C), more asphaltenes precipitates out and maximum asphaltene precipitation occurs at bubble point (Point-C). Below bubble point, there are vapor, oil and asphaltene phases. If pressure keeps decreasing (from Point-C to D), more gas comes out of oil and asphaltenes starts dissolving into oil. At specific temperature and pressure (Point-D), there are only vapor and oil phases and asphaltene phase disappears. This boundary is known as lower onset pressure (LOP) boundary since above it, asphaltene phase appears. In short, asphaltenes are generally stable at high pressure or in heavy oil with less content of lighter (volatile) compounds. The Pressure-Temperature plot, shown in Fig. 1.3, is known as Asphaltene phase envelope (APE), Asphaltene Onset Envelope (AOE), or Asphaltene Deposition Envelope (ADE). If the gas-oil separator condition is outside of APE (Point-E), one cannot see any trace of asphaltene precipitation inside the separator but there could be asphaltene precipitation inside the wellbore.



Fig. 1.3. Asphaltene phase envelope (APE).

1.5 Literature Survey on Thermodynamic Models for Asphaltene precipitation

There have been various models studied for asphaltene modeling for years in the literature. Generally, there are two types of thermodynamic modeling approach for asphaltene precipitation. The first approach assumes that asphaltenes are soluble in the oil and present as a true component. The second approach assumes that ashpaltenes present as a colloidal form whose stability depends upon the other constituents of the oil, temperature and pressure. In this section, we will discuss about the modeling approaches based on the Cubic Plus Association (CPA), Statistical Associating Fluid Theory (SAFT) and Cubic equation of state (EoS) from the literature. Our objective is to let the reader know about basic assumptions of these models and what kind of studies have been performed with them.

1.5.1 Ashpaltenes as True Components

Ting et al [19] propose the modeling approach based on the Perturbed Chain SAFT (PC-SAFT) EoS for asphaltene precipitation modeling. It is assumed that the asphaltene precipitation is due to nonpolar van der Waals forces. They also concede that the hydrogen bonding interactions are also important in a few situations, however, they have not considered them in their modeling. In other words, asphaltenes are present as pre-aggregated molecules in the oil and there is no association between molecules during and after precipitation. Therefore, the association term is not included. They studied their model for a recombined oil (separator gas+liquid) and a model oil (1 g asphaltenes in 100 ml toluene) with methane gas injection. It is concluded that the modeling results are in good agreement with the experimental data. Gonzalez et al [20-22] studied the effect of gas injections and contamination of oil based mud into the live oil after modifying the approach from Ting et al. [19]. Later Panuganti et al [23] modified the modeling approach from Gonzalez et al [20-22] and studied the effect of gas injection in live oils using both the PC-SAFT and Soave-Redlich-Kwong (SRK) equations of state. They concluded that the PC-SAFT model is able to predict the gas injection effect while the SRK model cannot do so. Punnapala & Vargas [24] then modified the modeling approach from Panuganti et al [23] by reducing three adjustable asphaltene PC-SAFT parameters to two parameters and studied the gas injection effect in live oils. AlHammadi et al [25] studied both PC-SAFT and CPA using modeling approaches from Panuganti et al [23] and Zhang et al [26] respectively. They compared the results with the experimental data and concluded that the PC-SAFT predictions for the effect of gas injections are better than the CPA predictions. However, they have compared the asphaltene precipitation onset results only for one live oil and therefore their conclusion cannot be generalized for all fluids. Panuganti et al [27] and Tavakkoli et al [28] applied the PC-SAFT EoS to model asphaltene precipitation from degassed crudes. For the PC-SAFT (without association term) model, discussed above, requires SARA analysis to characterize the oil.

Li & Firoozabadi [29,30] propose the CPA EoS to model asphaltenes. The Peng-Robinson (PR) EoS is used as a physical part while the association term is used from Werthiem [31,32]. Asphaltenes are considered as an associating component and can cross-associate with resins or heavy fraction of oil. Two studied are presented; the first one is on heavy/degassed oil while the second one is on live oil. In the first article, seven different heavy oils and four model oils (10 kg asphaltenes in 1m³ of toluene) are studied. In the second article, seven live oils are studied. They have not studied the gas injection effect on upper onset boundary of asphaltene phase envelope.

Zhang et al [26] compared the CPA and PC-SAFT EoS with respect to asphaltene modeling. The CPA model has the SRK EoS as a physical part and an association term is from Wertheim [31-32]. Self-association between the asphaltene molecules and cross-association between the apshaltene and resin molecules are considered. For the PC-SAFT, the same modeling approach is used as proposed by Gonzalez et al [20-22]. A total number of six live oils and one heavy oil are studied and concluded that the CPA EoS correlates the experimental data better than the PC-SAFT EoS, which contradicts the conclusion from AlHammadi et al [25], discussed above.

Shirani et al [33] also propose a modeling approach based on the CPA EoS. They compared both the PR and SRK EoS as a physical part in addition to an association part. The association term is the same as that used by Zhang et al [26] and Li et al [29,30]. Asphaltenes are considered to be self-associating component. There is no cross association between resins and asphaltene molecules. Three live oils are studied and it is concluded that the SRK term in the CPA EoS is better than the PR term. They also concluded that the CPA model is better than Victorov et al.'s model [34] and Pan et al.'s model [35].

Hustad et al [36] compare the PC-SAFT (without association term) and SRK EoS based modeling approaches with respect to asphaltene precipitation. The experimental results of constant mass expansion (CME) of four samples with different amount of N₂ are obtained. The C_{50+} aromatic fraction is considered to be the asphaltene fraction. The SARA analysis is not required for this modeling approach. It is concluded that the PC-SAFT model is better than the SRK model.

Pedersen et al [37] also studied live oils with the SRK/PR EoS and concluded that the models can correlate the asphaltene phase boundary after tuning critical pressure and temperature of asphaltene component. However, they have not extensively studied the gas injection effect on the asphaltene phase boundary.

Jamaluddin et al [38] studied the SRK EoS to describe two live oils. They could correlate asphaltene upper onset pressure boundary by tuning the model parameters and predict lower onset pressure boundary. However, they have not studied the gas injection effect on the asphaltene phase boundary extensively.

Sabbagh et al [39] use the PR EoS to study asphaltene yield from the heavy oil. The deasphalted heavy oil (maltene) is divided into single component of saturates, aromatics and resins fractions. They divide the asphaltene fraction into multiple components of different molar mass in the range of [1800-30000 Da] based on the gamma distribution function. They concluded that the PR model is not a universal predictor and not better than the previously developed regular solution model.

1.5.2 Ashpaltenes as Colloids

Wu et al [40,41] propose the modeling approach based on the HS-SAFT (Hard Sphere SAFT) EoS. Asphaltenes and resins are assumed to be present as colloids in the solvent (oil excluding asphaltenes and resins). The asphaltene precipitation is governed by the interactions between asphaltene-asphaltene, resin-resin and asphaltene-resin molecules. The solvent is considered as a medium, which affects the van der Waal interactions among asphaltene and resin molecules through average pair-dispersion energy. This pair-dispersion energy depends upon Hamaker constants of the medium, asphaltenes and resins. Asphaltene molecules are associating hard spheres while the resins molecules are chains of hard spheres. There can be cross association between asphaltene and resin molecules but no association between resins molecules. The PR EoS with Peneloux correction factor is used to calculate VLE since the oil density and composition is required to calculate Hamaker constant of medium. It is assumed that the asphaltene concentration is very small in oil and their precipitation

will not affect VLE. Different live and dead oils are studied and results are in agreement with the experimental data.

Buenrostro-Gonzalez et al [42] also propose the same model like Wu et al [40,41], but with the VR-SAFT (variable range SAFT) instead of the HS-SAFT. Asphaltenes and resins pair potential is given by the sum of hard sphere potential and variable range attractive potential, changing of which the shape of the attractive well is modified. Effect of this potential is considered in monomers interaction, chain formation and associating contribution to overall Helmholtz free energy whereas Wu et al [40,41] consider this potential (not variable but fixed range) in monomer interaction contribution only. Variable range potential can be given by either Square Well or Sutherland. It is concluded that there is not much difference in the results when using either Square Well or Sutherland since the asphaltene precipitation is governed by the association energy. Energy depth is given by Hamkar's constants of asphaltnes (H^A) , resins (H^R) and solvent (H^S) (oil excluding asphaltenes and resins). Solvent is considered structurless continuum, which screens out interaction between asphaltene-asphaltene, resin-resin and asphaltene-resin molecules. When density of solvent decreases (due to pressure drop or gas addition), H^S decreases, which increases the difference between H^A and H^S . It will result in increased interaction between asphaltene-asphaltene molecules, which leads to precipitation. H^{S} is density dependent and therefore the PR EoS with Peneloux volume correction is used for VLE. Two different oils are studied and concluded that one set of parameters obtained from the experimental data is enough to predict the asphaltene precipitation at different temperature, pressure and composition.

Fahim et al [43] also use the same approach as proposed by Wu et al [40]. Total Helmholtz energy is considered due to association contribution only and other contributions (ideal gas, hard spheres repulsion, van der Waals interactions, and resins chain formation) are neglected. Asphaltene molecules are considered self-associating and resins molecules are not self-associating. Resins molecules can cross-associate with asphaltene molecules. The SRK EoS is used to calculate phase equilibrium (in terms of P^{SRK}) considering all components and only binary mixture of asphaltenes and resins are considered to calculate the association effect on the phase equilibrium (in terms of P^{assoc}). In other words the total pressure is given by the sum of SRK and association contributions ($P = P^{SRK} + P^{assoc}$). Several live oils are studied but no reference to the experimental data is provided. There is no study done with respect to gas injection.

The asphaltene modeling study can be categorized into modeling of asphaltene precipitation onset condition from live oil, gas injection effect on asphaltenes containing live/dead oil, asphaltene yield from dead oil, and asphaltene precipitation onset condition from blend of different crudes. Table 1.1 shows the different equations of state modeling approaches studied for the different categories of asphaltene modeling study.

Table 1.2 shows different experimental data used by the different modeling studies, mentioned above. It also gives us an idea about how different models could correlate or predict the experimental data.

For example, the experimental data of reference [44] are used in modeling studies with the CPA and PC-SAFT (without association term) EoS.

		Asphaltene Modeling Study			
EoS	Reference	Asp Onset from Live Oil	Gas Injection Effect	Asp Yield from Dead Oil	Asp Onset from Blend of Dead Oils
	[26]	Yes	Yes	Yes	No
	[29]	No	No	Yes	No
CPA	[30]	Yes	No	No	No
	[33]	Yes	Yes	No	No
	[43]	Yes	No	No	No
CAET HS	[40]	No	No	Yes	No
SAF I-115	[41]	Yes	Yes	No	No
SAFT-VR	[42]	Yes	No	Yes	No
DC SAET	[19]	No	Yes	Yes	No
(w/o association term)	[20-25,36]	Yes	Yes	No	No
(w/o association term)	[27-28]	No	No	Yes	No
	[23 36]	Yes	Yes	No	No
SRK	[37]	Yes	No	No	No
חח	[37]	Yes	No	No	No
РК	[39]	No	No	Yes	No

 Table 1.1. Equations of state used for different categories of asphaltene modeling study.

Reference (Exp. Data)	СРА	PC-SAFT (w/o assoc. term)	SRK	PR	SAFT-HS	SAFT-VR	This work
[11]	[26]	[27, 28]			[41]		Х
[19]		[19, 20,27]					Х
[21]		[21]					
[23]		[23]	[23]				Х
[24]		[24]					Х
[36]		[36]	[36]				
[38]			[38]	[37]			
[39]	[29]	[28]		[39]			
[42]						[42]	Х
[43]	[43]						
[44]	[26,30]	[20,22]		[37]			Х
[45]		[22]					
[46]		[21]					
[47]							
[49]	[30]						Х
[50]	[30]						
[51]	[30]						Х
[52]	[30]						Х
[53]	[30] [33] [26]				[41]		Х
[54]	[33]				[41]		
[55]	[26]						Х
[56]	[26]						Х
[57]	[26]				[41]		Х
[58]	[26]						Х
[59]			[37]				
[60]		[28]					
[61]							Х
[62]							Х
[63]							Х
[64]							Х
[65]							Х

Table 1.2. Experimental data from the literature used by different groups to compare thier modeling results.

1.6 Scope of Research

From the literature study, we came to know that the association models (e.g. SAFT, CPA) are theoretical models and have potential to represent asphaltene system. Li et al [30] propose simple modeling approach with the CPA EoS but do not show any result with gas injection effect on upper onset boundary. AlHammadi et al [25] concluded that the PC-SAFT (without association term) model is better than the CPA model. On the other hand, Zhang et al [26] also proposed a modeling approach with the CPA EoS and showed variety of results including gas injection. They also concluded that the CPA results are better than the PC-SAFT results, studying the modeling approach from Gonzalez et al [20-22] for the PC-SAFT (without association term). Therefore, there are two different opinions in the literature about asphaltene modeling results with the CPA and PC-SAFT. Tavakkoli et al [24] concluded that single set of parameters of the PC-SAFT model (without association term), used for saturation and upper onset pressure predictions, do not show a good match for the amount of precipitated asphaltenes. Hustad et al [36] showed that the PC-SAFT is better than the SRK. Panuganti et al [23] concluded that the SRK EoS is not able to predict the gas injection effect while the PC-SAFT (without association term) can predict it. Panuganti et al [23] also mentioned that an accurate SARA analysis is required to characterize the given oil. There is no study about sensitivity of SARA analysis and model parameters in the literature. Also, there is no information about whether these models are reliable at temperature and pressure conditions away from the experimental conditions. In addition, there is no study, as shown in Table 1.1, on asphaltene precipitation from the blend of different dead oils using the association models. Nobody has ever tried the asphaltene modeling using the PC-SAFT EoS including the association term.

1.7 Objectives of Thesis

Motivated by the need and importance of reliable predictions of asphaltene precipitation in oil industries, this work aims to achieve the following objectives:

- (a) Develop a modeling approach for asphaltene precipitation based on the equations of state, which account for association forces between molecules, for example the CPA and PC-SAFT equations of state. The modeling approach should be as simple as possible and easy to be implemented into reservoir PVT simulation software.
- (b) Study several fluids and compare the results with experimental data in order to show the reliability of the modeling approach to predict asphaltene precipitation.
- (c) Study the modeling approach based on the PC-SAFT (without association term) from the literature and compare it with the modeling approach, developed in this work, in order to find out differences.
- (d) Check the sensitivity of SARA analysis and model parameters to the modeling approach.
- (e) Compare the developed model with the cubic EoS (eg. SRK or PR).
- (f) Apply the modeling approach to study the asphaltene precipitation from crudes.
- (g) Apply the modeling approach to study the asphaltene precipitation from the blend of crudes.

(h) Develop a tool based on the modeling approach, which can be disseminated to consortium member companies for the calculation of asphaltene phase envelope.

1.8 Organization of Thesis

This thesis is organized into following chapters. The work presented in each chapter is briefly described below.

<u>Chapter-1</u>: There is a discussion about what asphaltenes are and how they are defined and quantified as per the standard procedure. Generally for reservoir fluids, asphaltene precipitation flow assurance problem is studied by Pressure-Temperature plot, known as Asphaltene Phase Envelop, which is also explained. A literature survey on asphaltene precipitation modeling with association equations of state is also presented and the scope of research is identified. Finally, objectives of this PhD project and organization of thesis are mentioned.

<u>Chapter-2</u>: All equations of state (CPA, PC-SAFT, SRK, SRK with Huron-Vidal mixing rule), which are studied in this work, are described to understand the physics behind them and get an idea about model parameters. The reader can skip this chapter if he/she knows about them.

<u>Chapter-3:</u> A modeling approach based on the CPA EoS is developed based on the inspiration from the literature. Several reservoir fluids are studied and results are compared with the experimental data.

<u>Chapter-4</u>: The sensitivity of the modeling parameters are investigated and successfully shown that the modeling approach based on the CPA EoS can predict the gas injection effect. It is concluded that one model parameter (cross-association energy between asphaltene and heavy component molecules) is temperature dependent and the model results may not be reliable outside of the experimental temperature range.

<u>Chapter-5:</u> The developed modeling approach is applied to the PC-SAFT EoS. The modeling approach from the literature based on the PC-SAFT (without association term) EoS is studied. The results from the CPA, PC-SAFT and PC-SAFT (without association term) are compared for several reservoir fluids. It is concluded that the literature approach based on the PC-SAFT (without association term) cannot correlate the upper onset boundary of certain reservoir fluids and needs temperature dependency. On the other hand, the PC-SAFT model, developed here, can correlate the one kind of data and predict the other kind of data like the CPA model.

<u>Chapter-6:</u> The developed modeling approach is applied to the SRK (with classical mixing rule) and SRK with Huron-Vidal mixing rule (SRK+HV) EoS. The results from the CPA, SRK and SRK+HV are compared for several reservoir fluids. It is concluded that the SRK and SRK+HV models can predict the gas injection effect on asphaltene onset boundary only when the asphaltene molar composition in C_{6+} fraction is fixed to the reference value at which the binary interaction parameters of gas/*n*-alkane-asphaltene pairs are regressed. In other words, the SRK and SRK+HV models work only at the reference value of asphaltene molar amount in C_{6+} fraction.

<u>Chapter-7</u>: The CPA model is applied to degassed crude oil in order to model asphaltene yield and precipitation onset during the addition of *n*-paraffin. The asphaltene stability in the blend of more than two crudes is also studied. The results from the PC-SAFT (without association term) are also compared. It is concluded that both models cannot predict the asphaltene yield but can be fitted with a certain number of model parameters. The CPA model has potential to predict asphaltene stability in the blend of *n*-paraffin at the onset conditions.

<u>Chapter-8:</u> The thesis is concluded and possible future research tasks are recommended.

Reference

- 1. Speight J.G.; "Petroleum Aspahltenes Part 1 Asphaltenes, Resins and the Structure of Petroleum", Oil & Gas Science and Technology, Vol 59 (2004), No. 5, pp. 467-477.
- Vargas F.M.; Gracia-Bermudes M.; Boggara M.; Punnapala S.; Abutaqiya M.; Mathew N.; Prasad S.; Khaleel A.; Al Rashed M.; Al Asafen H.; "On the Development of an Enhanced Method to Predict Asphaltene Precipitation", Presented at the Offshore Technology Conference held in Houston, Texas, USA, 5-8 May 2014.
- 3. Suatoni, J. C., & Swab, R. E. (1975). Rapid hydrocarbon group-type analysis by high performance liquid chromatography. Journal of Chromatographic Science, 13(8), 361-366.
- 4. Suzuki, Y. (1972). Studies on Quantitative TLC by means of a Hydrogen FID. II Rapid Analysis of Fuel Oil Constituents,". In 21st Annual Meeting of the Japan Society for Analytical Chemistry (Vol. 47).
- ASTM D2007-93: "Standard Test Method for Characteristic Groups in Rubber Extender and Processing Oils by the Clay-Gel Adsorption Chromatographic Method," ASTM, 1993
- 6. Fan, T., & Buckley, J. S. (2002). Rapid and accurate SARA analysis of medium gravity crude oils. Energy & Fuels, 16(6), 1571-1575.
- 7. Yarranton, H. W. (2005). Asphaltene self-association. Journal of dispersion science and technology, 26(1), 5-8.
- 8. Strausz, O. P., Peng, P. A., & Murgich, J. (2002). About the colloidal nature of asphaltenes and the MW of covalent monomeric units. Energy & fuels, 16(4), 809-822.
- 9. L. Buch, H. Groenzin, E. Buenrostro-Gonzalez, S.I. Andersen, C. Lira-Galeana, O.C. Mullins, Molecular size of asphaltene fractions obtained from residuum hydrotreatment, Fuel 82-9 (2003) 1075-1084.
- 10. S. Badre, C.C. Goncalves, K. Norinaga, G. Gustavson, O.C. Mullins, Molecular size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils and bitumen, Fuel 85-1 (2006) 1-11.
- 11. Hirschberg A.; de-Jong L.N.J.; Schipper B.A.; Meijer J.G.; "Influence of Temperature and Pressure on Asphaltene Flocculation", Society of Petroleum Engineers Journal, June 1984.
- 12. Speight J.G.; Plancher H.; "Molecular models for petroleum asphaltenes and implications for asphalt science and technology", Proceedings of the International Symposium on the Chemistry of Bitumens, 1991.
- 13. Wang J.X.; "Predicting Asphaltene Flocculation in Crude Oils", Ph.D thesis, Socorro, NM, 2000.
- 14. Wiehe I.A.; Fuel Sci. Tech. Intl., 14:289, 1996.
- 15. Long R.B. (1979) Preprints, Div. Petrol. Chem. Am. Chem. Soc., 24, 4, 891.
- 16. Long, R.B. (1981) The Chemistry of ASpahltene Constituents. In : Advances in Chemistry, Series No. 195, J.W. Bunger and N.Li (eds), American Chemical Society, Washington, DC.
- 17. Long R.B. and Speight J.G. (1989) Revue de l'Institut Francais du Petrole, 44, 205.
- 18. Cimino, R., Correrra, S., Del Bianco, A. and Lockhart T.P. (1995) In: Asphaltne constituents: Fundamentals and Applications, Chapter III, E.Y. Sheu and O.C. Mullins (eds.), Plenum Press, New York.
- 19. Ting P.D.; Hirasaki G.J.; Chapman W.G.; "Modeling of Asphaltene Phase Behavior with the SAFT Equation of State", Petroleum Science and Technology, Vol. 21, Nos. 3 & 4, 647-661,2003.
- 20. Gonzalez D.L.; Ting P.D.; Hirasaki G.J.; Chapman W.G.; "Prediction of Asphaltene Instability under Gas Injection with the PC-SAFT Equation of State", Energy & Fuels 2005, 19, 1230-1234.
- 21. Gonzalez D.L.; Hirasaki G.J.; Creek J.; Chapman W.G.; "Modeling of Asphaltene Precipitation Due to Changes in Composition Using the Perturbed Chain Statistical Association Fluid Theory Equation of State", Energy & Fuels, 2007, 21, 1231-1242.
- 22. Gonzalez D.L.; Vargas F.M.; Hirasaki G.J.; Chapman W.G.; "Modeling Study of CO2-Induced Asphaltene Precipitation", Energy & Fuels 2008, 22, 757-762.
- 23. Panuganti S.R.; Vargas F.M.; Gonzalez D.L.; Kurup A.S.; Chapman W.G.; "PC-SAFT characterization of crude oils and modeling of asphaltene phase behavior", Fuel 93 (2012) 658-669.
- 24. Punnapala, S., & Vargas, F. M. (2013). Revisiting the PC-SAFT characterization procedure for an improved asphaltene precipitation prediction. Fuel, 108, 417-429.
- 25. AlHammadi, A. A., Vargas, F. M., & Chapman, W. G. (2015). Comparison of Cubic-Plus-Association and Perturbed-Chain Statistical Associating Fluid Theory Methods for Modeling Asphaltene Phase Behavior and Pressure–Volume–Temperature Properties. Energy & Fuels.

- 26. Zhang X.; Pedrosa N.; Moorwood T.; "Modeling Asphaltene Phase Behavior: Comparison of Methods for Flow Assurance Studies", Energy fuels 2012, 26, 2611-2620.
- Panuganti, S. R., Tavakkoli, M., Vargas, F. M., Gonzalez, D. L., & Chapman, W. G. (2013). SAFT model for upstream asphaltene applications. Fluid Phase Equilibria, 359, 2-16.
- 28. Tavakkoli, M., Panuganti, S. R., Taghikhani, V., Pishvaie, M. R., & Chapman, W. G. (2014). Understanding the polydisperse behavior of asphaltenes during precipitation. Fuel, 117, 206-217.
- 29. Li, Z., & Firoozabadi, A. (2010). Modeling asphaltene precipitation by n-alkanes from heavy oils and bitumens using cubic-plus-association equation of state. Energy & Fuels, 24(2), 1106-1113.
- Li, Z., & Firoozabadi, A. (2010). Cubic-plus-association equation of state for asphaltene precipitation in live oils. Energy and Fuels, 24(5), 2956.
- 31. Wertheim, M.S.; J. Stat. Phys., 1984, 35, 19.
- 32. Wertheim, M.S.; J. Stat. Phys., 1986, 42, 459.
- 33. Shirani B.; Nikazar M.; Seyyed A.; Dehghani M.; "Prediction of asphaltne phase behavior in live oil with CPA equation of state", Fuel 97, 89-96, 2012.
- 34. Victorov AI; Firoozabadi A.; "Thermodynamic micellization model for asphaltene precipitation from petroleum fluids"", AICHE Journal 19996, 42, 1753-64.
- 35. Pan H.; Firoozabadi A.; "Thermodynamic mecellization model for asphaltene precipitation inhibition", AICHE Journal 2000, 46, 416-26.
- Hustad O.S.; Jia N.J.; Pedersen K.S.; Memon A.; Leekumjorn S.; "High Pressure Data and Modeling Results for Phase Behavior and Asphaltene Onsets of GoM Oil Mixed with Nitrogen", SPE 166097, 2013.
- Pedersen, K. S., Christensen, P. L., & Shaikh, J. A. (2014). Phase behavior of petroleum reservoir fluids. CRC Press.
- Jamaluddin, A. K. M., Creek, J., Kabir, C. S., McFadden, J. D., D'Cruz, D., Manakalathil, J. & Ross, B. (2002). Laboratory techniques to measure thermodynamic asphaltene instability. Journal of Canadian Petroleum Technology, 41(07).
- Sabbagh, O., Akbarzadeh, K., Badamchi-Zadeh, A., Svrcek, W. Y., and Yarranton, H. W. (2006). Applying the PR-EoS to asphaltene precipitation from n-alkane diluted heavy oils and bitumens. Energy & fuels, 20(2), 625-634.
- 40. Wu J.; Prausnitz J.M.; Firoozabadi A.; "Molecular-thermodynamic Framework for Asphaltene-Oil Equilibria", AICHE Journal, May 1998, Vol.44, No. 5.
- 41. Wu, J., Prausnitz, J. M., & Firoozabadi, A. (2000). Molecular thermodynamics of asphaltene precipitation in reservoir fluids. AIChE journal, 46(1), 197-209.
- 42. Buenrostro-Gonzalez E.; Galeana C.L.; Villegas A.G.; Wu J.; "Asphalten Precipitation in Crude Oils: Theory and Experiments", AICHE Journal, October 2004, Col. 50, No. 10.
- 43. Fahim M.A.; Andersen S.I.; "Tuning EOS Using Molecular Thermodynamics To Construct Asphaltne Deposition Envelope (ADE)", SPE 93517, 2005.
- 44. Jamaluddin A.K.M., Joshi N., Iwere F., Gurpinar O., "An Investigation of Asphaltene Instability Under Nitrogen Injection", SPE 74393, 2002.
- 45. Verdier S.; Carrier H.; Andersen S.I.; Daridon J.L.; "Study of Pressure and Temperature Effects on Asphaltene Stability in Presence of CO2", Energy & Fuels 2006, 20, 1584-1590.
- 46. Muhammad, M.; Joshi, N.; Creek, J.; McFadden, J.; "In Effect of Oil Based Mud Contamination on Live Fluid Asphaltene Precipitation Pressure", Presented at the 5th International Conference on Petroleum Phase Behavior and Fouling, Banff, Alberta, Canada, 2004; pp 13-17.
- 47. Kokal S.; Al-Ghamdi A.; Krinis D.; "Asphaltene Precipitation in High Gas-Oil-Ratio Wells", SPE 81567, Society of Petroleum Engineers: Richardson, TX, 2003; p. 1-11.
- 48. Sabbagh, O.; Akbarzadeh, K.; Badamchi-Zadeh A.; Svrcek W.Y.; Yarranton H.W.; "Applying the PR-EoS to Asphaltene Precipitation from n-Alkane Diluted Heavy Oils and Bitumens", Energy Fuels 2006, 20, p. 625-634.
- 49. Szewczyk V.; Thomas M.; Behar E.; "Prediction of Volumetric Properties and (Multi-) Phase Behaviour of Asphaltenic Crudes". Institut Francais du Petrole. Vol. 53. No. 1. Janvier-Fevrier 1998.

- 50. Szewczyk, V.; Behar E.; "Compositional model for predicting asphaltenes flocculation", Fluid Phase Equilibria, 1999, 158, 459.
- 51. Buenrostro G.E.; Galeana C.L.; Villegas A.; Wu J.; "Asphaltene Precipitation in Crude Oils: Theory and Experiments". AICHE Journal. Vol. 50. No. 10. 2004.
- 52. Fahim M.A.; "Empirical Equations for Estimating ADE of Crude Oils", Petroleum Science and Technology, 95, 949-965, 2007.
- Srivastava R.K.; Huang S.S.; Dyer S.B.; Mourits F.M.; "Quantification of Asphaltene Flocculation During Miscible CO2 Flooding in the Weyburn Reservoir". The Journal of Canadian Petroleum Technology. Vol. 34. No. 8. 1995.
- 54. Burke NE.; Hobbs RE.; Kashou SF.; "Measurement and modeling of asphaltene precipitation", JPT Trans AIME 1990, 289;1440-6.
- 55. Kabir C.S.; Jamaluddin A.K.M.; "Asphaltene Charactrerization and Mitigation in South Kuwait's Marrat Reservoir". SPE 53155. 1999.
- 56. Yonebayashi H.; Masuzawa T.; Dabbouk C.; Urasaki D.; "Ready for Gas Injection: Asphaltene Risk Evaluation by Mathematical Modeling of Asphaltene-Precipitation Envelope (APE) With Integration of All Laboratory Deliverables". SPE 125643. 2011.
- 57. Fotland P.; Anfinsen H.; Foerdedal H.; Hjermstad H.P.; "The Phae Diagrams of Asphaltenes: Experimental Technique, Results and Modeling on Some North Sea Crude Oils", Symposium on the Chemistry of the Asphaltene and Related Substances, Cancun, Mexico (1997).
- 58. Leontaritis, K.J.; Mansoori, G.A.; "Proceedings of the Society of Petroleum Engineers International Symposium on Oilfield Chemistry; San Antonio, TX, Feb 4-6, 1987.
- 59. Rydahl, A. K., Pedersen, K. S., & Hjermstad, H. P. (1997). Modelling of Live Oil Asphaltene Precipitation. American Institute of Chemical Engineers.
- 60. Wang, J. (2000). Predicting asphaltene flocculation in crude oils. PhD. thesis 2000. In: Petroleum and chemical engineering, New Mexoco Institure of Mining and Technology. Socorro.
- Tharanivasan, A. K., Svrcek, W. Y., Yarranton, H. W., Taylor, S. D., Merino-Garcia, D., and Rahimi, P. M. (2009). Measurement and modeling of asphaltene precipitation from crude oil blends. Energy & Fuels, 23(8), 3971-3980.
- 62. Memon, A. I., Qassim, B., Al-ajmi, M. F., Tharanivasan, A. K., Gao, J., Ratulowski, J. & Khan, R. A. (2012, January). Miscible Gas Injection and Asphaltene Flow Assurance Fluid Characterization: A Laboratory Case Study for Black Oil Reservoir. In SPE EOR Conference at Oil and Gas West Asia. Society of Petroleum Engineers.
- Gonzalez, D. L., Garcia, M. E., & Diaz, O. (2012, January). Unusual asphaltene phase behavior of fluids from Lake Maracaibo, Venezuela. InSPE Latin America and Caribbean Petroleum Engineering Conference. Society of Petroleum Engineers.
- 64. Gonzalez, D. L., Mahmoodaghdam, E., Lim, F. H., & Joshi, N. B. (2012, January). Effects of Gas Additions to Deepwater Gulf of Mexico Reservoir Oil: Experimental Investigation of Asphaltene Precipitation and Deposition. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.
- Marcano, F., Antonieta Ranaudo, M., Chirinos, J., Castillo, J., Daridon, J. L., & Carrier, H. (2013). Study of Asphaltenes Aggregation in Toluene/n-Heptane/CO2 Mixtures under High-Pressure Conditions. Energy & Fuels, 27(8), 4598-4603.

Chapter 2. Equations of State

In this chapter, we will briefly discuss about equations of state (EoS), which are used in this thesis. For more details, the reader is requested to refer the respective references. If the reader is familiar with below equations of state, he/she can skip this chapter. The objective of this chapter is to familiarize the reader with the model parameters used by each equation of state.

In thermodynamics, an equation of state represents the relationship between pressure, temperature and molar volume of the fluid. An equation of state can also be derived from the mathematical description of intermolecular forces. Van der Waal [1] proposed an equation of state to calculate different physical properties of the fluid. After van der Waal's work, several equations of state have been proposed and studied. Among these equations of state, the SRK [2] and PR [3] equations of state are the most used equations in the petroleum industries. In late 20th century, Chapman et al [4,5] proposed an equation of state, known as Statistical Associating Fluid Theory (SAFT), based on statistical thermodynamic perturbation theory. They referred the work of Wertheim [6] in order to describe associating fluid. Afterwards, many researchers have modified the original SAFT EoS and proposed different versions. Among these versions, the most used version is the Perturbed Chain (PC-SAFT) EoS, proposed by Gross and Sadowski [7]. Kontogeorgis et al [8] also combined the association term with the SRK EoS and proposed the Cubic Plus Association (CPA) EoS, which have been successful in describing many complex associating systems like glycols, alcohols.

2.1 Cubic Plus Association

The Cubic Plus Association (CPA) equation of state (EoS), proposed by Kontogeorgis et al [8], can be expressed for mixtures in terms of pressure P, as shown in equation (2.1). Please consult the "List of Symbol" section for the meaning of each symbols used in the following equations. The addition of the association term in the CPA EoS can fairly describe the polar and hydrogen bonding forces between molecules. The CPA EoS has been successful to describe the association system (e.g. glycols) [8].

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho}\right) \sum_i x_i \sum_{A_i} \left(1 - X_{A_i}\right)$$
2.1

$$a(T) = \sum_{i} \sum_{j} x_i x_j a_{ij}(T)$$
2.2

$$a_{ij}(T) = \sqrt{a_i(T)a_j(T)} (1 - k_{ij})$$
2.3

$$b = \sum_{i} x_i b_i$$
 2.4

When the CPA EoS is used for mixtures, the conventional mixing rules are employed in the physical term (Soave-Redlich-Kwong: SRK) for the energy and co-volume parameters. The geometric mean rule is used for the energy parameter $a_{ij}(T)$. The interaction parameter k_{ij} is the only binary adjustable parameter of CPA in the applications for self-associating mixtures, e.g. glycol with *n*-alkanes.

The pure compound energy parameter (a_i) of the EoS is given by temperature dependency proposed by Mathias-Copeman [9], while co-volume parameter (b_i) is temperature independent:

$$a_{i}(T) = a_{0,i} \left[1 + c_{1,i} \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) + c_{2,i} \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right)^{2} + c_{3,i} \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right)^{3} \right]^{2}; for \frac{T}{T_{c,i}} < 1;$$
2.5

$$a_{i}(T) = a_{0,i} \left[1 + c_{1,i} \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^{2}; \quad for \quad \frac{T}{T_{c,i}} \ge 1;$$
2.6

where $T_{c,i}$ is the critical temperature of the i^{th} component.

The energy parameter temperature dependency proposed by Mathias-Copeman can be reduced to temperature dependency proposed by Soave [2] as below:

$$c_{1,i} = 0.480 + 1.574\omega - 0.176\omega^2; \quad c_{2,i} = c_{3,i} = 0;$$
 2.7

The key element of the association term is X_{A_i} , which represents the mole fraction of site-A in molecule of component *i* not bonded to other sites, while x_i is the mole fraction of component *i*. X_{A_i} is related to the association strength $\Delta^{A_iB_j}$ between two sites belonging to two different molecules, e.g. site A on molecule *i* and site B on molecule *j*, determined from:

$$X_{A_{i}} = \frac{1}{1 + \rho \sum_{j} X_{j} \sum_{B_{j}} X_{B_{j}} \Delta^{A_{i}B_{j}}}$$
2.8

where the association strength $\Delta^{A_iB_j}$ in CPA is expressed as:

$$\Delta^{A_i B_j} = g\left(\rho\right) \left[exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j}$$
2.9

where:

$$b_{ij} = \frac{b_i + b_j}{2}$$

with the radial distribution function:

$$g(\rho) = \frac{1}{1 - 1.9n}; \qquad n = \frac{1}{4}b\rho;$$
 2.11

In the expression for the association strength $\Delta^{A_i B_j}$, the parameters $\varepsilon^{A_i B_j}$ and $\beta^{A_i B_j}$ are called the association energy and the association volume, respectively. These two parameters are used only for associating components, and along with the three additional parameters of the SRK term ($a_{0,i}$, b_i , $c_{1,i}$), they are the five pure-compound parameters of the model. They are obtained by fitting vapor pressure and liquid density data. For inert components such as hydrocarbons, only the three parameters of the SRK term are required, which can either be obtained from vapor pressures and liquid densities or be calculated in the conventional manner (from critical data, acentric factor).

Following are the combining rules (CR), which are required for cross-associating systems. CR-1 and Elliott CR are generally used. Modified CR-1 and Customized CR-1 are used for solvating systems only.

(i) CR-1:

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2}; \quad \beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \quad ; \qquad 2.12$$

(ii) Elliott CR:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}}$$

(iii) Modified CR-1:

Cross association volume $\beta^{A_iB_j}$ is fitted to experimental data and CR-1 rule is used for cross association energy $\epsilon^{A_iB_j}$.

(iv) Customized CR-1:

Cross association volume $\beta^{A_iB_j}$ and cross association energy $\epsilon^{A_iB_j}$ are fitted to experimental data.

For an associating compound, the number and type of associating sites need to be determined before parameterize the five CPA parameters. Huang and Radosz [10] propose the association scheme for various compounds. They label the association scheme with a number (corresponding to number of sites) followed by a letter (A: any site can associate with any other, B: one site is positive/negative and other sites have opposite charge, C: two sites are positive/negative and other sites have opposite charge, C: two sites are positive/negative and other sites have opposite charge, and so on) [11]. Table 2.1 shows a few examples of the association scheme.

Compound	Formula	Scheme	Compound	Formula	Scheme
Water	А В :О:Н С Н D	4C (2+ve,2-ve)	Alcohol	— О:: в Н с	3B (1+ve,2-ve)
Ammonia	D H:N:H B H C	4B (1-ve,3+ve)	Alcohol	— ;;; H B	2B (1-ve,1+ve)
Benzene		Non- Selfassociating (solvating with single –ve site)			

Table 2.1. Association Scheme for pure compound molecules as per Huang and Radosz [10] temrminology.

2.2 Perturbed-Chain-Statistical-Associating-Fluid-Theory

The Perturbed-Chain-Statistical-Associating-Fluid-Theory (PC-SAFT) EoS was developed by Gross and Sadowski [7]. It has its basis on SAFT EoS, which was originally developed by Chapman et al [5]. The PC-SAFT EoS uses hard-chain fluid as a reference for the perturbation theory while the SAFT EoS uses hard spherical segments. The PC-SAFT EoS can be written in terms of residual Helmholtz free energy (A^{res}) as shown in equation (2.14). Please consult the "List of Symbol" and "Greek Letters" sections for the meaning of each symbols used in the following equations.

$$A^{res} = A^{hs} + A^{chain} + A^{disp} + A^{assoc}$$

$$2.14$$

where A^{hs} , A^{chain} , A^{disp} and A^{assoc} are the Helmholtz free energy contributions for the hard sphere repulsion, hard chain formation from the hard spherical segments, dispersion forces and association contributions between chains respectively. For more details of the PC-SAFT EoS, the reader is referred to literature [8,7]. There are five model parameters for a pure compound, (1) number of spherical segments per chain/molecule (m) (2) temperature independent diameter of spherical segment ($\sigma(\dot{A})$) (3) potential energy (ϵ/k (K)) (4) association energy (ϵ/R (K)) and (5) association volume \mathcal{K} . For non-associating pure compounds, only the first thee parameters are required while for associating pure compounds, all the five parameters are needed.

$$\frac{A^{hs}}{RT} = \frac{m}{\xi_0} \left[\frac{3\xi_1 \xi_2}{\left(1 - \xi_3\right)} + \frac{\xi_2^3}{\xi_3 \left(1 - \xi_3\right)^2} + \left(\frac{\xi_2^3}{\xi_3^2} - \xi_0\right) \ln\left(1 - \xi_3\right) \right]$$
2.15

$$\frac{A^{chain}}{RT} = \sum_{i} x_i \left(1 - m_i\right) \ln\left(g_{ii}^{hs}\right)$$
2.16

$$g_{ij}^{hs} = \frac{1}{\left(1 - \xi_{3}\right)} + \left(\frac{d_{i}d_{j}}{d_{i} + d_{j}}\right) \frac{3\xi_{2}}{\left(1 - \xi_{3}\right)^{2}} + \left(\frac{d_{i}d_{j}}{d_{i} + d_{j}}\right)^{2} \frac{2\xi_{2}^{2}}{\left(1 - \xi_{3}\right)^{3}}$$
2.17

$$\xi_n = \frac{\pi}{6} \hat{\rho} \sum_i x_i m_i d_i^n$$
2.18

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-3\frac{\epsilon_i}{kT}\right) \right]$$
 2.19

$$\frac{A^{disp}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT}$$
2.20

$$\frac{A_{i}}{RT} = -2\pi\hat{\rho} \left(\sum_{i=0}^{6} a_{i}(m)\eta^{i}\right) \left(\sum_{i} \sum_{j} x_{i}x_{j}m_{i}m_{j}\left(\frac{\epsilon_{ij}}{kT}\right)\sigma_{ij}^{3}\right)$$
2.21

$$\frac{A_2}{RT} = -\frac{\pi \hat{\rho} m}{C} \left(\sum_{i=0}^{6} \mathbf{b}_i(m) \eta^i \right) \left(\sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{kT} \right)^2 \sigma_{ij}^{3} \right)$$
 2.22

$$C = 1 + m \frac{8\eta - 2\eta^2}{(1 - \eta)^2} + (1 - m) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{\left[(1 - \eta)(2 - \eta)\right]^2}$$
 2.23

$$m = \sum_{i} x_{i} m_{i}$$
 2.24

Conventional combining rules are applied to calculate the parameters for a pair of two different segments.

$$\sigma_{ij} = \frac{1}{2} \left(\sigma_i + \sigma_j \right)$$
 2.25

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \left(1 - k_{ij} \right)$$
2.26

$$a_{i}(m) = a_{0i} + \frac{m-1}{m} a_{1i} + \left(\frac{m-1}{m}\right) \left(\frac{m-2}{m}\right) a_{2i}$$
 2.27

$$b_{i}(m) = b_{0i} + \frac{m-1}{m}b_{1i} + \left(\frac{m-1}{m}\right)\left(\frac{m-2}{m}\right)b_{2i}$$
2.28

The universal constants (total 42) for the a_{0i} , a_{1i} , a_{2i} , b_{0i} , b_{1i} , b_{2i} can be found from Gross and Sadowski [2]. These 42 constants are regressed from pressure-volume-temperature (PVT) data of pure *n*-alkane series.

$$\eta = \frac{\pi \hat{\rho}}{6} \sum_{i} x_i m_i d_i^3$$
 2.29

$$\rho = \frac{\hat{\rho}}{N_{AV}}$$
 2.30

$$\frac{A^{assoc}}{RT} = \sum_{i} x_i \left[\sum_{A_i} \left(\ln X_{Ai} - \frac{X_{Ai}}{2} \right) + \frac{M_i}{2} \right]$$
2.31

$$X_{A_{i}} = \left[1 + \sum_{j} \sum_{B_{j}} \rho_{j} X_{B_{j}} \Delta^{A_{i}B_{j}}\right]^{-1}$$
 2.32

$$\Delta^{A_i B_j} = g_{ij}^{hs} \left[exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] \left(d_{ij}^{3}\right) \left(\mathcal{K}^{A_i B_j}\right)$$
2.33

$$\beta^{A_i B_j} = \mathcal{K}^{A_i B_j}$$

Same combining rules, as mentioned in the section of CPA EoS, are applied for cross association energy and cross-association volume.

2.3 Soave-Redlich-Kwong with Classical Mixing Rule

The CPA EoS, described above, is reduced to the SRK EoS, as shown in equation (2.35), when association term is not considered:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m (V_m + b)}$$
2.35

Equations (2.2) to (2.7) are also applicable to SRK EoS.

Unlike the CPA EoS, the pure compound energy $(a_{0,i})$ and co-volume (b_i) parameters are calculated from the critical temperature and pressure:

$$a_{0,i} = 0.42747 \frac{R^2 T_{c,i}^2}{P_{c,i}}; \quad b_i = 0.08664 \frac{R T_{c,i}}{P_{c,i}}$$
 2.36

2.4 Soave-Redlich-Kwong with Huron-Vidal Mixing Rule

The Soave-Redlich-Kwong with Huron-Vidal mixing rule (SRK+HV) is the same as the SRK with classical mixing rule, described above, except the mixing rule for the energy parameter.

The liquid activity coefficient models (like NRTL, UNIFAC) are generally temperature dependent (and not pressure dependent) and describe the liquid properties very well at ambient pressure. Huron-Vidal [12] assumed that the excess Gibbs free energy value at infinite pressure from the Cubic EoS should be same as the excess Gibbs free energy value from the liquid activity coefficient model. The SRK+HV EoS can successfully describe the multicomponent system including both polar and non-polar compounds but the SRK EoS with classical mixing rule cannot.

Huron-Vidal [12] showed that the mixture energy parameter (*a*) for the SRK EoS can be calculated as:

$$a = b \left[\sum_{i=1}^{N} x_i \frac{a_{ii}}{b_{ii}} - \frac{g_{\infty}^E}{\ln 2} \right]$$
2.37

Huron-Vidal modified the classical NRTL [13] model as below:

$$g_{\infty}^{E} = \sum_{i=1}^{N} x_{i} \frac{\sum_{j=1}^{N} x_{j} b_{j} G_{ji} \exp\left(-\alpha_{ji} \frac{G_{ji}}{RT}\right)}{\sum_{k=1}^{N} x_{k} b_{k} \exp\left(-\alpha_{ki} \frac{G_{ki}}{RT}\right)}$$
2.38

$$G_{ji} = GO_{ji} + GT_{ji} \times T$$

$$2.39$$

$$G0_{ji} = g0_{ji} - g0_{ii}, \quad GT_{ji} = gT_{ji} - gT_{ii}$$
2.40

The difference between the classical NRTL and modified NRTL, presented above, is the presence of co-volume parameter both in numerator (b_j) and denominator (b_k). The parameter gO_{ji} is the interaction energy between molecules of component-*i* and *j*. The parameter gT_{ji} is the temperature correction to interaction energy between molecules of component-*i* and *j*. The parameter α_{ij} represents the degree of randomness of molecules of component-*i* and *j* in the binary system of component-*i* and *j*. When the value of α_{ij} is zero, it means molecules are completely random and the

probability of finding the molecule of component-j is the same as the probability of finding the molecule of component-i around the molecule of component-i and j respectively.

The Huron-Vidal mixing rule can be reduced to the classical mixing rule when the interaction energies (G_{ji}) and randomness factor (α_{ij}) are calculated as:

$$G_{ji} = \left(-\frac{2a_{ji}}{b_j + b_i} + \frac{a_{jj}}{b_{jj}}\right) \ln 2; \quad \alpha_{ij} = \alpha_{ji} = 0;$$
 2.41

References

- 1 Van der Waals (1873) The equation of state for gases and liquids, Nobel Lectures in Physics, 1, 254-265, Elsevier, Amsterdam (1967).
- 2 Soave, G. (1972) Equilibrium constants for a modified RedlichKwong equation of state, Chem. Eng. Sci, 27, 1197-1203.
- 3 Peng, D-Y. and Robinson, D.B. (1976) A new two-constant equation of state, Ind. Eng. Chem. Fundam., 15, 59-64.
- 4 Chapman, W. G., Jackson, G., & Gubbins, K. E. (1988). Phase equilibria of associating fluids: chain molecules with multiple bonding sites. Molecular Physics, 65(5), 1057-1079.
- 5 Chapman, W. G., Gubbins, K. E., Jackson, G., & Radosz, M. (1990). New reference equation of state for associating liquids. Industrial & Engineering Chemistry Research, 29(8), 1709-1721.
- 6 Wertheim, M. S. (1986). Fluids with highly directional attractive forces. III. Multiple attraction sites. Journal of statistical physics, 42(3-4), 459-476.
- 7 Gross, J., & Sadowski, G. (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & engineering chemistry research*, *40*(4), 1244-1260.
- 8 G.M. Kontogeorgis, G.K. Folas, Thermodynamic models for industrial applications: from classical and advanced mixing rules to association theories. John Wiley & Sons (2009).
- 9 Mathias, P. M., & Copeman, T. W. (1983). Extension of the Peng-Robinson equation of state to complex mixtures: evaluation of the various forms of the local composition concept. Fluid Phase Equilibria, 13, 91-108.
- 10 Huang, S. H., & Radosz, M. (1990). Equation of state for small, large, polydisperse, and associating molecules. Industrial & Engineering Chemistry Research, 29(11), 2284-2294.
- 11 De Hemptinne, J. C., Mougin, P., Barreau, A., Ruffine, L., Tamouza, S., & Inchekel, R. (2006). Application to petroleum engineering of statistical thermodynamics-based equations of state. Oil & Gas Science and Technology-Revue de l'IFP, 61(3), 363-386.
- 12 Huron, M. J., & Vidal, J. (1979). New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. Fluid Phase Equilibria, 3(4), 255-271.
- 13 Renon, H., & Prausnitz, J. M. (1968). Local compositions in thermodynamic excess functions for liquid mixtures. AIChE journal, 14(1), 135-144.

Chapter 3. Modeling of Asphaltene Onset Condition using the CPA Equation of State

Entire content of this chapter is from our journal article "Alay Arya; Nicolas von Solms; Georgios M. Kontogeorgis. Determination of asphaltene onset conditions using the cubic plus association equation of state. Fluid Phase Equilibria 2015, Vol. 400, pp. 8-19".

Abstract

The Cubic-Plus-Association (CPA) equation of state (EoS) has already been proven to be a successful model for phase equilibrium calculations for systems containing associating components and has already been applied for asphaltene modeling by few researchers. In the present work, we apply the CPA EoS to determine asphaltene precipitation onset conditions for various reservoir fluids but with a different modeling approach than literature approaches. A simple oil characterization technique, based on SARA analysis, is adopted which divides the C_{6+} fraction of the oil into "heavy component" and asphaltene. Self-association between asphaltene molecules and cross-association between asphaltene and heavy component molecules are considered. Experimental data of several reservoir fluids are compared with model results and it is found that the temperature dependent cross-association energy correlates asphaltene phase envelope quite well in agreement with the experimental data. Two experimental asphaltene onset points at different temperature dependent cross-association energy and critical pressure of heavy component respectively. The effect of gas injection on asphaltene precipitation is also correlated with experimental data by tuning a single binary interaction parameter of the injected gas component and asphaltene pair.

3.1 Introduction

Asphaltene does not have a specific structure but is defined as a solubility fraction, which is not soluble in *n*-pentane/*n*-heptane according to the ASTM D6560 and IP 143 but soluble in an aromatic solvent [1-3]. It is also the heaviest fraction of the oil. Resins can be defined as the fraction of the oil not soluble in ethyl acetate but soluble in n-heptane, toluene, and benzene at room temperature [2,4]. Asphaltene and resins are hetero-compounds and form the most polar part in the oil compared to other components [2,4]. Resins and to some extent aromatic compounds cross-associate with asphaltene molecules, which is believed to be the main reason for asphaltene solubility in the oil. Asphaltene precipitation and agglomeration is a significant problem in the oil production, transmission and

processing facilities. Asphaltene stability depends upon the composition of the oil, pressure, temperature and properties of asphaltene [2,4-6]. The effect of composition and pressure change on asphaltene stability is generally believed to be stronger than the effect of temperature change. Asphaltene precipitation does not depend upon the amount of asphaltene. For example, low asphaltene content such as 0.2 wt% of the heavy oil does not imply that precipitation will not cause any severe production problems [2]. On the other hand, asphaltene content more than 17 wt% may not create any deposition problems [7]. In addition asphaltene solubility may increase or decrease with temperature. Thus the mechanism of asphaltene deposition is very complex.

The growing market of oil production and need for enhanced oil recovery by miscible displacement increases the risk of asphaltene deposition and hence loss of production and cost of remediation [4]. We cannot get a clear picture of the asphaltene precipitation conditions and related problems just by doing the limited experimental studies. Moreover, they often are not feasible economically and may not be possible in some cases. Therefore, it is imperative to model asphaltene precipitation to predict the above issues with reasonable accuracy and minimal experimental measurements.

There are two types of hypothesis about asphaltene precipitation. One type of hypothesis says that asphaltenes are dissolved in the oil in a true liquid state and may precipitate depending on the thermodynamic conditions of temperature, pressure and composition. The second type of hypothesis says that asphaltenes are insoluble and suspended in the oil whose stability depends on the interactions with resins molecules [5]. Some of the modeling approaches based on these two types of hypothesis are mentioned in Table 3.1.

Asphaltene as soluble compound		Asphaltene as insoluble compound		
Model	Reference	Model	Reference	
СРА	[8,9,17,16,18]	SAFT-HS	[23,24]	
PC-SAFT	[3,10-15, 20]	SAFT-VR	[4]	
Flory-Huggins	[2,21,22,26]			
AEOS	[19]			
SRK/SRK-P	[3,20]			
PR/PR-P	[25]			

Table 3.1. List of models used for asphaltene phase equilibria in the literature.

From the literature, we can observe that association models (e.g. SAFT, CPA) have been previously used and have potential to represent asphaltene system. Other models based on Flory-Huggins are not compared extensively for live oils asphaltene phase envelope with/w/o gas injection and they consider that precipitated material contains only pure asphaltene. In addition, Flory-Huggins theory based models calculate VLE from well-known EoS like SRK or PR followed by calculation of LLE using Flory-Huggins theory rather than calculating VLE and LLE simultaneously. Therefore their application in the industry might be limited. Model based on SRK and PR EoS have not been proved reliable. The SAFT-VR model [4] based on the colloidal approach requires more experimental data

to determine seven adjustable model parameters. On the other hand the SAFT-HS model [23-24] also based on colloidal approach requires only two adjustable model parameters. Both the SAFT-VR and SAFT-HS models are also promising approaches for asphaltene modeling but need further validation by applying them to calculate asphaltene phase envelopes (APEs) of a number of reservoir fluids. They have not been extensively used so far. One disadvantage with these colloidal based models is that, like Flory-Huggins theory based models, it needs an EoS to calculate VLE. Li et al [8] proposed a simple modeling approach with CPA considering that the asphaltene component is monodispersed but did not show any result with gas injection. On the other hand, Zhang et al [9] also proposed a less complicated approach with CPA considering asphaltene and resins components are polydispersed and showed a variety of results including gas injection. Li et al [8] do not predict any maximum while Zhang et al [9] predict the existence of a maximum in upper onset pressure-temperature curve at low temperature. Zhang et al [9] also concluded that CPA results are better than PC-SAFT results by studying six fluids, considering the modeling approach from Gonzalez et al [10-12] for PC-SAFT. Gonzalez et al [10-12] did not use association term in PC-SAFT EoS whereas Buenrostro-Gonzalez et al [4] mentioned that association contribution to the total free energy dominates over the meanattractive energy contribution in their use of SAFT-VR. Tavakkoli et al [13] concluded that a set of parameters (of PC-SAFT without the association term) used for saturation and onset pressure predictions, do not show a good match for the amount of precipitated asphaltene.

Even though CPA EoS have been proposed earlier for asphaltene modeling, in this work we demonstrate how it can effectively be applied to calculate asphaltene onset conditions considering asphaltene phase behavior as liquid-liquid equilibrium. At the same time, inspired from Li et al [8], we make the modeling approach less complex using a simple fluid characterization. This approach requires fewer experimental measurements, and can easily be used by industry. Modeling results are compared with different types of experimental data of several reservoir live oils in order to check the reliability of the model.

3.2 Modeling Approach

There could be different ways to characterize the oil with asphaltene, however, in this work we characterize it based on SARA analysis. Ideally, we should have separator gas and oil molar compositional analysis, gas to oil ratio and SARA analysis to calculate the composition of reservoir oil. SARA analysis gives the composition of heavy oil as weight fraction. To convert it to molar fraction, we need molecular weight information of each fraction, which is generally not available or measured. In addition, asphaltene has tendency to cross associate with resins and partially with aromatics, which means that we need to determine cross associating energies for asphaltene-resins and asphaltene-aromatics pairs. Asphaltene molecules are self-associating, which means we need to determine one more parameter that is the self-associating energy for the asphaltene-asphaltene pair. To reduce the degree of freedoms (number of unknown model parameters to be determined), we merge three different fractions (Saturates, Aromatics, Resins) into a single fraction termed as heavy component (HC) in this work. We also assume that the amount of components lighter than n-hexane
in the heavy oil is negligible and therefore the composition of C_{6+} fraction is the same as the SARA composition. Asphaltenes are considered as monomeric molecules with four association sites and its molecular weight is assumed to be 750 Da [29,30]. Critical properties of asphaltene (P_c = 15.4 bar, $T_c = 1040$ K, $\omega = 1.54$) are also fixed based on its solubility parameter. Asphaltene solubility parameters are 19.14 MPa^{1/2} ($\varepsilon^{AA} = 0$) and 21.51 MPa^{1/2} ($\varepsilon^{AA} = 3000$) at 298K and 1 atm. Self-association energy ($\epsilon^{AA}/R = 3000$ K) and self-association volume fraction of asphaltene $(\beta^{AA} = 0.05)$ are also fixed based on the preliminary calculations during this work. For the heavy component, one cross-association site is selected and the normal boiling point is calculated from Pedersen relationship [31]. Critical parameters (P_c, T_c) and acentric factor (ω) of HC are calculated from the Kesler–Lee relationship [32]. Critical pressure (P_c) of HC is adjusted to match bubble point pressures of the oil. Cross-association energy (ϵ^{AH}/R) between HC and asphaltene is assumed to be temperature dependent and is calculated from experimental data of upper onset pressures at two different temperatures. Any change in the value of ε^{AH}/R does not have any effect on bubble pressure due to very small mole fraction of asphaltene. However, change in the value of P_c of HC does alter the onset conditions. Cross-association volume fraction ($\beta^{AH} = 0.05$) is also fixed. Table 3.2 shows a comparison of modeling parameters for this work, Li et al [8] and Zhang et al [9]. The main difference between the modeling approach of this work and that of Li et al [8] is the asphaltene parameters, cross-association parameters and number of pseudo-components.

Parameters	This Work	Li et al [8]	Zhang et al [9]
No. of association site on Asp molecule	4	4	4
Asp MW	750	1800	Whitson Characterization Method
$\varepsilon^{\rm AA}/R$ (K)	3000	2000	3000
β^{AA}	0.050	0.100	0.050
Asp Critical Parameters	Based on Solubility Parameter of 18 MPa ^{1/2}	From Li et al [16]	Based on Solubility Parameter of 18-21 MPa ^{1/2}
Pseudo-components (PCs)	HC, Asp	Multiple SCNs ^a , HC, Asp	Multiple SCNs, Multiple resins, Asp
Pseudo-components Critical Parameters	Lee-Kesler	Cavett, Firoozabadi	Lee-Kesler & Riazi
Cross Association	Between HC and Asp	Between HC and Asp	Between resins and Asp
No. of cross-association sites	1	4	2
Tuned Parameter with respect to Bubble Points	Pc of HC	Pc of HC	Mathias Copeman/Accentric Factors of PCs
Tuned Parameter with respect to two Onset Points	Temp Dependent ε^{AH}/R	Temp Dependent $\varepsilon^{\rm AH}/R$	Temp Independent ε^{AR}/R , β^{AR}
Cross-association volume fraction	$\beta^{AH}=0.050$	$\beta^{AH} = 0.100$	β^{AR} is adjusted
Tuned Parameter with respect to Gas Injection Data	<i>k</i> _{<i>ij</i>} of Asp-Gas	No results presented	not mentioned

Table 3.2. Comparison of Modeling Approach of this work, Li et al [8] and Zhang et al [9].

^{*a*} There could be multiple SCN PCs in case of plus fraction (=HC+Asp) is considered above C7+. For example if the plus fraction is C12+ (=HC +Asp) then multiple SCN pseudo-components would be from C7 to C11.

Table 3.3 shows binary interaction parameter (k_{ij}) used in our CPA model. Parameter k_{ij} of asphaltene-component pair is assumed to be the same as that of the benzene/toluene-component pair unless otherwise tuned. Parameter (k_{ij}) of HC-component pair is assumed to be same as that of any heavy alkane-component pair for which data are available.

2	1 (1)/	2	1		
Component	N ₂	CO_2	H_2S	HC ^b	Asp ^c
N ₂				0.10	0.24
CO ₂	-0.06			0.10	0.10
H_2S	0.678-0.0018T			0.05	
methane	0.141-12.6448/T	0.0882*	0.0760*		0.01
ethane	0.04	0.1335*	0.0847*		0.01
propane	0.04	0.1522*	0.0917*		0.01
isobutane	0.05ª	0.1122 ^a	0.0761*		
nbutane	0.05	0.1122*	0.0897*		
isopentane	0.06 ^a	0.10 ^a			
npentane	0.06	0.10			

Table 3.3. Binary interaction parameter (k_{ij}) used by CPA model. T is temperature in K.

* From reference [40,41] and others are estimated in this work.

^a Binary parameter with *i*-butane and *i*-pentane are assumed to be the same as that of with the *n*-butane and *n*-pentane respectively.

^b Binary parameter is assumed from binary of heavy alkanes (heavier than *n*-hexane) with given component unless tuned with respect to onset data.

^c Binary parameter is assumed from binary of benzene/toluene with given component unless tuned with respect to onset data.

3.3 Results and Discussion

We now perform the calculations for the different oil systems with the proposed modeling approach and compare them with experimental data of different reservoir oils mentioned in Table 3.4. Compositions of reservoir oils are reduced to C_{6+} fraction as per the modeling approach requirement. The information of amount of asphaltene in STO, MW and SG of STO or C_{6+} fraction should be available in order to characterize C_{6+} fraction. We also divide our discussion into two sections. In the first section, only one type of experimental data is available for the reservoir oil, for example, asphaltene phase envelope only. In the second section, at least two types of experimental data are available, for example, asphaltene phase envelope and gas injection results or amount of precipitated asphaltene.

	Buenrostro 2004 [4] (Fluid C1)	Buenrostro 2004 [4] (Fluid Y3)	Szewczyk 1998 [33]	Fotland 1997 [34]	Srivastava 1995 [35]	Kabir 1999 [36]	Jamaluddin 2002 [37]	Yonebayashi 2009 [38]	Fahim 2007 [39]
Comp.	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%	mol%
N ₂	0.91	0.47	0.27	1.26	0.96	0.09	0.49	0.17	0.09
CO_2	1.57	1.59	4.07	0.23	0.58	1.02	11.37	1.75	1.02
H_2S	5.39	1.44	0	-	0.30	0.05	3.22	2.04	0.05
C1	24.02	32.22	30.53	40.00	4.49	42.42	27.36	16.47	42.41
C2	10.09	12.42	7.13	9.10	2.99	10.80	9.41	8.66	10.78
C3	9.58	10.29	5.92	8.88	4.75	6.92	6.70	8.21	6.92
iC4	1.83	2.03	2.43	1.34	0.81	0.96	0.81	1.35	1.55
nC4	4.83	4.87	1.11	4.22	1.92	3.52	3.17	4.84	2.92
iC5	2.27	2.22	0.82	1.46	1.27	1.21	1.22	1.88	1.47
nC5	2.74	2.71	0.79	1.93	2.19	2.09	1.98	3.15	1.82
C ₆₊	36.77	29.74	46.92	31.59	79.74	30.93	34.28	51.48	30.95
C_{6+} MW	302.4	256.9	239.7	207.1	230.0	204.4	236.3	205.2	198.1
C_{6+} SG	0.852	0.784	0.815		0.870	0.840	0.873	0.848	0.834
Saturates (wt%)	54.67	55.14	-	-	46.60	63.30	57.40	47.98	-
Aromatics (wt%)	28.89	30.73	-	-	39.60	24.90	30.80	44.42	-
Resins (wt%)	12.66	10.88	-	2.80	8.90	11.30	10.40	6.29	7.30
Asphaltenes (wt%)	3.80	3.25	4.35	0.90	4.90	0.50	1.40	1.32	0.50

Table 3.4. Composition and SARA information of reservoir oils required for CPA model.

Oils with a Single Type of Data

Buenrostro 2004

Buenrostro et al [4] studied two Mexican crude oils, Fluid-C1 and Fluid-Y3. A series of titration experiments were carried out to determine asphaltene precipitation amounts in tank oil samples with several n-alkanes. Using bottom-hole samples of the same oils, high pressure/temperature flocculation experiments were carried out to obtain the experimental APEs of these fluids. As shown in Fig.3.1 & 3.2, CPA is able to correlate the experimental APEs quite well. Fig.3.1 shows that onset pressure decreases, below temperature of around 335 K, as temperature decreases. Fig. 3.2 shows that upper onset pressure increases as temperature decreases in agreement to the experimental data. Both Fluid-C1 and Fluid-Y3 have also been studied by Li et al [8] and their results are also in agreement with experimental data, however, there is no maximum in upper onset pressure curve for Fluid-C1.



Fig.3.1. Fluid-C1 upper/lower asphaltene onset pressures and bubble points vs temperature. Symbols (squares for upper onset, circles for bubble points) represent experimental data from Buenrostro et al [4] and lines for upper onset and bubble pressures are the correlations by CPA with $\varepsilon^{AH} / R = 1594 + 16166/T K$ and P_c of HC = 17.79 bar. Line for lower onset pressure is the prediction by CPA after determination of ε^{AH} / R and P_c of HC. No experimental data for lower onset pressure are available.



Fig. 3.2. Fluid-Y3 upper/lower asphaltene onset pressures and bubble points vs temperature. Symbols (squares for upper onset, circles for bubble points) represent experimental data from Buenrostro et al [4] and lines for upper onset and bubble pressures are the correlations by CPA with $\varepsilon^{AH} / R = 1507-5136/T K$ and P_c of HC = 23.91 bar. Line for lower onset pressure is the prediction by CPA after determination of ε^{AH} / R and P_c of HC. No experimental data for lower onset pressure are available.

Szewczyk 1998

Szewczyk et al [33] studied a sample of crude oil taken off at a pressure above the bubble point. The amount of precipitated asphaltene and volume are measured at different pressure and a constant temperature of 303 K. Fig. 3.3a shows that CPA is able to correlate experimental data of relative

volume (ratio of the volume of liquid oil at given pressure to the volume of liquid oil at bubble point) after tuning the P_c of HC. Fig. 3.3b shows that CPA is not able to correlate the fraction of precipitated asphaltene (ratio of the mass of precipitated asphaltene to the mass of asphaltene present initially) at pressures higher than around 250 bar after tuning the value of ε^{AH}/R . This oil has also been studied by Li et al [8] and their results match the experimental data for pressure higher than around 70 bar, however, there is a poor agreement for the pressure range 10-70 bar. At this point it is good to know that as Tavakkoli et al [13] mentioned that a small experimental error during filtration procedure or gravimentric method for measuring the amount of precipitated asphaltene can lead to a significant difference between model and experimental results.



Fig. 3.3. Szewczyk 1998 crude oil: (a) Relative volume vs pressure at 303 K. (b) Fraction of asphaltene precipitated vs pressure at 303K. Symbols represent experimental data from Szewczyk [33] and lines are correlations by CPA with $\varepsilon^{AH} / R = 1690$ K and P_c of HC = 16.85 bar.

Fotland 1997

Fotland et al [34] studied North Sea crude with respect to gas injection. Separator gas of flashed reservoir oil was injected in different amounts and then measured the onset pressures. It was found that there was asphaltene precipitation at 35 mol% of gas injection or more at 365 K. Hence we tuned ε^{AH}/R at this point. Fig. 3.4 shows that CPA is able to correlate upper onset pressures with different amount of gas injection only after tuning k_{ij} of the binary pairs of methane, ethane, propane with asphaltene to the value of (-0.2). However, this value of k_{ij} is far from the default values of k_{ij} of n-alkanes with asphaltene as mentioned in Table 3.3. We believe that more information on the asphaltene envelope would be required to check the reliability of the model. The composition of injected gas is given in Table 3.5. This oil has also been studied by Zhang et al [9] and their results also match the experimental data similarly to this work as Fig. 3.4b, however, there is no discussion about whether they use any k_{ij} to match the data.



Fig. 3.4. Fotland 1997: Upper onset and bubble point pressure vs amount of gas injection at 365 K. Symbols (squares for upper onset and circles for bubble points) represent experimental data from Fotland [34] and lines are correlations by CPA with $\varepsilon^{AH} / R = 1428$ K and P_c of HC = 20.21 bar. (a) with default values of k_{ij} mentioned in Table 3.3 (b) when methane/ethane/propane-asphaltene pairs $k_{ij} = (-0.2)$.

Srivastava 1995

Weyburn Oil-A2 was from the southeast Saskatchewan reservoir, Weyburn. The initial asphaltene content of the oils collected from the Weyburn pool was about 5 wt% and suggested the possibility of formation plugging and wettability alteration during CO₂ injection. Srivastava et al [35] undertook the laboratory study to find out the effect of CO₂ injection on Weyburn oil. It was heavy oil with C_{6+} content of 79.74 mol%. Fig. 3.5a shows that CPA is able to correlate experimental data of bubble point pressures at different CO₂ concentraitons at 332 K after tuning the P_c of HC. Fig. 3.5b shows that CPA is also able to correlate the fraction of precipitated asphaltene (ratio of mass of precipitated asphaltene to mass of asphaltene present initially) after tuning the values of ε^{AH}/R at 160 bar and 332 K. However, we feel that experimental data of APE is required to check the model reliability. This oil also been studied by Li et al [8] and their results are also in agreement with experimental data.



Fig. 3.5. Srivastava 1995 Weyburn Oil-A2: (a) Bubble point pressures vs mole fraction of CO_2 at 332 K (b) Fraction of asphaltene precipitated vs mole fraction of CO_2 at 160 bar and 332 K. Symbols represent experimental data from Srivastava [35] and lines are correlations by CPA with $\varepsilon^{AH} / R = 1652$ K and P_c of HC = 20.20 bar.

Oils with Two & More Types of Data

For a rigorous test or to check the reliability of the model, two types of experimental data of the same oil are encouraged. One type of data is used to determine model parameters and a second type of data is used for checking the model without adjusting any new parameters.

Kabir 1999

Kabir et al [36] studied an oil from south Kuwait's Marrat well (MG-OF4) in the Magwa area of the Greater Burgan field in order to mitigate production problems. A gravimetric technique was used to generate asphaltene phase envelope and an acoustic resonance technique (ART) is used for determination of both onset and bubble point pressure. Fig. 3.6a shows that CPA is able to correlate the upper onset and bubble points data well after tuning temperature dependent ε^{AH}/R and P_c of HC respectively. Calculation of lower onset curve, where no parameter is adjusted, is in agreement with the data. On the other hand, Fig. 3.6b shows the calculation of asphaltene content in the oil versus pressure at 322 K. We get good match of the experimental data with minor deviations. These results indicate that CPA is able to calculate other type of data than those used in parameter estimation. This oil has also been studied by Zhang et al [9]. Their results also show maximum in upper onset pressure curve as we see in Fig. 3.6a. Fig. 3.6a also shows the effect of N₂, CO₂ and methane (C1) injection on upper onset pressure boundary. The amount of injected gas is 10 mol% (0.1 mol of gas per 0.9 mol of reservoir oil). We see that, N₂ is strongest precipitant followed by methane and CO₂ respectively.



Fig. 3.6. Kabir 1999: (a) upper/lower asphaltene onset pressures and bubble points vs temperature. Symbols (squares for upper onset, circles for bubble points, and triangles for lower onset) represent experimental data from Kabir et al [36]. Lines for upper onset and bubble curves (for oil without gas injection) are the correlations by CPA with $\varepsilon^{AH} / R = 1257+81602/T K$ and P_c of HC = 19.97 bar. Line for lower onset curve and effect of 10 mol% of N_2 , CO₂ and methane (C1) injections on upper onset pressures are the predictions by CPA after determination of ε^{AH} / R and P_c of HC. (b) Asphaltene content in the oil vs pressure at 322 K. Symbols represent experimental data from Kabir et al [36] and the line represents the prediction by CPA.

Jamaluddin 2002

The reservoir has been under production with primary depletion for more than 20 years and was expected to decline below the saturation pressure soon. Therefore, Jamaluddin et al [37] undertook the feasibility study to evaluate the potential of improved oil recovery by pressure maintenance using nitrogen. Fig. 3.7a shows that CPA is able to correlate upper onset and bubble points data in agreement with experimental results after tuning the temperature dependent ε^{AH}/R and P_c of HC respectively. Calculation of lower onset curve, where no parameter is adjusted, is in agreement with the experimental data. Fig. 3.7b shows that CPA is also able to correlate onset pressure with different amounts of N_2 injection at 419 K but only after tuning the binary interaction parameter (k_{ij}) of asphaltene- N₂ pair to 0.24. Gonzalez et al [12] studied the same oil with PC-SAFT EoS and tuned the asphaltene- N_2 pair k_{ij} to the value of 0.25. Li et al [8] and Zhang et al [9] also studied the same oil, however, Li et al [8] have not shown the effect of N₂ injection and Zhang et al [9] have not mentioned anything about k_{ij} . Hustad et al [20] performed the study of N₂ injection on different oil with PC-SAFT and they also mentioned that the asphaltene- N_2 pair k_{ij} has the value of 0.17. Therefore, the asphaltene- N_2 pair k_{ij} value of 0.24 is quite reasonable and it is used as default value for all the oils studied in this work. In addition Zhang et al [9] show a maximum in upper onset curve whereas our results do not show any maximum in Fig. 3.7a.



Fig. 3.7. Jamaluddin 2002: (a) upper/lower asphaltene onset pressures and bubble points vs temperature. Symbols (squares for upper onset, circles for bubble points, triangles for lower onset) represent experimental data from Jamaluddin et al [37]. Lines for upper onset and bubble curves (for oil without gas injection) are the correlations by CPA with $\varepsilon^{AH} / R = 1540+6339/T$ K and P_c of HC = 19.04 bar. Line for lower onset curve and effect of 10 mol% of N_2 , CO_2 and methane (C1) injections on upper onset pressures are the predictions by CPA after determination of ε^{AH} / R and P_c of HC. (b) Upper onset and bubble point pressure vs amount of N_2 injection in mol% at 419 K. Symbols (triangles for upper onset, circles for bubble points) represent experimental data from Jamaluddin et al [37]. Lines represent the calculated trend by CPA.

Fig. 3.7a also shows the effect of N_2 , CO_2 and methane (C1) injection on upper onset pressure boundary. The amount of injected gas is 10 mol% (0.1 mol of gas per 0.9 mol of reservoir oil). We see that N_2 is strongest precipitant followed by methane, and CO_2 respectively. Gonzalez et al [12] also performed the same study with PC-SAFT (without the association term) by injecting the same amount of gas (10 mol%) and also concluded that N_2 is the strongest precipitant followed by methane and CO_2 respectively. However, they also concluded that for a given amount of CO_2 injection, there is a cross over temperature, below which asphaltene becomes stable, for this oil. It implies from their results that the attraction between CO_2 and asphaltene molecules becomes dominant below crossover temperature. More experimental data is needed for the validation of such results.

Yonebayashi 2009

This oil was from an offshore carbonate field in the Arabian Gulf, which was exhibiting asphaltene deposition inside the tubing of production wells completed in one of two main producible limestone reservoirs. EOR was planned and risk of enhancing the asphaltene problem was studied by Yonebayashi et al [38]. There are no experimental data on bubble point pressure and therefore tuning of the P_c of the HC is not possible. Fig. 3.8a shows that CPA is able to correlate the upper onset pressure of the oil without gas injection after tuning the temperature dependent ε^{AH}/R . The same parameters are used to calculate the upper onset pressure boundary with different amount of gas injection. Fig. 3.8b shows that CPA calculation results have minor deviations from experimental data.

Table 3.5 shows the composition of injected gas. Zhang et al [9] also studied the same oil and showed a maximum in upper onset curve with and without gas injection, whereas our results do not show any maximum.



Fig. 3.8. Yonebayashi 2009: (a) Lower Onset and bubble point pressures vs temperature without gas injection. Upper onset pressure vs temperature with/w/o gas injections. Symbols (square for 0 mol% gas, circle for 2.9 mol% gas, upward triangle for 5.4 mol% of gas, downward triangle for 10.7 mol% gas, star for 14.1 mol%, plus for 22.6 mol%) represent experimental data of upper onset pressure from Yonebayashi [38]. Lines for upper onset (with 0 mol% gas injection) and bubble pressure are the correlations by CPA with $\varepsilon^{AH} / R = 1597 + 24786/T K$ and P_c of HC = 16.91 bar. While lines for lower onset curve and effect of gas injections on upper onset pressures are the predictions with CPA after determination of ε^{AH} / R and P_c of HC. (b) Upper onset temperature vs amount of injected gas in mol% at 278 bar. Symbols represent experimental data of upper onset pressure from Yonebayashi [38]. Solid line is the calculation by CPA.

Common on onto	Fotland 1997	Yonebayashi 2009
Components	Composition (mol%)	Composition (mol%)
H_2	-	0.21
H_2S	-	7.28
CO_2	0.43	4.37
N ₂	2.36	0.42
methane	67.50	39.71
ethane	12.79	20.79
propane	9.73	21.41
<i>i</i> -butane	1.22	1.66
<i>n</i> -butane	3.03	2.49
<i>i</i> -pentane	0.82	0.62
<i>n</i> -pentane	0.76	0.42
<i>n</i> -hexane	0.62	0.21
<i>n</i> -heptane	0.76	0.21
C_{8+}	-	0.21

	Table	3.5.	Iniecte	ed Gas	Com	position.
--	-------	------	---------	--------	-----	-----------

Fahim 2007

Fahim [39] presented the experimental data of upper onset, lower onset and bubble point pressures data for the different crude oils, most of them are from Middle East. He presented the asphaltene envelope data of the reservoir oil for two values of asphaltene amount. Fig. 3.9a shows that CPA is able to correlate the upper onset and bubble point pressures after tuning the temperature dependent ε^{AH}/R and P_c of HC respectively while the prediction of lower onset curve deviates from experimental data when asphaltene amount is 0.5 wt% in the heavy oil. Fig. 3.9b shows that CPA is able to calculate upper and bubble point pressures in agreement with experimental data, however lower onset pressure calculation shows minor deviations, when asphaltene amount is changed from 0.5 wt% to 0.4 wt%. No parameters are adjusted while generating Fig. 3.9b. Li et al [8] also studied this oil and concluded that upper onset pressure were overestimated when the asphaltene content is 0.4 wt%. However, our results are in agreement as shown in Fig. 3.9b. Li et al [8] also concluded that asphaltene becomes less stable above 400 K whereas our results show that asphaltene becomes more stable with temperature.



(a)

(b)

Fig. 3.9. Fahim 2007: Asphaltene phase envelope (a) when asphaltene in heavy oil is 0.5 wt% (b) when asphaltene in heavy oil is 0.4 wt%. Symbols (squares for upper onset, circles for bubble points, and triangles for lower onset) represent experimental data from Fahim [39]. (a) Lines for Upper onset and bubble curves are the correlations by CPA with $\varepsilon^{AH} / R = 1368 + 47643/T K$ and P_c of HC = 20.33 bar. Line for lower onset curve is the prediction with CPA after determination of ε^{AH} / R and P_c of HC. (b) Lines are the predictions with CPA after determination of ε^{AH} / R and P_c of HC.

Ting 2003

Ting et al [14] prepared a model oil by dissolving 1g of asphaltene in 100 ml of toluene. Titrating different n-alkanes with model oil, the volume fraction of each n-alkane was found at the onset of asphaltene precipitation. Methane was then injected isothermally and upper onset and bubble point pressures were found. We assumed cross-association between toluene and asphaltene and then

calculated the cross-association energy (ε^{AT}/R) from the onset data with different n-alkanes. Fig. 3.10a shows that CPA is able to correlate experimental data. We used the same parameters to check the effect of methane injection. Fig. 3.10b shows that CPA is able to calculate results in agreement with experimental data. Ting et al [14] used PC-SAFT (without the association term) and could also correlate the experimental data. However, they tuned total three asphaltene pure component parameters and we tuned only one parameter from Fig. 3.10a. Since the difference between the two experimental temperatures is not large, we kept the ε^{AT}/R as temperature independent parameter and this results to minor deviations in the upper onset pressure results at 339 K.



Fig. 3.10. Ting 2003: (a) Volume fraction of different n-alkane at the onset of asphaltene precipitation at 293 K and 1 bar vs carbon number of respective n-alkane. Circles represent experimental data from Ting et al [14] and cross marks represent the correlation by CPA with $\varepsilon^{AH} / R = 2132$ K. (b) Upper onset and bubble point pressures vs amount of methane injected in terms of mass fraction. Symbols represent experimental data and lines are the predictions with CPA.

Hirschberg 1984

Hirschberg et al [2] carried out a series of titration experiments on heavy oil. The onset of asphaltene precipitation upon the dilution of the oil with various liquid alkanes and gases was determined. The amount of *n*-pentane insoluble asphaltene in the heavy oil was 3.9 wt%. MW and SG of heavy oil were 221.5 g/mol and 0.875 g/cm³ respectively. Onset measurements with different n-alkanes are used to calculate ε^{AH}/R and P_C of HC and the correlation between experimental data and CPA results can be seen in Fig. 3.11. The results of lower onset pressure with different gases at different temperatures are calculated by the model, without adjusting any parameters, and compared with experimental data in Table 3.6. In most cases, results are in agreement with the experimental data. In some cases the oil was diluted with *n*-decane in order to decrease the lower onset pressure to keep the pressure reading in the measurement range of the apparatus used. We kept ε^{AH}/R as temperature independent since the experimental temperature variation is not large.



Fig. 3.11. Hirschberg 1984: Amount of n-alkane (in cm3) per g of oil at the onset of precipitation vs n-alkane number at 295.15 K and 1 bar. Symbols (solid circles) represent experimental data from Hirschberg et al [2] while symbols (cross marks) are the correlations by CPA with $\varepsilon^{AH} / R = 1730$ K and P_c of HC = 20.98 bar.

Table 3.6. Comparison of lower onset pressure between experimental data and CPA predictions for propane, methane and CO_2 as precipitants.

Precipitant	Dilution (cm ³ <i>n</i> -decane/g of tank	Temp.	Experimental onset P	CPA onset P	RD ^a in Onset P
	oil)	(K)	(bar)	(bar)	(%)
Propane	0	295.15	7.9	6.65	15.8
	0	313.15	12.3	9.99	18.8
	0	334.15	>21	15.06	-
	0.49	297.15	5.3	5.06	4.5
	0.49	310.15	9.1	6.65	26.9
	0.49	333.15	13	10.13	22.1
	0.49	333.15	14	10.13	27.6
	0.98	297.15	4.2	2.74	34.8
	1.41	297.15	1.8	1.14	36.7
Methane	0	295.15	>200	485.51	-
	0.98	295.15	>200	70.93	-
CO_2	0	296.15	>53	305.69	-
	0.49	296.15	40	47.31	18.3
	0.98	297.15	29	26.37	9.1
	1.41	295.15	31	1.29	95.8

^a Relative Deviation $= \frac{|P_{exp} - P_{calc}|}{P_{exp}} \times 100$

Table 3.7 shows the calculated values of ε^{AH}/R and P_c of HC for all the oils studied in this work. One can observe that for most of the oils, ε^{AH}/R is decreasing with temperature and for Fluid Y3 it is increasing with temperature. We suspect that some of the upper onset pressure data for Fluid Y3 may

be in error. One can also observe that P_c of HC varies around 20 bar and is always above P_c of asphaltene (15.4 bar).

Fluid	$arepsilon^{ m AH}$ / R (K)	P_c of HC (bar)
Kabir 1999	1257+81602/T	19.97
Jamaluddin 2002	1540+6339/T	19.04
Yonebayashi 2009	1597+24786/T	16.91
Fotland 1997	1428 @365K	20.21
Buenrostro 2004 (Fluid C1)	1594+16166/T	17.79
Buenrostro 2004 (Fluid Y3)	1507-5136/T	23.91
Fahim 2007	1368+47643/T	20.33
Szewczyk 1998	1690 K @303K	16.85
Srivastava 1995	1652 @332K	20.20
Ting 2003	2132 K @ 293K	-
Hirschberg 1984	1730 K @ 296 K	20.98

Table 3.7. Value of cross-association energy ε^{AH} / R (K) and P_c of HC after tuning for all fluids studied.

Table 3.8 shows SARA analysis of five reservoir fluids, ratio of amount of resins (R) to aromatics (A) and calculated value of ε^{AH}/R (K) at 298 K. We considered only five fluids because of availability of SARA analysis and APE data. Since heavy component is a lumped component of saturates, aromatics and resins fractions, cross association energy of heavy component towards asphaltene decreases with amount of saturates and increases with amount of resins and aromatics. Out of resins and aromatics, resins contribute more to cross association energy compared to aromatics. Fig. 3.12 shows that calculated ε^{AH}/R (K) at 298 K depends upon both amount of saturates and R/A ratio. In other words, if amount of saturates increases and at the same time there is considerable increase in R/A ratio (points 1 & 2 in Fig. 3.12) then change in ε^{AH}/R (K) may not be significant. One can also observe that value of ε^{AH}/R (K) for Fluid Y3 (point-5 with triangle symbol) is not consistent with the values of ε^{AH}/R (K) of other fluids, which further corroborates our suspicion of wrong onset data in addition of negative sign in temperature dependency of ε^{AH}/R (K).

Table 3.8. SARA analysis and cross-association energy ε^{AH} / R (K) at 298 K for five reservoir fluids.

		Kabir 1999	Yonebayashi 2009	Jamaluddin 2002	Buenrostro 2004 Fluid C1	Buenrostro 2004 Fluid Y3
Saturates (S)	wt%	63.3	47.98	57.4	54.67	55.14
Aromatics (A)	wt%	24.9	44.42	30.8	28.89	30.73
Resins (R)	wt%	11.3	6.29	10.4	12.66	10.88
Asp	wt%	0.5	1.32	1.4	3.8	3.25
R/A	wt/wt	0.45	0.14	0.34	0.44	0.35
$\varepsilon^{\rm AH}/R$ @298K	Κ	1531	1680	1561	1648	1501



Fig. 3.12. Relationship between cross-association energy ε^{AH} / R (K) at 298 K and SARA analysis. (a) cross-association energy ε^{AH} / R (K) at 298 K vs Saturates (wt%) (b) R/A ratio (wt/wt) vs Saturates (wt%). Triangle symbol represents data for Fluid Y3. Point 1 for Kabir 1999, 2 for Yonebayashi 2009, 3 for Jamaluddin 2002, 4 for Buenrostro 2004 Fluid C1 and 5 for Buenrostro 2004 Fluid Y3 (triangle symbols).

3.4 Conclusions

By studying the nine reservoir oils, the model oil and the heavy oil, it can be concluded that CPA is able to correlate experimental data of the onset of precipitation after tuning the temperature dependent cross-association energy and the critical pressure of HC. The modeling approach is quite simple and does not require splitting C_{6+} fraction into multiple components. The CPA model is also able to predict asphaltene phase envelope for different amount of gas injection, however, only in one case (Fotland 1997) we had to adjust the k_{ij} of asphaltene-gas pair to match the experimental data. Like Li et al [8], we could not find any physical meaning for the temperature dependent cross-association energy between HC and asphaltene (ε^{AH}/R). Like Gonzalez et al [12], we found that N₂ is the strongest precipitant followed by methane and CO₂ respectively. We also feel that more experimental data on CO₂ injection effect on live reservoir oil in terms of onset pressure are required to validate whether asphaltene becomes stable at low temperature. It is also found that there is not always a maximum in upper onset curve, which contradicts the results from Zhang et al [9] for some of the oils (Yonebayashi 2009 and Jamaluddin 2002) studied in this work. One of the key points found during this work is that the calculated values of ε^{AH}/R (K) are the function of SARA fractions and are not any random fitting values.

References

- 1 J. G. Speight, Petroleum Asphaltenes-Part 1: Asphaltenes, resins and the structure of petroleum, Oil & gas science and technology 59-5 (2004) 467-477.
- 2 A. Hirschberg, L.N.J. DeJong, B.A. Schipper, & J.G. Meijer, Influence of temperature and pressure on asphaltene flocculation, Society of Petroleum Engineers Journal 24-03 (1984) 283-293.
- F. Vargas, M. Garcia-Bermudes, M. Boggara, S. Punnapala, M.I. Abutaqiya, N.T. Mathew, H.Y. Al Asafen, On the Development of an Enhanced Method to Predict Asphaltene Precipitation, In Offshore Technology Conference held in Houston, Texas, USA, May-(2014).
- 4 E. Buenrostro-Gonzalez, C. Lira-Galeana, A. Gil-Villegas, J. Wu, Asphaltene precipitation in crude oils: Theory and experiments, AIChE Journal 50-10 (2004) 2552-2570.
- 5 S. Kokal, A. Al-Ghamdi, D. Krinis, Asphaltene precipitation in high gas-oil ratio wells, Middle East Oil Show, SPE 81567 (2003).
- 6 S. Verdier, H. Carrier, S.I. Andersen, J.L. Daridon, Study of pressure and temperature effects on asphaltene stability in presence of CO2, Energy & Fuels 20-4 (2006) 1584-1590.
- 7 K.J. Leontaritis, G.A. Mansoori, Asphaltene deposition: a survey of field experiences and research approaches, Journal of Petroleum Science and Engineering 1-3 (1988) 229-239.
- 8 Z. Li, A. Firoozabadi, Cubic-plus-association equation of state for asphaltene precipitation in live oils, Energy & Fuels 24-5 (2010) 2956-2963.
- 9 X. Zhang, N. Pedrosa, T. Moorwood, Modeling asphaltene phase behavior: comparison of methods for flow assurance studies, Energy & Fuels 26-5 (2012) 2611-2620.
- 10 D.L. Gonzalez, P.D. Ting, G.J. Hirasaki, W.G. Chapman, Prediction of asphaltene instability under gas injection with the PC-SAFT equation of state, Energy & Fuels 19-4 (2005) 1230-1234.
- 11 D.L. Gonzalez, G.J. Hirasaki, J. Creek, W.G. Chapman, Modeling of asphaltene precipitation due to changes in composition using the perturbed chain statistical associating fluid theory equation of state, Energy & Fuels 21-3 (2007) 1231-1242.
- 12 D.L. Gonzalez, F.M. Vargas, G.J. Hirasaki, W.G. Chapman, Modeling Study of CO2-Induced Asphaltene Precipitation, Energy & Fuels 22-2 (2007) 757-762.
- 13 M. Tavakkoli, S.R Panuganti, V. Taghikhani, M.R. Pishvaie, W.G. Chapman, Precipitated Asphaltene Amount at High-Pressure and High-Temperature Conditions, Energy & Fuels, 28-3 (2013) 1596-1610.
- 14 P.D. Ting, G.J. Hirasaki, W.G. Chapman, Modeling of asphaltene phase behavior with the SAFT equation of state, Petroleum Science and Technology 21-3&4 (2003) 647-661.
- 15 P.D. Ting, Thermodynamic Stability and Phase Behavior of Asphaltenes in Oil and of Other Highly Asymmetric Mixtures, PhD Thesis, Rice University May (2003).
- 16 Z. Li, A. Firoozabadi, Modeling asphaltene precipitation by n-alkanes from heavy oils and bitumens using cubic-plus-association equation of state, Energy & Fuels, 24-2 (2010) 1106-1113.
- 17 B. Edmonds, R.A.S Moorwood, R. Szczepanski, X. Zhang, M. Heyward, R. Hurle, Measurement and prediction of asphaltene precipitation from live oils. In 3rd International Symposium on Colloid Chemistry in Oil Production, Asphaltenes and Waxes Deposition, Huatulco, Mexico, November (1999).
- 18 B. Shirani, M. Nikazar, S.A Mousavi-Dehghani, Prediction of asphaltene phase behavior in live oil with CPA equation of state, Fuel 97 (2012) 89-96.
- 19 B. Shirani, M. Nikazar, A. Naseri, S.A. Mousavi-Dehghani, Modeling of asphaltene precipitation utilizing Association Equation of State, Fuel 93 (2012) 59-66.
- 20 O.S. Hustad, N. Jia, K.S. Pedersen, A. Memon, S. Leekumjorn, High-Pressure Data and Modeling Results for Phase Behavior and Asphaltene Onsets of Gulf of Mexico Oil Mixed With Nitrogen, SPE Reservoir Evaluation & Engineering 17-3 (2014) 384-395.
- 21 G.R. Pazuki, M. Nikookar, A modified Flory-Huggins model for prediction of asphaltene precipitation in crude oil, Fuel 85-7 (2006) 1083-1086.
- 22 G.R. Pazuki, M. Nikookar, M.R. Omidkhah, Application of a new cubic equation of state to computation of phase behavior of fluids and asphaltene precipitation in crude oil, Fluid phase equilibria 254-1 (2007) 42-48.

- 23 J. Wu, J.M. Prausnitz, A. Firoozabadi, Molecular-thermodynamic framework for asphaltene-oil equilibria, AIChE Journal 44-5 (1998) 1188-1199.
- 24 M.A. Fahim, U. Kuwait, S.I. Andersen, Tuning EOS Using Molecular Thermodynamics To Construct Asphaltene Deposition, Society of Petroleum Engineering SPE 93517 (2005).
- O. Sabbagh, K. Akbarzadeh, A. Badamchi-Zadeh, W.Y. Svrcek, H.W. Yarranton, Applying the PR-EoS to asphaltene precipitation from n-alkane diluted heavy oils and bitumens, Energy & Fuels 20-2 (2006) 625-634.
- 26 N.E. Burke, E.H. Roland, F.K. Samir, Measurement and modeling of asphaltene precipitation, J. Pet. Technol 42-11 (1990) 1440-1446.
- 27 V. Szewczyk, E. Behar, Compositional model for predicting asphaltenes flocculation, Fluid Phase Equilibria 158 (1999) 459-469.
- 28 G.M. Kontogeorgis, G.K. Folas, Thermodynamic models for industrial applications: from classical and advanced mixing rules to association theories. John Wiley & Sons (2009).
- 29 L. Buch, H. Groenzin, E. Buenrostro-Gonzalez, S.I. Andersen, C. Lira-Galeana, O.C. Mullins, Molecular size of asphaltene fractions obtained from residuum hydrotreatment, Fuel 82-9 (2003) 1075-1084.
- 30 S. Badre, C.C. Goncalves, K. Norinaga, G. Gustavson, O.C. Mullins, Molecular size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils and bitumen, Fuel 85-1 (2006) 1-11.
- 31 K.S. Pedersen, P.L. Christensen, J.A. Shaikh, Phase behavior of petroleum reservoir fluids, CRC Press (2014).
- 32 M.G. Kesler, B.I. Lee, Improve prediction of enthalpy of fractions, Hydrocarbon processing 55-3 (1976) 153-158.
- 33 V. Szewczyk, M. Thomas, E. Behar, Prediction of volumetric properties and (multi-) phase behaviour of asphaltenic crudes, Oil & Gas Science and Technology 53-1 (1998) 51-58.
- 34 P. Fotland, H. Anfinsen, H. Foerdedal, H.P. Hjermstad, The phase diagrams of asphaltenes: experimental technique, results and modeling on some north sea crude oils, In Proceedings of the Symposium on the Chemistry of the Asphaltene and Related Substances, Cancun, Mexico, November (1997) 11-15.
- 35 R.K. Srivastava, S.S. Huang, S.B. Dyer, Quantification of asphaltene flocculation during miscible CO2 flooding in Weyburn reservoir, The Journal of Canadian Petroleum Technology 34-8 (1995) 31-40.
- 36 C.S. Kabir, A.K.M. Jamaluddin, Asphaltene characterization and mitigation in south Kuwait's Marrat reservoir, SPE production & facilities 17-04 (2002) 251-258.
- 37 A.K.M. Jamaluddin, N. Joshi, F. Iwere, O. Gurpinar, An investigation of asphaltene instability under nitrogen injection, In SPE International Petroleum Conference and Exhibition in Mexico, Society of Petroleum Engineers January (2002).
- 38 H. Yonebayashi, T. Masuzawa, C. Dabbouk, D. Urasaki, Ready for gas injection: Asphaltene risk evaluation by mathematical modeling of asphaltene precipitation envelope (APE) with integration of all laboratory deliverables, In SPE/EAGE Reservoir Characterization & Simulation Conference, October (2009).
- 39 M.A. Fahim, Empirical equations for estimating ADE of crude oils, Petroleum Science and Technology 25-7 (2007) 949-965.
- 40 I. Tsivintzelis, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Modeling phase equilibria for acid gas mixtures using the CPA equation of state. Part II: Binary mixtures with CO2, Fluid Phase Equilibria 306-1 (2011) 38-56.
- 41 I. Tsivintzelis, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Modeling phase equilibria for acid gas mixtures using the CPA equation of state. I. Mixtures with H2S, AIChE Journal 56-11 (2010) 2965-2982.

Chapter 4. Study of Gas Injection Effect and Sensitivity of the CPA Model

Entire content of this chapter is from our journal article "Alay Arya; Nicolas von Solms; Georgios M. Kontogeorgis. Investigation of the Gas Injection Effect on Asphaltene Onset Precipitation Using the Cubic-Plus-Association Equation of State. Energy Fuels. 2016, Vol. 30(5), pp.3560-3574".

Abstract

Miscible and Immiscible gas flooding is one of the enhanced oil recovery (EOR) techniques that has been widely used to increase the oil production. One of the critical problems with gas flooding is that it generally aggravates the asphaltene precipitation, which further creates a flow assurance problem. Therefore, it is imperative to investigate beforehand, the effect of gas injection into the reservoir, from the modeling results. The Cubic-Plus-Association (CPA) equation of state (EoS) has previously been applied to model asphaltene onset precipitation condition. In this work, we adopt the modeling approach from the previous work and provide the conceptual base for it. Five different reservoir fluids are studied to validate whether the model is able to calculate the effect of different types (e.g. N_2 , CO_2 , methane) and amounts (e.g. 10/20/30 mol%) of gas injections in agreement with experimental data from the literature. We also investigate the model behavior in order to show the importance of the association term in the EoS for the selected modeling approach. Sensitivity of the model results when we calculate either two or three model parameters from the experimental data is also studied. Model dependency on Saturates-Aromatics-Resins-Asphaltenes (SARA) analysis or molecular weight (MW) of asphaltene is also analyzed. In addition, a unique characteristic of the model for the given stock tank oil (STO) is identified, which does not change with different types and amounts of gas injections, and also remains same at upper and lower onset pressure boundaries. Based on this unique characteristic, a simple procedure to predict asphaltene phase envelope (APE) for the reservoir oil with relatively simple and few experimental data, performed on STO with n-pentane/n-heptane as precipitant, is proposed. This proposed procedure avoids the need of high pressure measurements of upper onset pressure (UOP).

4.1 Introduction

Asphaltenes are high MW organic compounds and are characterized as the fraction of the reservoir oil that is soluble in toluene, but insoluble in n-pentane/n-heptane [1]. Asphaltene solubility depends upon temperature, pressure and composition of the oil and they may precipitate out during improved oil recovery (IOR) operation by gas injection [2]. Once the asphaltene precipitation occurs, it causes

severe permeability reduction and wettability alteration in the reservoir, and plugging in the wellbore and surface facilities. Remedial measures, which are expensive and disruptive, usually include chemical treatments. Therefore, one must investigate the possibility of asphaltene precipitation prior to implementing a gas injection scheme [3,4].

After the primary and secondary oil recovery, the remaining oil in the most of the reservoir is around 50-60% of the Original Oil in Place (OOIP) [5-6]. Literature survey reveals that EOR technique with gas injection can produce up to 40% of the remaining oil in the field after water flooding [7,8]. Gas injection has been the most widely used EOR method for light, condensate and volatile oil reservoirs, compared to chemical and thermal methods. Light reservoirs with even small asphaltene content are susceptible to asphaltene precipitation not only through pressure depletion during the primary recovery but also through the composition change in fluid during gas injection [9-11]. Therefore gas injection in the light oil reservoir is more likely to cause asphaltene precipitation [3]. For reservoir fields, where hydrocarbon gas is in abundance, EOR is generally performed either by gas injection or by Water-Alternating-Gas (WAG) scheme. For fields, where CO_2 is economically available, pure CO_2 injection or Water-Alternating-Gas scheme is applied for the enhanced oil recovery. CO_2 -EOR is long-practiced method and CO_2 -EOR projects are being considered globally [12]. If there is no access of other gases, N_2 injection might be economical and suitable scheme for high pressure and high temperature (HP/HT) light oil reservoirs [13]. Reservoir field with sour and under saturated light oil with large gas content has the option of high pressure miscible acid gas (H_2S+CO_2) injection for enhanced oil recovery as well as for sulfur & CO_2 management [14].

Gas injection effect on asphaltene precipitation has been studied by several researchers using SAFT, PC-SAFT, and CPA. Wu et al [15] used modeling approach based on SAFT within the McMillan-Mayer description of liquid solutions and studied only one reservoir fluid with respect to gas injection. Ting et al [16] and Arya et al [17] studied the methane injection on model oil using the PC-SAFT (without association term) and CPA respectively. They have shown that the ambient pressure nalkane titration data are enough to find the model parameters. However, no validation was provided to show if the ambient pressure n-alkane titration data for STO alone would be sufficient to predict the effect of injection of separator gas (or mixture of gases) into the STO. Gonzalez et al [18] studied the effect of N_2 and CO_2 injections into the reservoir fluid using PC-SAFT by modifying the approach from Ting et al. [16]. Later Panuganti et al [19] modified the modeling approach from Gonzalez et al [18] and studied the effect of hydrocarbon gases for two reservoir fluids using both PC-SAFT and SRK-P. They concluded that PC-SAFT is able to predict the gas injection effect while SRK-P cannot do so. Punnapala & Vargas [20] then modified the modeling approach from Panuganti et al [19] by reducing three adjustable asphaltene parameters to two parameters and studied gas injection effect on five reservoir fluids. AlHammadi et al [21] studied both PC-SAFT and CPA using modeling approach from Panuganti et al [19] and Zhang et al [22] respectively. They compared the results with the experimental data and concluded that the PC-SAFT predictions for the effect of gas injections are better than the CPA predictions. However, they have compared the asphaltene precipitation onset results only for one reservoir fluid and therefore their conclusion cannot be generalized for all fluids.

On the other hand Zhang et al [22] also studied both PC-SAFT and CPA using the modeling approach from Gonzalez et al [18] and a self-developed approach (CPA) respectively. They concluded that CPA results are better than PC-SAFT results for two out of three reservoir fluids studied with respect to gas injection. It can be analyzed that for some fluids, the CPA approach of Zhang el al [22] is better while for some fluids, the PC-SAFT approach from Gonzalez et al [18] or Panuganti et al [19] is better and therefore it opens the door of further understanding. Moreover, from analyzing the results of the PC-SAFT modeling approach in the above mentioned publications and results of the CPA modeling approach from Li & Firoozabadi [23], it can be seen that the upper onset pressure (UOP) boundaries are always of the shape of concave up decreasing. While, the results of CPA modeling approach from Zhang et al [22] for UOP boundary show always maximum in the pressure at lower temperature and shape of the UOP boundary is more like concave down decreasing. Li & Firoozabadi [23], Zhang et al [22] and Arya et al [17] applied the CPA with a different modeling approach but no analysis was provided for the sensitivity of model parameters on the results. Li & Firoozabadi [23] have not shown any gas injection effect on UOP of reservoir oil. Vafaie-Sefti & Mousavi-Dehghani [24] considered asphaltene sub-fractions as aggregated components and used the Peng-Robinson (PR) EoS. However, they have shown only CO_2 injection effect on asphaltene precipitation at fixed temperature and pressure but not on UOP boundary of reservoir oil at different temperatures. Yonebayashi et al [25] studied the effect of acid gas (H_2S+CO_2) injection using CPA for two reservoir fluids. They used only two experimental measurements of UOP at two different temperatures for the first fluid and only one measurement of UOP for the second fluid to calculate model parameters. In all of these works, mentioned above, no discussion is provided about model reliability away from experimental temperature range and model sensitivity with respect to SARA analysis and MW of asphaltene. Panuganti et al [19] mentioned that accurate SARA analysis is necessary to characterize the oil using PC-SAFT but did not show any sensitivity results. Table 4.1 shows the brief overview of the available work and corresponding references, based on asphaltene modeling study with CPA and PC-SAFT, and how this study is different from them.

siuay win CFA and FC-SAF1.								
EoS	APE without GI	APE with GI	Asphaltene Precipitation in dead oil	PVT Properties	Sensitivity of Model Inputs/Parameters			
СРА	[17,22,23]	[17,22]	[26]	[21]	This Work			
PC-SAFT	[16]	[18,19,20]	[27,28]	[20,21]	NA			

Table 4.1. Overview of how this work is different than the available work in the literature, based on asphaltene modeling study with CPA and PC-SAFT.

In this work, we first go through the CPA EoS in order to understand the model parameters. In the next section, we mention the framework based on which the modeling approach is derived. Then we discuss the results of five reservoir fluids with different types and amounts of gas injections and their comparison with experimental data. We also analyze the model behavior with respect to association

term and find its importance. Based on the model behavior, relatively simple experimental measurements with STO are proposed as model input to predict the asphaltene onset boundary for the given reservoir oil with/without gas injections. Effect of model adjustable parameters and MW of asphaltene (or in other words, amount of asphaltene from SARA analysis) on the modeling results are also discussed. Model results, away from experimental temperature range, are analyzed with different set of model parameters.

4.2 Hypothesis behind Modeling Approach

In this work we assume the same modeling approach as presented by Arya et al [17], which is also represented in Fig. 4.1. Asphaltenes are considered as single self-associating compounds. The saturates, aromatics and resins are lumped into single component named as heavy component (HC), generally known as maltene fraction. This heavy component is cross associating with asphaltene. Asphaltene phase is modeled as liquid phase [30]. The binary interaction parameters are the same as mentioned by Arya et al [17], also shown in Table 4.2, and kept constant for all the fluids studied in this work. Since the modeling approach uses n-hexane plus (C_{6+}) fraction and STO contains negligible amount of lighter component than n-hexane, we can reasonably approximate STO as the C_{6+} fraction, which is further divided into the heavy component and asphaltene. In reality, asphaltene fraction is poly-dispersed in the medium of heavy component in the form of many sub-fractions as shown in the Fig. 4.2 as pictorial representation. Buch et al [31] and Badre et al [32] conducted several experiments using fluorescence depolarization techniques and concluded that the asphaltene molecules are always present as monomer in the oil with MW around 750 DA. Our model results are also consistent with this finding, which is discussed in the "Results & Discussion" section. Each subfraction of asphaltene may have different self-associating energy (ε^{AA}). Since the heavy component is the lumped component, each asphaltene sub-fraction may encounter different cross-association energy (ε^{AH}) in the medium due to different local composition. In this modeling approach we assume that asphaltene sub-fraction, which has the highest value of ε^{AA} precipitates first and is responsible for the onset of precipitation. One can assume asphaltene sub-fractions as insoluble fractions in nheptane, n-octane, and n-nonane and so on respectively. Since in this study we are only concerned about onset conditions of asphaltene precipitation and therefore to make the approach simple we assume that all the sub-fractions of asphaltene have the same highest value of ε^{AA} . In addition, asphaltenes are treated as single component with 4C scheme (molecule has two proton donor and two proton acceptor sites). Asphaltene critical parameters are fixed based on the assumption that its solubility parameter is 19-23 MPa^{1/2} [33]. Asphaltene solubility parameters are 19.14 MPa^{1/2} (ε^{AA} = 0) and 21.51 MPa^{1/2} (ε^{AA} = 3000) at 298K and 1 atm. User should note that we can use different set of critical parameters of asphaltene since model adjustable parameters will set accordingly for the same final results. The default value of ε^{AA} is 3000K [34] but can be treated as adjustable model parameter if sufficient experimental data are available. Local composition of the medium of heavy component varies with temperature, which also varies the location dependent ε^{AH} . We are interested in ε^{AH} , which is faced by the asphaltene sub-fraction of the highest value of ε^{AA} . Therefore, we assume that the entire heavy component medium has same ε^{AH} , which is temperature dependent. Cross-association volume (β^{AH}) and self-association volume (β^{AA}) have constant values (0.05). One can note that the value of association strength ($\Delta^{A_iB_j}$) is dependent upon two model parameters ($\varepsilon^{A_iB_j} \& \beta^{A_iB_j}$). Hence if we fix $\beta^{A_iB_j}$, we can calculate $\varepsilon^{A_iB_j}$ from the experimental data at given temperature. However, the temperature extrapolation of $\Delta^{A_iB_j}$ will be different for different values of $\beta^{A_iB_j}$. For the heavy component, one cross-association site is selected and the normal boiling point is calculated from the Pedersen relationship [35]. Critical parameters (P_c, T_c) and acentric factor (ω) of HC are calculated from the Kesler–Lee relationship [36]. Critical pressure (P_c) of HC is adjusted to match bubble point pressures of the oil. In addition, this modeling approach does not require SARA analysis since it does not depend upon asphaltene amount or asphaltene MW. In other words, for the fixed value of asphaltene ε^{AA} , increase in asphaltene amount increases ε^{AH} with heavy component at the onset temperature and pressure. While decrease in asphaltene amount decreases ε^{AH} at the onset temperature and pressure. We discuss these points in detail in the "Results & Discussion" section.



Fig. 4.1. Representation of the characterization procedure of STO/C_{6+} fraction into two pseudo-components (heavy component and asphaltene).



Fig. 4.2. Graphical representation of the assumptions made for the modeling approach used in this work. (a) Real condition, where asphaltene subfractions are scattered in the medium of heavy component in the heavy oil/STO. (b) All asphaltene subfractions are assumed of having same physical properties. (c) The cross-association energy (ε^{AH} / R) assumed to be the same everywhere but it is temperature dependent.

Table 4.2. Binary interaction parameter (k_{ij}) used by CPA model from Arya et al [17]. T is temperature in K. A missing value means that the binary interaction parameter is set to zero.

	2 1	-			
Component	N ₂	CO_2	H_2S	HC	Asp
N ₂				0.10	0.24
CO ₂	-0.06			0.10	0.10
H_2S	0.678-0.0018T			0.05	
methane	0.141-12.6448/T	0.0882	0.0760		0.01
ethane	0.04	0.1335	0.0847		0.01
propane	0.04	0.1522	0.0917		0.01
<i>i</i> -butane	0.05	0.1122	0.0761		
<i>n</i> -butane	0.05	0.1122	0.0897		
<i>i</i> -pentane	0.06	0.10			
<i>n</i> -pentane	0.06	0.10			

4.3 Results and Discussion

In this work, five reservoir fluids are studied with respect to different type and different amount of gas injection in order to show the predictive ability and reliability of the model. In general, experimental data of asphaltene onset precipitation are used to calculate model parameters and then the model is used to predict the results of different types and/or amounts of gas injections. Model behavior and effect of model parameters are also analyzed. Calculated values of model parameters are mentioned in Table 4.3 for all the fluids. Reservoir oil compositions and properties required for the model are mentioned in Table 4.4. Please note that we do not need SARA analysis and information about amount of asphaltene is optional. Model behavior is same for all the fluids studied; however, results are shown only for fluid-1 in this work. The effect of different model parameters have been analyzed for fluid-1 to fluid-4. Four out of these five reservoir fluids have been studied by Punnapala

& Vargas [20] with PC-SAFT and reader is referred to their publication if interested. Relative deviations between experimental data and calculated results of all the fluids are mentioned in the Supplementary Information.

5		5 5			
Fluid	Asp MW	$\varepsilon^{\mathrm{AA}}/R$ (K)	$\varepsilon^{\rm AH}/R$ (K)	$eta^{ m AH}$	P_c of HC (bar)
Fluid-1	1800	7000	3444-5305/T	0.05	18.21
	750*	7000	3604-24123/T	0.05	18.21
	750	3000	1207+97519/T	0.05	18.21
Fluid-2	750	3000	1243+65231/T	0.05	20.12
	750*	7000	3550-23918/T	0.05	20.12
	750	3000	3876-378860/T	0.01	20.12
Fluid-3	750	3000	1887-33418/T	0.05	19.13
	750*	7000	3977-58536/T	0.05	19.13
Fluid-4	750	3000	1269+71943/T	0.05	21.4
	750*	7000	3863-116110/T	0.05	21.4
Fluid-5	750*	3000	1540 at 373K	0.05	21.5

Table 4.3. Values of Model Parameters for all fluids studied in this work.

* Relative deviations for this case are mentioned in the Supplementary Information

Table 4.4. Composition, properties and asphaltene amount (optional) of reservoir fluids required for the CPA model.

	Fluid-1 ^[20]	Fluid-2 ^[20]	Fluid-3 ^[37]	Fluid-4 ^[20]	Fluid-5 ^[20]
Comp.	mol%	mol%	mol%	mol%	mol%
N ₂	0.17	0.15	0.34	0.09	0.96
H ₂ S	2.11	1.72	0.16	3.68	0.58
CO ₂	0	0	0	5.27	0.30
methane	34.95	32.51	32.9	45.84	4.49
ethane	7.77	7.97	8.15	5.35	2.99
propane	6.81	7.7	6.28	4.21	4.75
<i>i</i> -butane	1.81	1.93	0	1.18	0.81
<i>n</i> -butane	4.26	4.66	1.13	2.79	1.92
<i>i</i> -pentane	2.10	2.08	0	1.39	1.27
<i>n</i> -pentane	2.69	2.75	3.5	1.8	2.19
C ₆₊	37.17	38.55	47.54	28.4	79.74
<i>C</i> ₆₊ MW	207.5	191.07	250.64	199.05	230.21
<i>C</i> ₆₊ SG	0.823	0.817	0.919	0.8464	0.867
Asphaltenes (wt%)	0.21	0.17	15.5	0.17	1.73

Components	Fluid-1	Fluid-2	Fluid-5 ^a		
		_	Hydrocarbon gas	Associated gas	
N ₂	0.398	0.462	0.40	0.53	
H ₂ S	3.891	4.510	2.44	3.18	
CO ₂	0.000	0.000	0.19	0.17	
methane	71.312	87.449	74.87	59.40	
ethane	11.912	7.192	14.36	17.64	
propane	7.224	0.370	6.20	13.52	
<i>i</i> -butane	1.189	0.006	0.49	1.40	
<i>n</i> -butane	2.254	0.005	0.85	3.04	
<i>i</i> -pentane	0.567	0.001	0.09	0.44	
<i>n</i> -pentane	0.616	0.001	0.08	0.52	
C ₆₊	0.637	0.004	0.03	0.16	

Table 4.5. Injected Gas Composition in mol% for Fluid-1, Fluid-2 and Fluid-5 from Punnapala & Vargas [20].

^a Composition of two different injected gases (Hydrocarbon gas and Associated gas) are mentioned for fluid-5.

<u>Fluid-1</u>

Fig. 4.3 shows the hydrocarbon gas injection effect on the reservoir fluid-1. Composition of injected hydrocarbon gas is shown in Table 4.5. Model parameters are calculated by correlating experimental data for 5 mol% gas injection case as shown in Fig. 4.3a. P_c of HC is calculated from one bubble point and association parameters ($\varepsilon^{AA} \& \varepsilon^{AH}$) are calculated from three upper onset pressures. Cases with 10, 15 and 30 mol% gas injection are then predicted using the model and compared with the experimental data as shown in Fig. 4.3b, 4.3c and 4.3d respectively. Model predictions are in agreement with experimental data. Also the sensitivity of the model with respect to asphaltene MW is analyzed by considering two cases. In the first case, the value of asphaltene MW is considered 750 Da (which is also the default value) while in the second case it is considered 1800 DA. Model results with both cases are in agreement with experimental data. It proves that our modeling approach is not sensitive to the asphaltene MW or in other words it does not need accurate amount of asphaltene from SARA analysis. SARA analysis usually varies from one standard to another and therefore it is one of the benefits of this modeling approach that it does not depend upon SARA analysis. It can also be analyzed that decreasing the molar amount of asphaltene by increasing the MW to 1800 Da for the fixed mass fraction of asphaltene, ε^{AH} value also decreases compared to that of for 750 Da case in the experimental temperature range. In addition, Fig. 4.4 shows comparison between model results for UOP boundary with the three adjustable parameters approach and the two adjustable parameters approach. In the three adjustable parameters approach P_c , ε^{AH}/R and ε^{AA}/R are calculated from one bubble point and three upper onset pressures. While in the two adjustable parameters approach P_c and ε^{AH}/R are calculated from one bubble point and two UOP points for default value of ε^{AA}/R = 3000K. One can see that the three parameters approach is, as expected, more accurate than the two parameters approach. Moreover, extrapolation of upper onset pressures at lower and higher temperatures, away from the experimental temperature range, is quite different. As per Fig. 4.4b, there is no UOP at higher temperature. We are not sure whether the model can extrapolate the results away from the experimental temperature range either with the three parameters approaches or with the two parameters approaches. However, we can confidently say that it predicts accurate results of

gas injection effect within the experimental temperature range. In addition, with two parameters approach, there is a maximum in UOP at lower temperature. The three parameters approach show concave up decreasing shape.



Fig. 4.3. Fluid-1: UOP and bubble points vs temperature for different amounts of gas injection. Symbols (squares for UOP, circles for bubble points) represent experimental data from Punnapala & Vargas [20]. (Plot-a) Lines for UOP and bubble pressures for 5 mol% gas injection case are the correlations by CPA with $\varepsilon^{AH} / R = 3604-24123/T \text{ K}$, $\varepsilon^{AA} / R = 7000\text{ K}$, P_c of HC =18.21 bar for MW of 750 (case-1/solid line) and $\varepsilon^{AH} / R = 3444-5305/T \text{ K}$, $\varepsilon^{AA} / R = 7000\text{ K}$, P_c of HC =18.21 bar for MW of 1800 (case-2/dashed line). Lines for 10 mol% (Plot-b), 15 mol% (Plot-c) and 30 mol% (Plot-d) gas injections are the predictions after determination of ε^{AH} / R , ε^{AA} / R and P_c of HC using 5 mol% gas injection case.



Fig. 4.4. Fluid-1 (with asphaltene MW=750): Comparison between three vs two adjustable parameters approaches with respect to UOP boundary. (Plot-a) Three adjustable parameters approach, $\varepsilon^{AH} / R = 3604-24123/T K$, $\varepsilon^{AA} / R = 7000K$, P_c of HC =18.21 bar. (Plot-b) Two adjustable parameters approach, $\varepsilon^{AH} / R = 1207+97519/T K$, P_c of HC =18.21 bar for default value of $\varepsilon^{AA} / R = 3000K$. Symbols represent experimental data from Punnapala & Vargas [20].

Investigation of Model Behavior for Fluid-1

At the upper onset boundaries of fluid-1 with different amounts of gas injections, there is asphaltene rich phase in equilibrium with asphaltene lean phase. The asphaltene rich phase is analyzed with respect to SRK ($P^{SRK,R}$) and association ($P^{Assoc,R}$) contributions to the upper onset pressure (P^{UOP} = $P^{SRK,R} + P^{Assoc,R}$). The reader should note that, for the asphaltene lean phase, association ($P^{Assoc,L}$) contribution is negligible and SRK (P^{SRK,L}) contribution is almost equal to the upper onset pressure $(P^{UOP} \approx P^{SRK,L})$ since the mole fraction of asphaltene in asphaltene lean phase is very small. Table 4.6 shows that P^{Assoc,R} contribution remains constant for different amounts of gas injections for a given temperature. Since the association contribution is due to HC (which is cross-associating with asphaltene) and asphaltene (which is self-associating) components, we further show in Table 4.6 that asphaltene mole% in the binary mixture of HC and asphaltene in the asphaltene rich phase remains constant for different amounts of gas injections for a given temperature. Table 4.7 shows that even if we inject n-heptane (nC7) at ambient pressure into the mixture of HC and asphaltene, which is STO/heavy oil, the PAssoc,R term and mole % of asphaltene in asphaltene rich phase remain almost the same as in the case of gas injection into the reservoir fluid for a given temperature shown in Table 4.6. Hence, the P^{Assoc,R} term is the characteristic property for a given STO and can be calculated from the ambient or near ambient pressure titration data, which shows the amount of n-heptane/npentane required per amount of STO at asphaltene onset condition for different temperatures. For our modeling approach, we need these ambient pressure titration data at least at three different temperatures, which should cover the temperature range of interest. It is also observed that the PAssoc,R also remains constant for UOP and lower onset pressure (LOP) for a given temperature (results are not shown here). In other words, one can say that the Helmholtz energy contribution due

to the association term of asphaltene rich phase at the onset condition is independent of gas/n-heptane injection for given temperature.

An asphaltene (Asp) molecule can associate with other Asp molecules or with other HC molecules. If Asp molecules are only bonded with sites of HC molecules and Asp molecules are not bonded with each other, ratio of the bonded sites of Asp molecules to the bonded sites of HC molecules will be unity. On the other hand if Asp molecules are bonded with each other and also with HC molecules, ratio of the bonded sites of Asp molecules to the bonded sites of HC molecules will be greater than unity. Asp monomer fraction (fraction of molecules without any bond/s with other molecules), HC monomer fraction and ratio of bonded sites of Asp molecules to the bonded sites of HC molecules in both Asp rich phase and Asp lean phase at upper onset boundary are shown in Table 4.8 for the 5 mol% gas injection case. One can observe that Asp monomer fraction is almost zero in both Asp rich and Asp lean phases. In Asp lean phase, all Asp molecules are bonded with HC molecules, which results zero value of Asp monomer fraction and unity value of ratio of bonded sites. In Asp rich phase, Asp-Asp molecules self-association is more since the ratio of bonded sites of Asp molecules to bonded site of HC molecules are much higher than unity and Asp monomer fraction is close to zero. Thus, model behavior is consistent with the conclusion made by Badre et al [32] that Asp molecules in the oil (corresponds to Asp lean phase) are dispersed as single molecule (one fused aromatic ring) and not as a lumped molecule (multiple fused aromatic rings cross-linked with each other) of more than one Asp molecules associated with each other.

Temp.	P ^{Assoc,R} (bar) (Asp rich phase)				Asp mol% in Asp and HC mixture (Asp rich phase)			
(K)	5 mol% GI	10 mol% GI	15 mol% GI	30 mol% GI	5 mol% GI	10 mol% GI	15 mol% GI	30 mol% GI
281.3	-159.3	-158.6	-157.9	-154.7	94.5	94.5	94.6	94.7
302.1	-171.2	-170.8	-170.2	-168.2	93.6	93.6	93.7	93.8
322.9	-182.1	-181.6	-181.2	-179.6	92.6	92.6	92.7	92.8
343.8	-192.1	-191.8	-191.4	-190.0	91.5	91.5	91.6	91.8
364.6	-201.7	-201.3	-201.0	-199.6	90.3	90.4	90.5	90.8
385.4	-210.6	-210.4	-210.0	-208.8	89.2	89.2	89.3	89.7
406.3	-219.3	-219.0	-218.7	-217.5	88.0	88.1	88.2	88.6
427.1	-227.5	-227.2	-226.9	-225.8	86.8	87.0	87.1	87.5
447.9	-235.3	-235.0	-234.8	-233.7	85.8	85.9	86.0	86.5
468.8	-242.8	-242.6	-242.3	-241.3	84.7	84.8	85.0	85.5
489.6	-249.9	-249.7	-249.5	-248.6	83.7	83.8	84.0	84.5
500.0	-253.5	-253.3	-253.0	-252.1	83.2	83.3	83.5	84.1

Table 4.6. Fluid-1 (Asp MW=750 DA): Pressure contribution due to the association term ($P^{Assoc,R}$) and Asp mol% in the binary mixture of Asp and HC components for the asphaltene rich phase at the upper onset boundary.

	At onset of precipitation				
Temp. (K)	P ^{Assoc,R}	Asp composition in Asp and HC mixture (Asp rich phase)	amount of nC7 (cm^3 of nC7/g of oil)		
	(bar)	(mol%)			
281.3	-160.1	94.7	0.46		
302.1	-169.3	94.1	0.68		
322.9	-178.3	93.3	0.84		
343.8	-187.2	92.5	0.96		
364.6	-195.9	91.6	1.05		

Table 4.7. Fluid-1 (Asp MW=750 DA): Pressure contribution due to the association term ($P^{Assoc,R}$), Asp mol% in the mixture of Asp and HC components for asphaltene rich phase and amount of nC7 required at the onset of asphaltene precipitation during nC7 injection into STO at 1.01325 bar.

Table 4.8. Fluid-1 (Asp MW=750 DA), 5 mol% GI: Asp monomer fraction, HC monomer fraction and ratio of bonded sites of Asp molecules to bonded sites of HC molecules in Asp rich phase and Asp lean phase at upper onset boundary.

Temperature (K)	Asp monomer fraction		HC monomer fraction		Bonded sites of Asp molecules/Bonded sites of HC molecules in one mole of fluid	
	Asp Rich Phase	Asp Lean Phase	Asp Rich Phase	Asp Lean Phase	Asp Rich Phase	Asp Lean Phase
291.7	0.0003	0.0001	0.0765	0.9979	68.65	0.99
302.1	0.0003	0.0001	0.0933	0.9980	64.28	1.03
322.9	0.0004	0.0002	0.1341	0.9980	57.40	1.03
343.8	0.0006	0.0004	0.1799	0.9980	52.15	1.04
364.6	0.0008	0.0008	0.2344	0.9980	48.70	1.03
385.4	0.0009	0.0014	0.2982	0.9980	46.79	1.03
406.3	0.0011	0.0023	0.3683	0.9980	46.37	1.03
427.1	0.0014	0.0036	0.4262	0.9980	45.95	1.03
447.9	0.0016	0.0054	0.4843	0.9980	46.54	1.03
468.8	0.0018	0.0079	0.5484	0.9980	48.85	1.02
489.6	0.0020	0.0113	0.5988	0.9980	50.95	1.02
500.0	0.0021	0.0133	0.6217	0.9980	52.34	0.99

Non-associating CPA EoS for Fluid-1

Since the association term remains constant for given temperature as explained above, it does not mean that only SRK term is important and in order to prove that we studied the non-associating CPA EoS as shown in Fig. 4.5 for fluid-1. Association parameters are $\varepsilon^{AA}/R = 0K$ and $\varepsilon^{AH}/R = 0K$. Binary interaction parameter $(k_{ij} = -0.6893 + 1507.85 \times 10^{-6} \text{T} + 92.66/\text{T})$ between HC and asphaltene is considered temperature dependent and calculated from three UOP points. All other parameters are kept same as in the case of the associating CPA EoS. Fig. 4.5 shows that with non-associating CPA (essentially SRK), the model is able to correlate 5 mol% gas injection case but is unable to predict the 10, 15 and 30 mol% gas injection cases. It also shows the opposite physical behavior that is higher amount of gas injection decreases the upper onset pressure.



Fig. 4.5. Fluid-1: UOP and bubble points vs temperature for different amounts of gas injections using non-associating CPA EoS. Lines for upper onset and bubble pressures for 5 mol% gas injection case are the correlations by non-associating CPA EoS with k_{ij} between HC and Asp =-0.6893+1507.85x10⁻⁶T+92.66/T and P_c of HC =18.21 bar. Lines for 10, 15 and 30 mol% gas injections are the predictions after determination of k_{ij} and P_c of HC using 5 mol% gas injection case. Symbols represent experimental data of UOP from Punnapala & Vargas [20].

Fluid-2

Similar to Fluid-1, Fluid-2 is studied for the hydrocarbon gas injection effect. Composition of injected gas is mentioned in Table 4.5. Fig. 4.6 shows the effect of 10, 15 and 30 mol% of gas injection into reservoir fluid-2. Experimental data for 10 mol% gas injection is used to calculate the model parameters. Two cases are considered. In the first case, one bubble point is used to calculate P_c of HC and three upper onset pressures are used to calculate ε^{AA}/R and ε^{AH}/R . In the second case, one bubble point is used to calculate P_c of HC and three upper onset pressures are used to calculate ε^{AH}/R and β^{AH} for the default value of $\varepsilon^{AA}/R = 3000K$. Fig. 4.6 shows that after calculating the model parameters, the model is able to predict 15 mol% and 30 mol% gas injection cases for both the cases. However, the results beyond the experimental temperature range are different. It should also be noted that bubble point pressure does not get affected by association parameters (due to very small mole fraction and high vapor pressure of asphaltene) and that is why only one bubble point curve is shown in the Fig. 4.6. For fluid-2, we also compared three and two parameters approaches, as shown in Fig. 4.7. The conclusion is the same as previously mentioned for fluid-1. The injected gas in the case of fluid-2 is lighter than the injected gas in the case of fluid-1. Light hydrocarbon gas injection reduces the asphaltene stability more compared to heavy hydrocarbon gas. The composition for fluid-1 and fluid-2 are almost similar since they are from the same field but from different wells, however, from the experimental data (eg. of 10 mol% gas injection case in Supplementary Information), it can be observed that fluid-2 asphaltenes are more stable compared to fluid-1 asphaltenes even though the light hydrocarbon gas is injected into fluid-2.



Fig. 4.6. Fluid-2: UOP and bubble points vs temperature for different amounts of gas injections. Symbols (squares for upper onset, circles for bubble points) represent experimental data from Panuganti et al [19]. (Plot-a) Lines for upper onset and bubble pressures for 10 mol% gas injection case are the correlations by CPA, case-1/solid lines- ε^{AH} / R =3550-23918/T K & ε^{AA} / R =7000K for default value of β^{AH} =0.05, case-2/dashed lines- ε^{AH} / R =3876-378860/T K & β^{AH} =0.01 for default value of ε^{AA} / R =3000K. P_c of HC =20.12 bar and bubble point curves are same for both cases. Lines for 15 mol% (Plot-b) and 30 mol% (Plot-c) gas injections are the predictions after determination of ε^{AH} / R , ε^{AA} / R or β^{AH} and P_c of HC using 10 mol% gas injection case.



Fig. 4.7. Fluid-2: comparison between three vs two adjustable parameters approach with respect to UOP boundary. (Plot-a) Three adjustable parameters approach: case-1/solid lines- $\varepsilon^{AH} / R = 3550-23918/T \text{ K} \& \varepsilon^{AA} / R = 7000 \text{ for } default value of \beta^{AH} = 0.05, case-2/dashed lines- <math>\varepsilon^{AH} / R = 3876-378860/T \text{ K} \& \beta^{AH} = 0.01$ for default value of $\varepsilon^{AA} / R = 3000 \text{ K}$. (Plot-b) Two adjustable parameters approach: $\varepsilon^{AH} / R = 1243+65231/T \text{ K}$ for default value of $\varepsilon^{AA} / R = 3000 \text{ K}$. (Plot-b) Two adjustable parameters approach: $\varepsilon^{AH} / R = 1243+65231/T \text{ K}$ for default value of $\varepsilon^{AA} / R = 3000 \text{ K}$.

Fluid-3

Anadarko Petroleum Corporation and Schlumberger have jointly investigated the effects of gas addition on the Deepwater Gulf of Mexico reservoir fluid with respect to asphaltene precipitation and deposition. Three common EOR injection gases (N_2 , CO_2 and CH_4) have been studied experimentally. In addition, n-heptane (nC7) injection was also studied in order to analyze the phase behavior of the reservoir oil during reservoir depressurization. In this work, we use 0 mol% gas injection case to calculate model parameters using two cases and then the model is used to predict 10 mole% N_2 , CO_2 , CH_4 and nC7 injection effect. In the first case, the value of ε^{AA}/R and ε^{AH}/R are calculated from the three upper onset pressures. In the second case, the value of ε^{AA}/R is fixed to the default value of 3000K and ε^{AH}/R is calculated from the two upper onset pressures. In both cases, P_c of HC is the same since it is calculated from the same single bubble point information. Both cases are able to predict the different types of gas injections effect in agreement with experimental data as shown in Fig. 4.8. We can also observe that the extrapolations beyond the experimental temperature range are different for the two cases. Fig. 4.8f shows only the second case, and it can be observed that N_2 gas is the strongest precipitant followed by CH_4 , nC7 and CO_2 in decreasing order respectively, which is also true for the first case.



Fig. 4.8. Fluid-3: UOP and bubble points vs temperature for different types of gas injections. Symbols (squares for upper onset, circles for bubble points) represent experimental data from Gonzalez et al [37]. (Plot-a) Lines for upper onset and bubble pressures for 0 mol% gas injection case are the correlations by CPA with $\varepsilon^{AH} / R = 3977-58536/T K$, P_c of HC = 19.13 bar, $\varepsilon^{AA} / R = 7000K \& \beta^{AH} = 0.05$ (case-1/solid lines) and $\varepsilon^{AH} / R = 1887-33418/T K$, P_c of HC = 19.13 bar for default values of $\varepsilon^{AA} / R = 3000K \& \beta^{AH} = 0.05$ (case-2/dashed lines). Lines for 10 mol% of N_2 (Plot-b), CO_2 (Plot-c), CH_4 (Plot-d) and nC7 (plot-e) injections are the predictions after determination of ε^{AH} / R , ε^{AA} / R and P_c of HC using the 0 mol% gas injection case. (Plot-f) Comparison of UOP boundaries for different types of gas injections using the two parameters approach (case-2).

Fluid 4

The effect of CO_2 gas injection on reservoir fluid-4 is studied by Punnapala & Vargas [20]. Experimental data of bubble points of reservoir fluid-4 (0 mol% gas injection) and UOP with 20 & 30 mol% CO_2 gas injections are available. Fig. 4.9 shows that the model is able to correlate the bubble points after calculating P_c of HC from one bubble point information. Two cases are considered to calculate UOP boundary. In the first case, the value of ε^{AA}/R is fixed to the value of 7000K and in the second case, the value of ε^{AA}/R is fixed to the default value of 3000K. The model parameter ε^{AH}/R is calculated from the two upper onset pressures of 20 mol% CO_2 injection case. The model with both cases are able to predict 30 mol% CO_2 injection case. However, as mentioned above for other fluids, temperature extrapolations are very much different from each other. Note that, in the second case, there is no UOP above around 450K for 20 mol% CO_2 injection case. One can observe that higher value of ε^{AA}/R makes the UOP boundary concave up decreasing.



Fig. 4.9. Fluid-4: UOP for 20 & 30 mol% CO₂ injection and bubble points for 0 mol% CO₂ injection vs temperature. Symbols (upward & downward triangles for upper onset, circles for bubble points) represent experimental data from Punnapala & Vargas [20]. Lines for upper onset, for 20 mol% CO₂ injection, and bubble pressure, for 0 mol% CO₂ injection case, are the correlations by CPA with $\varepsilon^{AH} / R = 3863 \cdot 116110/T K$, P_c of HC = 21.4 bar, $\varepsilon^{AA} / R = 7000K \& \beta^{AH} = 0.05$ (case-1/solid lines) and $\varepsilon^{AH} / R = 1269 + 71943/T K$, P_c of HC = 21.4 bar for default values of $\varepsilon^{AA} / R = 3000K \& \beta^{AH} = 0.05$ (case-2/dashed lines). Lines (both solid and dashed) for 30 mol% of CO₂ injection cases.

Fluid 5

For this reservoir fluid, we will study different types and different amounts of gas injection effect at the constant temperature of 373K. The model parameter ε^{AH}/R is calculated from the hydrocarbons (*HCs*) gas injection case for the default value of $\varepsilon^{AA}/R = 3000K$. At constant temperature, model requires only one experimental data for the onset condition to calculate ε^{AH}/R . The composition of HCs and associated gases are mentioned in the Table 4.5. The effect of different type of gas injections $[HCs (90\%) + N_2(10\%)$ in Fig.4.10b, $HCs (80\%) + CO_2(20\%)$ in Fig.4.10c, HCs (96.4%) + $H_2S(3.6\%)$ in Fig.4.10d, $HCs(67\%) + CO_2(22\%) + N_2(11\%)$ in Fig.4.10e, associated gas in Fig.4.10f] are then predicted and compared with the experimental data. The model results are satisfactory. Fig. 4.11 shows that when at least 10 mol% N_2 is present in the injected gas, UOP boundary moves upward compared to UOP boundary with only HCs gas injection. Whereas when CO_2 or H_2S are added to the HCs gas, upper onset pressure boundary moves downward compared to the one with only HCs gas injection. In the case of associated gas injection, UOP is minimum compared to other cases or, in other words, when the amount of alkanes, heavier than methane, increases in the injected gas, the asphaltene stability also increases. Since this reservoir fluid is relatively heavy, containing 79.74 mol% of C_{6+} , one can see that more than around 35 mol% of HCs gas is required to start the asphaltene precipitation at 373K.


Fig.4.10. Fluid-5: UOP and bubble points vs amount of different types of gas injections at 373 K. Symbols (triangles for upper onset, circles for bubble points) represent experimental data from Punnapala & Vargas [20]. Lines for upper onset and bubble pressures for HCs gas injection case are the correlations by CPA with $\varepsilon^{AH} / R = 1540$ K, P_c of HC =21.5 bar for default value of $\varepsilon^{AA} / R = 3000$ K & $\beta^{AH} = 0.05$ in (Plot-a). Lines for upper onset pressure and bubble pressure, for (Plot-b) $HCs(90\%) + N_2(10\%)$ (Plot-c) $HCs(80\%) + CO_2(20\%)$ (Plot-d) $HCs(96.4\%) + H_2S(3.6\%)$ (Plot-e) $HCs(66\%) + CO_2(22\%) + N_2(11\%)$ (Plot-f) associated gas, are the predictions after determination of ε^{AH} / R , ε^{AA} / R and P_c of HC using HCs gas injection case. Composition is in mole%.



Fig. 4.11. Fluid-5: Comparison of upper onset pressure boundaries for different types of gas injection at 373 K. ε^{AH} / R = 1540 K, P_c of HC = 21.5 bar and default value of ε^{AA} / R=3000 K & β^{AH} = 0.05 are used. Composition is in mole%.

4.4 Conclusions

From this work, it can be concluded that the applied modeling approach with the CPA EoS is able to predict the effect of different amounts and types of gas injections after the model parameters are calculated from a few experimental data. At least three asphaltene onset conditions at different temperatures, covering the temperature range of interest, and bubble point information should be available in order to calculate asphaltene phase envelope. If the study focuses on analyzing reservoir depressurization/pressurization at constant temperature, only one experimental onset condition is needed. It is shown that the temperature dependent $P^{Assoc,R}$ term or asphaltene solubility in the asphaltene rich phase is the characteristic property of STO (mixture of heavy component and asphaltene), which does not change with addition of defined components. Moreover, PAssoc,R is the same for both upper onset pressure and lower onset pressure boundaries, which gives benefit to verify one set of data (e.g. lower onset boundary) if the model is able to correlate another set of data (e.g. upper onset boundary). Higher pressure measurements for the asphaltene upper onset boundary are not required with reservoir oil but relatively simple ambient or near ambient pressure measurements of STO with n-pentane/n-heptane precipitant are sufficient. Once we have this characteristic of STO, we can add separator gas into STO, with known separator gas composition and GOR, and the model can then predict the asphaltene phase envelope for the given reservoir fluid. Moreover, the model does not require SARA analysis, which may vary from one standard to another. The effect of three and two parameters approaches is clearly distinguished in this work. Three parameters approach is evidently more accurate than two parameters approach; however, temperature extrapolations may not be reliable either with three or with two parameters approach. In addition, temperature extrapolations are different when you use either ε^{AA}/R or β^{AH} as a third model parameter to be calculated from experimental data. The shape of upper onset pressure boundary depends upon the temperature dependent value of $\Delta^{AA}/q(\rho)$ relative to the temperature dependent value of $\Delta^{AH}/q(\rho)$. If we increase the value of $\Delta^{AA}/g(\rho)$, the shape of upper onset pressure boundary tends to become concave up decreasing. On the other hand if we decrease the value of $\Delta^{AA}/g(\rho)$, the shape tends to become concave down decreasing. The model results show that asphaltene molecules in the reservoir oil and in the STO are associated with the molecules of heavy component but not with each other. Asphaltene-asphaltene molecules association is almost negligible in the reservoir oil whereas in the asphaltene rich phase, asphaltene-asphaltene molecules association is dominant. It is also shown that when we do not consider the association term, the non-associating CPA EoS is unable to predict the gas injection effect.

4.5 Supplementary Information

Relative deviations between experimental data and model results are mentioned in the Tables 4.9 to 4.13 for all the fluids studied in this work. However, only one case, out of different cases, of each fluid is presented. Reader should note that experimental data are obtained by digitization of the plots, from the respected references, and therefore, there could be minor deviations from the actual experimental data.

Table 4.9. Fluid-1: Relative Deviation (RD) between experimental data and calculated results for BP and UOP. Experimental data are from Punnapala & Vargas [20]. Model parameters ($\varepsilon^{AH} / R = 3604-24123/T K$, $\varepsilon^{AA} / R = 7000K$, P_c of HC =18.21 bar for MW of 750) are calculated from 5% GI case. Data for 10 mol%, 15 mol% and 30 mol% gas injections are the predictions after determination of ε^{AH} / R , ε^{AA} / R and P_c of HC using 5 mol% GI case.

9	•	2	5		U	5 0		
			BP				UOP	
Amount of Injected Gas	Т	Exp	Calc	RD	Т	Exp	Calc	RD*
	Κ	bar	bar	%	K	bar	bar	%
	327.9	121.0	125.8	4.04	327.6	237.0	239.4	1.00
5 mol%	347.1	140.7	138.1	1.87	346.8	190.1	193.3	1.71
	394.2	160.5	160.6	0.11	393.9	162.9	163.9	0.59
	328.1	130.8	135.2	3.34	328.1	322.0	302.4	6.07
10 mol%	347.2	142.5	148.0	3.84	347.2	259.9	249.2	4.11
	394.4	177.8	171.6	3.45	394.4	221.4	208.4	5.86
15 - 10/	347.1	159.2	158.2	0.61	346.8	294.4	314.0	6.67
15 mol%	394.4	188.8	183.0	3.12	394.1	253.6	257.6	1.58
20 - 10/	347.1	201.5	192.4	4.55	346.8	624.2	564.3	9.60
30 mol%	394.1	233.5	219.5	6.00	393.8	476.8	453.0	4.98

*RD (%) =
$$\frac{|P_{exp} - P_{calc}|}{P_{exp}} \times 100$$

1 5	·	2	<i>,</i>	c J	0			
			BP				UOP	
Amount of Injected Gas	Т	Exp	Calc	RD	Т	Exp	Calc	RD
	Κ	bar	bar	%	Κ	bar	bar	%
	328.4	148.7	143.4	3.6	327.9	232.8	230.3	1.0
10 mol%	347.6	157.3	156.4	0.6	347.1	202.6	199.7	1.4
	391.6	183.2	178.6	2.5	391.6	183.2	188.9	3.1
	328.1	165.5	158.2	4.4	328.5	322.8	307.2	4.8
15 mol%	347.5	173.7	172.2	0.9	347.5	280.2	269.0	4.0
	391.5	199.9	195.1	2.4	391.5	254.0	245.2	3.5
	328.4	205.6	210.5	2.4	347.7	583.0	549.3	5.8
30 mol%	347.5	240.6	225.8	6.1	391.5	426.7	470.3	10.2
	391.9	246.7	250.1	1.4	-	-	-	-

Table 4.10. Fluid-2: Relative Deviation (RD) between experimental data and calculated results for BP and UOP. Experimental data are from Panuganti et al [19]. Model parameters ($\varepsilon^{AH} / R = 3550-23918/T K$, $\varepsilon^{AA} / R = 7000K$, P_c of HC =20.12 bar for MW of 750) are calculated from 10% GI case. Data for 15 mol% and 30 mol% gas injections are the predictions after determination of ε^{AH} / R , $\varepsilon^{AA} / R = 0$, ε^{AH} / R , $\varepsilon^{AA} / R = 0$, ε^{AH} / R , $\varepsilon^{AA} / R = 0$, ε^{AH} / R , $\varepsilon^{AA} / R = 0$, ε^{AH} / R , $\varepsilon^{AA} / R = 0$, ε^{AH} / R , $\varepsilon^{AA} / R = 0$, $\varepsilon^{AH} / R = 0$, ε^{A

T Ć		E	3P			U	ЮР	
Type of	Т	Exp	Calc	RD	Т	Exp	Calc	RD
Injected Gas	Κ	bar	bar	%	Κ	bar	bar	%
	370.9	166.9	173.5	3.9	370.9	317.2	315.2	0.7
	338.7	146.8	152.0	3.5	338.7	348.3	362.6	4.1
0 mall/CI	310.9	127.6	129.9	1.8	310.9	462.1	493.7	6.8
0 1101% 01	304.3	120.7	124.1	2.8	304.3	551.7	549.3	0.4
	299.8	117.2	120.1	2.4	299.8	593.1	594.4	0.2
	277.6	105.7	99.0	6.4	-	-	-	-
	370.9	311.4	318.5	2.3	370.9	669.0	651.4	2.6
$10 \text{ mol}\% N_2$	338.7	311.4	307.5	1.3	338.7	841.4	804.5	4.4
Injection	324.8	310.3	301.4	2.9	324.8	931.0	932.2	0.1
	310.9	304.6	294.4	3.3	310.9	1351.7	1136.0	16.0
10 10/ 20	370.9	187.7	187.8	0.1	370.9	427.6	434.7	1.7
	338.7	166.8	161.0	3.5	338.7	489.7	483.4	1.3
$10 \text{ mol}\% \text{CO}_2$	310.9	145.9	133.8	8.2	310.9	675.9	614.8	9.0
Injection	294.3	125.4	116.2	7.4	304.3	758.6	672.7	11.3
	277.6	118.3	98.0	17.2	-	-	-	-
	370.9	241.7	219.7	9.1	370.9	565.5	498.5	11.8
10	338.7	221.0	195.2	11.7	338.7	724.1	580.0	19.9
IU mol% CH ₄	310.9	194.3	168.7	13.2	310.9	896.6	764.5	14.7
Injection	294.3	178.3	150.5	15.6	-	-	-	-
	277.6	177.6	130.5	26.5	-	-	-	-
	277.7	90.6	82.0	9.5	311.1	805.2	730.2	9.3
10 mol% nC7	311.0	107.4	107.2	0.2	338.8	495.0	544.4	10.0
Injection	338.8	121.8	126.0	3.5	371.1	444.5	465.2	4.6
	371.1	138.5	144.7	4.5	-	-	-	-

Table 4.11. Fluid-3: Relative Deviation (RD) between experimental data and calculated results for BP and UOP. Experimental data are from Punnapala & Vargas [20]. Model parameters ($\varepsilon^{AH} / R = 3977-58536/T K$, $\varepsilon^{AA} / R = 7000K$, P_c of HC =19.13 bar for MW of 750) are calculated from 0% GI case. Data for 10 mol% of N₂, CO₂, CH₄ and nC7 injections are the predictions after determination of ε^{AH} / R , ε^{AA} / R and P_c of HC using the 0 mol% gas injection case.

Table 4.12. Fluid-4: Relative Deviation (RD) between experimental data and calculated results for BP and UOP. Experimental data are from Punnapala & Vargas [20]. Model parameters (ε^{AH} / R = 3863-116110/T K & P_c of HC = 21.4 bar for ε^{AA} / R=7000K & MW of 750) are calculated from 0% CO₂ GI and 20% CO₂ GI cases. Data for 30 mol% CO₂ GI are the predictions after determination of ε^{AH} / R, ε^{AA} / Rand P_c of HC using 0% CO₂ GI & 20 mol% CO₂ GI cases.

	BP for () mol% GI		UOP for 20 mol% CO_2 GI				UOP for 30 mol% CO ₂ GI			
Т	Exp	Calc	RD	Т	Exp	Calc	RD	Т	Exp	Calc	RD
К	bar	bar	%	K	bar	bar	%	K	bar	bar	%
321.1	225.5	223.7	0.80	355.1	386.8	388.7	0.50	355.0	490.4	519.2	5.88
355.1	250.1	254.1	1.61	393.5	362.9	364.3	0.40	393.9	444.5	479.1	7.80
393.5	276.9	276.6	0.13	-	-	-	-	-	-	-	-

Table 4.13. Fluid-5: Relative Deviation (RD) between experimental data and calculated results for BP and UOP with respect to amount of GI at 373 K. Experimental data are from Punnapala & Vargas [20]. Model parameters ($\varepsilon^{AH} / R = 1540 \text{ K} \& P_c$ of HC =21.5 bar for $\varepsilon^{AA}/R = 3000 \text{ K} \& MW$ of 750) are calculated from HCs GI case. Data for HCs (90%) + N₂(10%), HCs (80%) + CO₂(20%), HCs (96.4%) + H₂S (3.6%), HCs (66%) + CO₂(22%) + N₂(11%), associated gas injections are the predictions after determination of ε^{AH}/R , ε^{AA}/R and P_c of HC using HCs gas injection case. Composition is in mole%.

		В	Р			UOP				
Type of Injected Gas	GI	Exp	Calc	RD	GI	Exp	Calc	RD		
	mol%	bar	bar	%	mol%	bar	bar	%		
	0.0	53.8	54.7	1.7	33.8	187.0	NA ^a	-		
	9.7	91.2	83.4	8.5	46.5	336.6	403.5	19.9		
HCs	29.8	156.6	155.1	1.0	-	-	-	-		
	49.9	264.2	252.3	4.5	-	-	-	-		
	59.9	339.0	312.5	7.8	-	-	-	-		
HCs (90%)	9.9	81.4	90.8	11.4	41.7	342.6	316.1	7.8		
$+ N_2(10\%)$	29.8	168.5	179.4	6.4	-	-	-	-		
HCs (80%)	9.8	75.5	81.5	7.9	40.1	256.2	219.4	14.4		
$+ CO_2(20\%)$	29.9	171.4	147.4	14.0	42.9	336.5	279.6	16.9		
HCs (96.4%)	9.8	82.5	82.5	-	33.8	192.9	NA^{a}	-		
$+ H_2 S (3.6\%)$	29.9	145.1	152.2	-	46.0	338.6	376.8	11.3		
HCs (66%)	30.0	182.4	176.8	-	34.0	193.1	191.4	0.9		
$+ CO_2(22\%) + N_2(11\%)$	-	-	-	-	44.0	341.1	347.2	1.8		
	-	-	-	-	34.1	193.3	NA^{a}	-		
associated gas	-	-	-	-	44.1	340.4	309.4	9.1		

^a Modeling results do not show UOP at these T and P conditions.

References

- 1 Negahban, S., Bahamaish, J. N. M., Joshi, N., Nighswander, J., & Jamaluddin, A. K. M. (2005). An experimental study at an Abu Dhabi reservoir of asphaltene precipitation caused by gas injection. SPE Production & Facilities, 20(02), 115-125.
- 2 Jamaluddin, A. K. M., Nighswander, J. N., Kohse, B. F., El Mahdi, A., Binbrek, M. A., & Hogg, P. F. (2000, January). Experimental and Theoretical Assessment of the Asphaltene Precipitation Characteristics of the Sahil Field Under a Proposed Miscible Gas Injection Scheme. In Abu Dhabi International Petroleum Exhibition and Conference. Society of Petroleum Engineers.
- 3 Sarma, H. K. (2003, January). Can we ignore asphaltene in a gas injection project for light-oils?. In SPE international improved oil recovery conference in Asia Pacific. Society of Petroleum Engineers.
- 4 Yonebayashi, H., Masuzawa, T., Dabbouk, C., & Urasaki, D. (2009, October). Ready for gas injection: Asphaltene risk evaluation by mathematical modeling of asphaltene precipitation envelope (APE) with integration of all laboratory deliverables. In SPE/EAGE Reservoir Characterization & Simulation Conference.
- 5 Nobakht, M., Moghadam, S., & Gu, Y. (2008). Mutual interactions between crude oil and CO 2 under different pressures. Fluid phase equilibria, 265(1), 94-103.
- 6 Nabipour, M., Escrochi, M., Ayatollahi, S., Boukadi, F., Wadhahi, M., Maamari, R., & Bemani, A. (2007). Laboratory investigation of thermally-assisted gas–oil gravity drainage for secondary and tertiary oil recovery in fractured models. Journal of Petroleum Science and Engineering, 55(1), 74-82.
- 7 Moritis, G. (2006). EOR/Heavy Oil Survey—Special Report" and "2006 Worldwide EOR Survey,". Oil & Gas Journal, 37-57.
- 8 Blunt, M., Fayers, F. J., & Orr, F. M. (1993). Carbon dioxide in enhanced oil recovery. Energy Conversion and Management, 34(9), 1197-1204.
- 9 Nagel, R. G., Hunter, B. E., Peggs, J. K., Fong, D. K., & Mazzocchi, E. (1990). Tertiary Application of a Hydrocarbon Miscible Flood: Rainbow Keg River" B" Pool. SPE Reservoir Engineering, 5(03), 301-308.
- 10 Srivastava, R. K., Huang, S. S., & Dong, M. (1999). Asphaltene deposition during CO2 flooding. SPE production & facilities, 14(04), 235-245.
- 11 Leontaritis, K. J., Amaefule, J. O., & Charles, R. E. (1994). A systematic approach for the prevention and treatment of formation damage caused by asphaltene deposition. SPE Production & Facilities, 9(03), 157-164.
- 12 Bank, G. C., Riestenberg, D. E., & Koperna, G. J. (2007, January). CO2-enhanced oil recovery potential of the appalachian Basin. In Eastern Regional Meeting. Society of Petroleum Engineers.
- 13 Alvarado, V., & Manrique, E. (2010). Enhanced oil recovery: an update review. Energies, 3(9), 1529-1575.
- 14 Yonebayashi, H., Takabayashi, K., Iizuka, R., & Tosic, S. (2014, October). How Acid Gas Affects Asphaltene Precipitation Behavior. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.
- 15 Wu, J., Prausnitz, J. M., & Firoozabadi, A. (2000). Molecular thermodynamics of asphaltene precipitation in reservoir fluids. AIChE journal, 46(1), 197-209.
- 16 Ting, D.P., Hirasaki, G. J., & Chapman, W. G. (2003). Modeling of asphaltene phase behavior with the SAFT equation of state. Petroleum Science and Technology, 21(3-4), 647-661.
- 17 Arya, A., von Solms, N., & Kontogeorgis, G. M. (2015). Determination of asphaltene onset conditions using the cubic plus association equation of state. Fluid Phase Equilibria, 400, 8-19.
- 18 Gonzalez, D. L., Vargas, F. M., Hirasaki, G. J., & Chapman, W. G. (2007). Modeling Study of CO2-Induced Asphaltene Precipitation[†]. Energy & Fuels, 22(2), 757-762.
- 19 Panuganti, S. R., Vargas, F. M., Gonzalez, D. L., Kurup, A. S., & Chapman, W. G. (2012). PC-SAFT characterization of crude oils and modeling of asphaltene phase behavior. Fuel, 93, 658-669.
- 20 Punnapala, S., & Vargas, F. M. (2013). Revisiting the PC-SAFT characterization procedure for an improved asphaltene precipitation prediction.Fuel, 108, 417-429.

- 21 AlHammadi, A. A., Vargas, F. M., & Chapman, W. G. (2015). Comparison of Cubic-Plus-Association and Perturbed-Chain Statistical Associating Fluid Theory Methods for Modeling Asphaltene Phase Behavior and Pressure–Volume–Temperature Properties. Energy & Fuels.
- 22 Zhang, X., Pedrosa, N., & Moorwood, T. (2012). Modeling asphaltene phase behavior: comparison of methods for flow assurance studies. Energy & Fuels, 26(5), 2611-2620.
- 23 Li, Z., & Firoozabadi, A. (2010). Cubic-plus-association equation of state for asphaltene precipitation in live oils. Energy & Fuels, 24(5), 2956-2963.
- 24 Vafaie-Sefti, M., & Mousavi-Dehghani, S. A. (2006). Application of association theory to the prediction of asphaltene deposition: Deposition due to natural depletion and miscible gas injection processes in petroleum reservoirs. fluid phase equilibria, 247(1), 182-189.
- 25 Yonebayashi, H., Takabayashi, K., Iizuka, R., & Tosic, S. (2014, October). How Acid Gas Affects Asphaltene Precipitation Behavior. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.
- 26 Li, Z., & Firoozabadi, A. (2010). Modeling asphaltene precipitation by n-alkanes from heavy oils and bitumens using cubic-plus-association equation of state. Energy & Fuels, 24(2), 1106-1113.
- 27 Panuganti, S. R., Tavakkoli, M., Vargas, F. M., Gonzalez, D. L., & Chapman, W. G. (2013). SAFT model for upstream asphaltene applications. Fluid Phase Equilibria, 359, 2-16.
- 28 Tavakkoli, M., Panuganti, S. R., Taghikhani, V., Pishvaie, M. R., & Chapman, W. G. (2014). Understanding the polydisperse behavior of asphaltenes during precipitation. Fuel, 117, 206-217.
- 29 G.M. Kontogeorgis, G.K. Folas, Thermodynamic models for industrial applications: from classical and advanced mixing rules to association theories. John Wiley & Sons (2009).
- 30 Sirota, E. B. (2005). Physical structure of asphaltenes. Energy & fuels, 19(4), 1290-1296.
- 31 Buch, L., Groenzin, H., Buenrostro-Gonzalez, E., Andersen, S. I., Lira-Galeana, C., & Mullins, O. C. (2003). Molecular size of asphaltene fractions obtained from residuum hydrotreatment*. Fuel, 82(9), 1075-1084.
- 32 Badre, S., Goncalves, C. C., Norinaga, K., Gustavson, G., & Mullins, O. C. (2006). Molecular size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils and bitumen. Fuel, 85(1), 1-11.
- 33 Marcano, F., Antonieta Ranaudo, M., Chirinos, J., Castillo, J., Daridon, J. L., & Carrier, H. (2013). Study of Asphaltenes Aggregation in Toluene/n-Heptane/CO2 Mixtures under High-Pressure Conditions. Energy & Fuels, 27(8), 4598-4603.
- 34 Wu, J., Prausnitz, J. M., & Firoozabadi, A. (1998). Molecular-thermodynamic framework for asphaltene-oil equilibria. AIChE journal, 44(5), 1188-1199.
- 35 Pedersen, K. S., Christensen, P. L., & Shaikh, J. A. (2014). Phase behavior of petroleum reservoir fluids. CRC Press.
- 36 Kesler, M. G., & Lee, B. I. (1976). Improve prediction of enthalpy of fractions. Hydrocarbon processing, 55(3), 153-158.
- 37 Gonzalez, D. L., Mahmoodaghdam, E., Lim, F. H., & Joshi, N. B. (2012, January). Effects of Gas Additions to Deepwater Gulf of Mexico Reservoir Oil: Experimental Investigation of Asphaltene Precipitation and Deposition. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.

Chapter 5. Modeling of Asphaltene Onset Condition using the CPA and PC-SAFT Equations of State

Entire content of this chapter is from our journal article "Alay Arya; Xiaodong Liang; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Onset Precipitation Conditions with Cubic Plus Association (CPA) and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) Equations of State. Energy Fuels. 2016, Vol. 30(8), pp.6835-6852".

Abstract

Asphaltene precipitation has been one of the major problems in the oil industry and its modeling is still believed to be a quite complex issue due to the different characteristics of thousands of heavy components in the crude oil. There have been several attempts to model asphaltene precipitation using various equations of state and empirical models. In the past few years, association models based on CPA and SAFT equations of state have been found to be promising models for studies of asphaltene precipitation. In this work, we compare asphaltene precipitation results obtained from different modeling approaches based on CPA, PC-SAFT with association (PC-SAFT (WA)) and PC-SAFT without association (PC-SAFT (WOA)) models. While the modeling approaches for the CPA and PC-SAFT (WOA) have been described before in various literatures, the modeling approach for PC-SAFT (WA) is proposed in this work. All three models require the same number of experimental data points (at least three upper onset pressures and one bubble pressure) in order to obtain model parameters. Different types of asphaltene phase behavior for different reservoir fluids, where asphaltene solubility either decreases or increases with temperature, asphaltene precipitation occurs during reservoir fluid depressurization and the effect of gas injection are studied in order to investigate thoroughly the potential and reliability of the models. A total of five reservoir fluids and one model oil are studied with all three models. It is found that the modeling approach with the CPA EoS is more reliable compared to the other two approaches used in this study. The advantage of the association term to describe interactions between asphaltene and other stock tank oil (STO) heavy components is also evident from this study. The sensitivity of SARA data to the modeling approach based on PC-SAFT (WOA) is also analyzed. Finally, the relationship between the binary interaction parameter of the asphaltene- CO_2 pair and cross-over temperature, below which asphaltene solubility increases in reservoir fluid, with CO_2 gas injection is also studied.

5.1 Introduction

Asphaltenes constitute the heaviest and most polar fraction of crude oil. Asphaltenes are not a welldefined components, rather they are solubility class, which can generally be defined as the fraction

of the oil which is insoluble in n-alkanes (typically n-pentane or n-heptane) [1-3], but soluble in aromatic compounds such as toluene and pyridine. Experimental results show that the amount of npentane insoluble asphaltenes is always greater than or equal to the n-heptane insoluble asphaltenes, which is always greater than or equal to the *n*-decane insoluble asphaltenes and so on [2]. A representative asphaltene molecule is believed to have polynuclear aromatic ring/s (PNA) connected with aliphatic chains. Asphaltene molecule also consists of heteroatoms (oxygen, sulfur, nitrogen, nickel and vanadium), which are believed to impart polarity [4]. At certain pressure, temperature and composition of oil, asphaltene precipitates out of oil and creates flow assurance problems by plugging the well bore and causing formation damage (plugging reduces the permeability of reservoir rock, through which oil flows to the oil wells). Enhanced oil recovery by gas injection is more susceptible to asphaltene precipitation due to composition change [5-7]. Experimental results show that injection of N_2/CO_2 / hydrocarbon gas aggravates the asphaltene precipitation [8]. Asphaltene phase behavior under reservoir conditions is generally represented by the Pressure-Temperature (PT) plot (Fig. 5.6a in Result section). There are two PT boundaries, the upper onset pressure (UOP) boundary, above which only one (liquid) phase exists, and the lower onset pressure (LOP) boundary, above which three phases (gas, asphaltene-lean liquid, and asphaltene-rich liquid) exist. Asphaltene precipitation occurs between these two boundaries. Maximum asphaltene precipitation occurs at bubble pressure (BP). Sometimes crude is also blended with hydrocarbon solvent to decrease the viscosity for ease of transportation. In addition, mixing of different crudes (at ambient pressure) at the inlet facility of refinery could also pose the threat of asphaltene precipitation and subsequent fouling of heat exchangers in crude oil refining operations [9].

There are generally two different hypotheses for interactions of asphaltene molecules with molecules of other components. In the first hypothesis, asphaltene molecules are solubilized in oil due to the interactions with other oil molecules. The Flory Huggins model [2] and equation of states based models [10-14] are some examples of the first hypothesis. In the second hypothesis, asphaltene molecules are peptized by the molecules of resins due to the polar forces between them and together they form colloids. Stability of these colloids in the oil depends upon temperature, pressure and composition of oil. Solid asphaltene colloidal model by Leontaritis & Mansoori [15], thermodynamic miscellization model by Pan et al [16] and McMillan-Mayer theory based model using HS-SAFT by Wu et al [17] are some examples of the second hypothesis. There are also different views on the mechanism of asphaltene precipitation. Ting [18] and Wiehe [19] mentioned that asphaltene precipitation is governed by non-polar van der Waal's forces and size of molecules to a large extent. Ting [18] also agreed upon that in some cases polar forces and hydrogen bonding also take part in the precipitation process of asphaltene. On the other hand, Arya et al [20] concluded from the analysis based on their modeling approach that asphaltene molecules are present as monomers in the oil and the association term helps to describe asphaltene precipitation. Arya et al [20] also concluded that the effect of gas injection is largely dependent upon the van der Waals forces and association contribution remains more or less the same with amount of injected gas. Similarly, Buenrostro-Gonzalez et al [4] also agreed upon that association energy is the main parameter in their model to describe asphaltene precipitation. Asphaltene molecular weight is also a topic of debate in literature.

Few researchers [21-25] maintain that asphaltene in the oil is present as monomers with single ring of polynuclear aromatics (PNA) with molecular weight of <1000 Da, while others [26-27] report that asphaltene consists of macromolecules with multiple rings of PNA with molecular weight of 1000-10000 Da. In this work, we use the first hypothesis and the models based on CPA and PC-SAFT equations of state.

One group of researchers have studied the asphaltene precipitation with different modeling approaches based on the CPA EoS [20,28-30], while other group of researchers have studied the asphaltene precipitation with different modeling approaches based on the SAFT versions (e.g. PC-SAFT) [4,13,17,31]. However, there is little work in the literature where these models are compared on equal terms. Zhang et al [29] compared the two modeling approaches, the first approach was selfproposed (their own approach) based on CPA and the second approach was from Gonzalez et al [32-34] based on PC-SAFT (WOA), with the experimental data. They concluded that the self-proposed (their own) approach based on the CPA is better than the PC-SAFT (WOA) based approach. Later, AlHammadi et al [35] compared the CPA approach from Zhang et al [29] and the PC-SAFT (WOA) approach from Panuganti et al [31], who modified the approach from Gonzalez et al [32-34], and concluded that both the CPA and PC-SAFT (WOA) are able to predict the gas injection effect but the PC-SAFT (WOA) based approach is more accurate than the CPA based approach. However, AlHammadi et al [35] have not shown the results for a number of fluids with different types of asphaltene phase behavior. On the other hand, Zhang et al [29] showed the results for a number of different fluids and also mentioned that it would be interesting to compare the results with SAFT based approach including association term. In these studies of Zhang et al [29] and AlHammadi et al [35] for comparing the CPA and PC-SAFT (WOA) based approaches, at most two experimental upper onset pressure (UOP) have been used to estimate the model parameters. It would also be interesting to compare the model results when we use more than two UOP data in order to calculate more optimized model parameters. Moreover, both studies resulted into contradicting conclusions and therefore in this work we try to clarify this contradiction. The difference between the CPA approach used in this work and the approach used by Zhang et al [29] can be found in Arya et al [12]. In this work, we also propose the asphaltene modeling approach based on PC-SAFT (WA) EoS, which, to the best of our knowledge, nobody has tried before.

In this work, we first describe the characterization of pseudo-components and the modeling approaches proposed by Arya et al [12,20] based on CPA, by Panuganti et al [31] based on PC-SAFT (WOA) and new approach proposed in this work based on PC-SAFT (WA). Then we study the five reservoir fluids and one model oil with all the three models. The fluids considered in this work have different asphaltene phase behaviors (PT boundaries) and different kinds of experimental data in order to check the reliability of the models. The effect of the association term on asphaltene phase behavior is analyzed from the results.

5.2 Modeling Approach with CPA & PC-SAFT (WA)

In this work we assume the same modeling approach as presented by Arya et al [12,20] as shown in Fig. 5.1. Arya et al [12,20] applied the modeling approach only to CPA EoS but in this work we also show how to use it for PC-SAFT (WA) EoS. Asphaltenes are considered as single self-associating compound. Since the modeling approach uses n-hexane plus (C_{6+}) fraction and stock tank oil (STO) contains negligible amount of lighter component than n-hexane, we can reasonably approximate STO as the C_{6+} fraction, which is further divided into the heavy component (HC) and asphaltene. This heavy component is cross associating with asphaltene. Asphaltene rich phase is modeled as a liquid phase [36]. The binary interaction parameters (k_{ij}) for the CPA model are shown in Table 5.1, which is same as reported by Arya et al [12,20], and kept constant for all fluids studied in this work. The k_{ij} s for the PC-SAFT (WA) model are taken from Panuganti et al [31] and are mentioned in Table 5.2. The k_{ii} s with HC are kept same as those with saturates in Panuganti et al [31]. The k_{ii} s with asphaltene are fixed after studying different fluids. In reality, asphaltene fraction is poly-dispersed in the medium of heavy component in the form of many sub-fractions as shown schematically in Fig. 5.2. We use asphaltene MW of 750 Da [22-23]. Each sub-fraction of asphaltene may have different self-association energy (ε^{AA}). Since heavy component is a lumped component, each asphaltene subfraction may encounter different cross-association energy (ε^{AH}) in the medium due to different local composition. In this modeling approach we assume that asphaltene sub-fraction having highest value of ε^{AA} precipitates first and is responsible for onset of precipitation. One can assume asphaltene subfractions as insoluble fractions in n-heptane, n-octane, and n-nonane and so on. Since, in this study, we are only concerned about onset conditions of asphaltene precipitation and to make the approach simple we assume that all sub-fractions of asphaltene have the same highest value of ε^{AA} . In addition, asphaltenes are treated as single component with the 4C scheme (molecule has two proton donor and two proton acceptor sites). Asphaltene parameters for CPA and PC-SAFT (WA) are different. Asphaltene critical parameters ($T_c(K) = 1040, P_c(bar) = 15.44, \omega = 1.535$) for CPA and PC-SAFT parameters (m = 15.25, $\sigma(\dot{A}) = 4.22$, ε/k (K) = 367) for PC-SAFT (WA) are fixed based on the assumption that the asphaltene solubility parameter varies from 19-23 MPa^{1/2} [2,37-39] at ambient condition. For CPA, asphaltene solubility parameters are 19.14 MPa^{1/2} ($\varepsilon^{AA} = 0$) and 21.51 MPa^{1/2} (ε^{AA} = 3000) at 298K and 1 atm. For PC-SAFT (WA), asphaltene solubility parameters are 20.23 MPa^{1/2} ($\varepsilon^{AA} = 0$) and 22.20 MPa^{1/2} ($\varepsilon^{AA} = 3000$) at 298K and 1 atm. These parameters are selected based on our experience. It is suspected that changing the asphaltene pure component parameters may also necessitate changing the k_{ii} values for asphaltene containing binaries, however, this is not studied yet. The default value of ε^{AA} is 3000K [40] but can be treated as an adjustable model parameter if sufficient experimental data are available. Local composition of the medium of heavy component varies with temperature, which also varies the location dependent ε^{AH} . We are interested in ε^{AH} , which is faced by the asphaltene sub-fraction of the highest value of ε^{AA} . Therefore, we assume that the entire heavy component medium has same ε^{AH} , which is temperature dependent. The cross-association volume (β^{AH}) and self-association volume (β^{AA}) have constant

values (0.05). From equations C.6 & C.30 (see supporting information), one can see that the value of association strength ($\Delta^{A_iB_j}$) is dependent upon two model parameters ($\varepsilon^{A_iB_j} \& \beta^{A_iB_j}$). Hence if we fix $\beta^{A_iB_j}$, we can calculate $\varepsilon^{A_iB_j}$ from the experimental data at a given temperature. However, the temperature extrapolation of $\Delta^{A_iB_j}$ will be different for different values of $\beta^{A_iB_j}$. For the heavy component, one cross-association site is selected, which can cross-associate with both positive and negative sites (total 4 sites) of asphaltene molecule. One can also assume that the HC has one crossassociation site, which can cross-associate only to positive or negative sites (total 2 sites) of asphaltene molecule. In both cases (total 4 vs 2 cross-association sites), values of the calculated model parameters (ε^{AH} , β^{AH} , ε^{AA}), from experimental data, will be different. The normal boiling point of HC is calculated from the Pedersen relationship [41]. Critical parameters (P_c, T_c) and acentric factor (ω) of HC are calculated from the Kesler–Lee relationship [42]. Critical pressure (P_c) and Peneloux volume correction factor of HC are then adjusted to match bubble point pressure and STO density of the oil for the CPA model. The PC-SAFT parameters for the HC are initially calculated from the MW correlations, which are shown in Table 5.3, with aromaticity (γ 1) value of 0.5, for the component consisting of saturates fraction and polynuclear aromatics (PNA) derivative fraction from Punnapala and Vargas [8]. Arya et al [20] showed that this modeling approach does not require SARA analysis since it does not depend upon asphaltene amount or asphaltene MW. In other words, for the fixed value of asphaltene ε^{AA} , increase in asphaltene amount increases ε^{AH} with heavy component at the onset temperature and pressure.



Fig. 5.1. Representation of the characterization procedure of STO/C_{6+} fraction into two pseudo-components (heavy component and asphaltene) for the CPA and PC-SAFT (WA) models.



Fig. 5.2. Graphical representation of the assumptions made for the modeling approach used in this work from Arya et al [12-20]. (a) Real condition, where asphaltene subfractions are scattered in the medium of heavy component in the heavy oil/STO. (b) All asphaltene subfractions are assumed of having same physical properties. (c) The cross-association energy (ε^{AH}) between asphaltene and heavy component is assumed to be the same everywhere but it is temperature dependent.

Component	N ₂	CO ₂	H_2S	НС	Asphaltene
N ₂	0.0	0.0	0.0	0.10	0.24
CO_2	-0.06	0.0	0.0	0.10	0.10
H_2S	0.678-0.0018T	0.0	0.0	0.05	0.0
methane	0.141-12.6448/T	0.0882	0.0760	0.0	0.01
ethane	0.04	0.1335	0.0847	0.0	0.01
propane	0.04	0.1522	0.0917	0.0	0.01
<i>i</i> -butane	0.05	0.1122	0.0761	0.0	0.011
<i>n</i> -butane	0.05	0.1122	0.0897	0.0	0.011
<i>i</i> -pentane	0.06	0.10	0.05	0.0	0.011
<i>n</i> -pentane	0.06	0.10	0.05	0.0	0.011
<i>n</i> -heptane ¹	0.0	0.10	0.0	0.0	0.011
Toluene ¹	0.0	0.10	0.0	0.0	0.0

Table 5.1. CPA binary interaction parameters (k_{ij}) from Arya et al [12,20]. T is temperature in K.

¹ \boldsymbol{k}_{ij} values are proposed in this work.

	()		1	(1) / 5	0			
Component	N ₂	CO ₂	H_2S	C1	C2	C3	<i>i</i> C5/ <i>n</i> C5 ¹	$nC7^1$
N ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.13
H_2S	0.09	0.0678	0.0	0.0	0.0	0.0	0.0	0.0
methane	0.03	0.05	0.062	0.0	0.0	0.0	0.0	0.0
ethane	0.04	0.097	0.058	0.0	0.0	0.0	0.0	0.0
propane	0.06	0.10	0.053	0.0	0.0	0.0	0.0	0.0
isobutane ¹	0.06	0.10	0.0	0.0	0.0	0.0	0.0	0.0
nbutane ¹	0.06	0.10	0.0	0.0	0.0	0.0	0.0	0.0
isopentane ¹	0.06	0.10	0.0	0.03	0.02	0.015	0.0	0.0
npentane ¹	0.06	0.10	0.0	0.03	0.02	0.015	0.0	0.0
HC^1	0.14	0.13	0.09	0.03	0.012	0.01	0.005	0.0
Asphaltene ¹	0.175	0.16	0.015	0.04	0.04	0.01	0.01	0.01
Toluene ¹		0.10	0.0	0.0	0.0	0.0	0.0	0.01

Table 5.2. PC-SAFT (WA) binary interaction parameters (k_{ii}) from Panuganti et al [31].

¹ $\boldsymbol{k_{ij}}$ values are proposed in this work.

Table 5.3. Empirical correlations for the initial estimation of the PC-SAFT (WA) model parameters for mixture of saturates and polynuclear aromatics (PNA) derivative components from Punnapala & Vargas [8].

$(\gamma 1)$ saturates correlation + $(1 - \gamma 1)$ PNA derivatives correlation	
$m = (1 - \gamma 1)[0.0257 \times MW + 0.8444] + \gamma 1[0.0101 \times MW + 1.7296]$	
$\sigma(\text{\AA}) = (1 - \gamma 1) \left[4.047 - \frac{4.8013 \times \ln(MW)}{MW} \right] + \gamma 1 \left[4.6169 - \frac{93.98}{MW} \right]$	
$\epsilon/k(K) = (1 - \gamma 1) \left[exp\left(5.5769 - \frac{9.523}{MW} \right) \right] + \gamma 1 \left[508 - \frac{234100}{(MW)^{1.5}} \right]$	

	, ,	2			ij v v	0			
Component	N ₂	CO ₂	H_2S	C1	C2	C3	Heavy gas	nC7 ²	Saturates
N ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.13	0.0
H_2S	0.09	0.0678	0.0	0.0	0.0	0.0	0.0	0.0	0.0
methane	0.03	0.05	0.062	0.0	0.0	0.0	0.0	0.0	0.0
ethane	0.04	0.097	0.058	0.0	0.0	0.0	0.0	0.0	0.0
propane	0.06	0.10	0.053	0.0	0.0	0.0	0.0	0.0	0.0
Heavy gas	0.075	0.12	0.07	0.03	0.02	0.015	0.0	0.0	0.0
Saturates	0.14	0.13	0.09	0.03	0.012	0.01	0.005	0.0	0.0
A+R	0.158	0.10	0.015	0.029	0.025	0.01	0.012	0.0	0.007
Asphaltene	0.16	0.191	0.015	0.07	0.06	0.01	0.01	0.01	-0.004
Toluene ²	0.0	0.10	0.0	0.0	0.0	0.0	0.0	0.01	0.0

Table 5.4. PC-SAFT (WOA) binary interaction parameters (k_{ii}) from Panuganti et al [31].

¹ k_{ij} for CO_2 -asphaltene pair is modified in this work to match the model results with experimental data. More information is provided into Result section. ² Proposed in this work considering Toluene and nC7 as (A+R) and Saturates respectively.

5.3 Modeling Approach with PC-SAFT (WOA)

In this work, the procedure suggested by Panuganti et al [31] is used to characterize the fluid for the PC-SAFT (WOA) model. Separator gas is modeled as a mixture of seven compounds (N_2 , CO_2 , H_2S , methane, ethane, propane and heavy gas (lumped C4+ components)) while STO (separator liquid) is characterized as a mixture of three compounds (saturates, aromatics+resins (A+R), asphaltene) as shown in the Fig. 5.3. They used the asphaltene MW of 1700 Da considering asphaltene molecules are pre-aggregated. Therefore, in this work, we use the asphaltene MW of 1700 Da for PC-SAFT (WOA) whereas 750 Da for CPA and PC-SAFT (WA). Detailed information about characterization can be found in Panuganti et al [31]. These authors [31] also mentioned that the MW of Cn+ saturates and Cn+ (A+R) pseudo-components are assumed such that the STO MW and Cn+ average MW are matched. However, this is not completely right since the STO MW is a function of STO composition, Cn+ average MW and MW of STO components lighter than Cn+. Fixing the Cn+ average MW by changing either the MW of saturates or MW of (A+R) fix the STO MW. Therefore, there can be multiple sets of Cn+ saturates and (A+R) MW, which can yield the same STO MW and Cn+ average MW. Hence, the characterization of STO may not comply with actual SARA fractions on molar basis. Panuganti et al [31] have not mentioned anything about how to use the approach when only reservoir fluid composition is available. We propose that when separator gas and STO compositions are not available but only reservoir oil composition is available, we can still use the same approach by assuming that C_{6+} fraction is 100% STO and lighter components (than C_{6+} fraction) are in the separator gas phase. This assumption is pragmatic since lighter components in the STO are always in small amount (around <10 mol %). Values of k_{ij} s used for the PC-SAFT (WOA) model are shown in Table 5.4.



Fig. 5.3. Characterization approach for separator gas and STO from Panuganti et al [31]. A=aromatics, R=resins.

Correlations for the PC-SAFT parameters of saturate components and mixture of polynuclear aromatics and benzene derivatives components are mentioned in Table 5.5. The value of aromaticity parameter (γ) defines the contribution from PNA (γ =1 means 100% PNA and γ =0 means 100% benzene derivative). Heavy gas and saturate components are defined by the correlation of saturates while (A+R) component is defined from the correlation of PNA+benzene derivatives.

Correlation for Saturates	(γ) PNA correlation + (1 – γ) benzene derivatives correlation
$m = 0.0257 \times MW + 0.8444$	$m = (1 - \gamma)[0.0223 \times MW + 0.751] + \gamma[0.0101 \times MW + 1.7296]$
$\sigma(\text{\AA}) = 4.047 - \frac{4.8013 \times \ln(MW)}{MW}$	$\sigma(\text{\AA}) = (1 - \gamma) \left[4.1377 - \frac{38.1483}{MW} \right] + \gamma \left[4.6169 - \frac{93.98}{MW} \right]$
$\ln(\epsilon/k)$ in $K = 5.5769 - \frac{9.523}{MW}$	(ϵ/k) in $K = (1 - \gamma)[0.00436 \times MW + 283.93] + \gamma \left[508 - \frac{234100}{(MW)^{1.5}} \right]$

Table 5.5. Empirical correlations for the estimation of the PC-SAFT (WOA) model parameters for saturates and mixture of Polynuclear Aromatics (PNA) and benzene derivative components from Panuganti et al [31].

5.4 Results and Discussion

In this work, a total of seven fluids are studied with the CPA, PC-SAFT (WA) and PC-SAFT (WOA) modeling approaches mentioned in previous sections. Among all fluids, fluid-3 is the model oil prepared by dissolving 0.04 wt% of asphaltene into the mixture of toluene (60 mol %) and n-heptane (40 mol %). Properties of all other fluids are shown in Table 5.6. Generally, three UOP points are used to calculate $\varepsilon^{AH}/R(K)$ and $\varepsilon^{AA}/R(K)$ for the CPA and PC-SAFT (WA) models unless mentioned otherwise. Only one bubble pressure point and STO density are used to calculate P_c and Peneloux volume correction of HC respectively for the CPA model. All available bubble pressure points and STO density are used to calculate the PC-SAFT parameters (m, σ, ϵ) of HC and aromaticity (y) of A+R component for the PC-SAFT (WA) and PC-SAFT (WOA) models respectively. All available UOP points are used to calculate the PC-SAFT parameters of asphaltene for the PC-SAFT (WOA) model. Results from all three models are compared with experimental data after calculating the model parameters from experimental data. Default values of $\beta^{AA} = 0.05$ and $\beta^{AH} = 0.05$ are used unless mentioned otherwise for both the CPA and PC-SAFT (WA) models. Values of calculated model parameters for the CPA and PC-SAFT (WA) models are presented in Table 5.7. Plot of calculated parameter ε^{AH}/R vs temperature is also shown for fluid-3, 5, and 6 in Fig. 5.7, 5.9, and 5.11 respectively. Composition of the reservoir fluids used for the CPA and PC-SAFT (WA) models are shown in Table 5.8. While composition of the reservoir fluids and model parameters used for the PC-SAFT (WOA) model are shown in Table 5.9. In addition, Supplementary Information is also provided, which shows a few more results. In all figures, shown in this section, UOP values are calculated only up to 900 bar since PC-SAFT (WOA) generally shows very high UOP with pure asphaltene phase and packing fraction above the packing fraction of face centered cubic structure, which is not a correct solution; more information regarding this issue can be found from Liang et al [43]. Relative deviations of all the models' results with respect to experimental data are given in Supplementary Information.

	Fluid-1	Fluid-2	Fluid-4	Fluid-5	Fluid-6
Saturates (wt%)	66.26	57.4	57.4*	63.3	53.75
Aromatics (wt%)	25.59	30.8	30.8*	24.9	28.50
Resins (wt%)	5.35	10.4	10.4^{*}	11.5	14.10
Asphaltenes (wt%)	2.8	1.4	1.4*	0.5	3.65
<i>C</i> ₆₊ MW	208.6	225.7	223.2	204.3	246.37
STO MW	193	229.2	-	-	243.30
STO SG	0.823	0.865	0.863	0.840	0.887
MW of reservoir fluid	97.75	102.0	102.6	81.7	116.1
GOR (m^3/m^3)	140	160	140	-	125

Table 5.6. Properties of fluids used in this work.

* SARA values are assumed, due to lack of data. Fluid-4 SARA data is assumed same as that of for Fluid-2 based on molar mass and SG of C_{6+} /STO.

 Table 5.7. Calculated values of the model parameters for the CPA and PC-SAFT (WA) for all fluids studied in this work.

 CDA

			CPA			PC-SA	.FI (W.	A)		
Fluid	ε^{AA}/R	$\varepsilon^{\rm AH}/R$		P_c of HC	ε^{AA}/R	$\varepsilon^{\rm AH}/R$			HC	
	(K)	(K)	$\beta^{ m AH}$	(bar)	(K)	(K)	β^{AH}	т	σ (Å)	$\epsilon/k(K)$
Fluid-1	3000	2088-92032/T	0.05	16.87	2400	1870-74929/T	0.05	6.16	3.92	252.0
Fluid-2	7000	5863-508383/T	0.005	18.92	7000	5290-420874/T	0.02	6.73	3.96	281.3
Fluid-3*	7000	4596-219166/T	0.006	-	7000	3895-129770/T	0.03	-	-	-
Fluid-4	7000	4155-177189/T	0.05	19.27	4200	3280-298690/T	0.05	6.33	3.86	260.8
Fluid-5	3700	1890-1864/T	0.05	20.11	3550	1953+19995/T	0.05	5.87	3.97	267.3
Fluid-6	3250	1738+15240/T	0.05	19.26	3350	2035+5347/T	0.05	6.86	3.88	270.3

* Fluid-3: Since fluid-3 is a model oil, toluene is treated as HC for CPA and PC-SAFT (WA).

Table 5.8. Composition of reservoir fluids used for the CPA and PC-SAFT (WA) model*.

	Fluid-1	Fluid-2	Fluid-4	Fluid-5	Fluid-6
Comp.	mol%	mol%	mol%	mol%	mol%
N ₂	0.163	0.496	0.390	0.088	0.315
H ₂ S	1.944	11.374	0.840	1.022	3.549
CO ₂	0.000	3.218	0.000	0.048	0.701
methane	33.600	27.350	36.630	42.420	32.555
ethane	7.673	9.445	8.630	10.800	8.423
propane	7.282	7.053	6.660	6.918	6.903
<i>i</i> -butane	1.885	0.948	1.210	0.957	1.094
<i>n</i> -butane	5.671	3.675	3.690	3.518	3.208
<i>i</i> -pentane	2.193	1.388	1.550	1.213	1.380
<i>n</i> -pentane	2.980	2.061	2.250	2.086	1.849
НС	36.302	32.831	37.991	30.888	39.542
Asphaltene	0.301	0.162	0.159	0.042	0.480

* C_{6+} mol % is the sum of mol % of HC and asphaltene.

-	Fluid-1	Fluid-1	Fluid-1	Fluid-2	Fluid-4	Fluid-5	Fluid-6
Comp.	SARA-1	SARA-2	SARA-3	10 /	10 /	10 /	10 /
	mol%						
N ₂	0.163	0.16	0.16	0.496	0.390	0.088	0.315
CO ₂	1.944	1.94	1.94	11.38	0.840	0.048	3.549
H ₂ S	0.000	0.00	0	3.219	0	1.022	0.701
methane	33.600	33.60	33.6	27.36	36.63	42.42	32.56
ethane	7.557	7.56	7.56	9.361	8.630	10.80	8.423
propane	6.742	6.74	6.74	6.470	6.660	6.918	6.729
Heavy Gas	8.198	8.21	8.21	6.116	8.700	7.774	7.168
Saturates	31.743	28.91	28.4	23.65	24.05	21.76	25.25
A+R	9.907	12.81	13.21	11.90	14.03	9.15	15.10
Asphaltenes	0.133	0.070	0.17	0.067	0.070	0.019	0.212
heavy Gas							
MW	65.5	65.56	65.57	67.1	58.12	58.12	67.3
m	2.53	2.53	2.53	2.57	2.34	2.34	2.58
σ (Å)	3.74	3.74	3.74	3.75	3.71	3.71	3.75
ϵ/k (K)	228.5	228.5	228.5	229.3	224.3	224.3	229.4
saturates							
MW	167.7	160.1	152.64	198.2	203.2	183.8	210.1
m	5.15	4.96	4.77	5.94	6.07	5.57	6.24
σ (Å)	3.90	3.89	3.89	3.92	3.92	3.91	3.92
$\epsilon/k(K)$	249.7	248.99	248.27	251.9	252.1	250.9	252.5
A+R							
MW	253.8	259.3	260.0	282.6	250	250.0	278.3
m	6.41	6.53	6.55	5.98	5.95	6.04	6.09
σ (Å)	3.99	3.99	3.99	4.13	4.03	4.02	4.10
ϵ/k (K)	285.0	285.06	285.06	360.7	314.8	307.9	347.2
Asphaltene							
MW	1700	1700	1700	1700	1700	1700	1700
m	40.2	50.14	41.93	28.00	33.21	33.21	35.82
σ (Å)	4.20	4.20	4.20	4.35	4.31	4.30	4.46
ϵ/k (K)	341.2	338.5	338.09	413.2	382.72	383.06	413.4

Table 5.9. Composition and PC-SAFT parameters of heavy gas, saturates, A+R and asphaltene required for the PC-SAFT (WOA) model.

<i>v</i> 1	·	
Components	Fluid-1	Fluid-4
N ₂	0.398	0.000
CO ₂	3.891	60.320
H ₂ S	0.000	0.000
methane	71.312	10.730
ethane	11.912	7.550
propane	7.224	9.090
<i>i</i> -butane	1.189	0.000
<i>n</i> -butane	2.254	6.470
<i>i</i> -pentane	0.567	0.030
<i>n</i> -pentane	0.616	5.820
C ₆₊	0.637	0.000

Table 5.10. Injected Gas Composition in mol% for Fluid-1 [8,31,35] and Fluid-4 [45].

<u>Fluid-1</u>

Fluid-1 has been studied by AlHammadi et al [35], who compared results of the PC-SAFT (WOA) and CPA models with respect to experimental data. They used the same modeling approach as Panuganti et al [31], which is also used in this work for the PC-SAFT (WOA). However, AlHammadi et al [35] used a different approach for the CPA than used in this work. Fig. 5.4 shows the comparison of the results from this work using the PC-SAFT (WOA), PC-SAFT (WA) and CPA with respect to experimental data. Experimental data for 5 mol% gas injection (i.e. 5 mol of gas added to 95 mol of fluid) scenario are used to calculate the model parameters (as explained in the previous section) and models correlation can be seen in panel (b) of Fig. 5.4. The composition of the injected gas is shown in Table 5.10. After calculating the model parameters, results for 0 mol%, 15 mol% and 30 mol% gas injection scenarios are predicted as shown in panels (a), (c) and (d) of Fig. 5.4. It can be observed that all three modeling approaches are able to correlate the UOP and BP data for 5 mol% gas injection in the experimental range. There are deviations between all three models outside the experimental temperature range. At lower temperature, deviations are more pronounced in UOP and BP results. The BP results from the PC-SAFT (WOA) and PC-SAFT (WA) are almost the same but different to the BP results from CPA. Predictions for 0 mol%, 15 mol% and 30 mol% scenarios by all three models are in agreement with experimental data but there are considerable deviations among the models' results for 30 mol% gas injection case. In other words, it can be concluded that as the composition changes from the reference composition (of correlated scenario, 5 mol% gas injection), predictions from three approaches differ largely from each other. It is believed that the difference between predictions can be due to interactions between asphaltene and other STO components, characterization of STO components and binary interaction parameters of different components with asphatlene. This fluid has also been studied by Punnapala and Vargas [8] with little modification of the modeling approach from Panuganti et al [31] for the PC-SAFT (WOA) and with different MW of asphaltene. Punnapala and Vargas [8] used a MW of 1474 Da while Panuganti et al [31] and AlHammadi et al [35] used a MW of 1700 Da for asphaltene. In other words, there are multiple sets of asphaltene parameters for different values of MW of asphaltene, which can correlate the experimental data. It should be noted that asphaltene PC-SAFT (WOA) parameters found in this work are also different to those used by AlHammadi et al [35]. As mentioned earlier, the CPA and PC-



SAFT (WA) modeling approaches are also independent of asphaltene MW and there could be multiple sets of asphaltene parameters, which would correlate experimental data.

Fig. 5.4. Fluid-1: Upper onset and bubble pressure boundaries for reservoir fluid without gas injection (Panel-a) and with gas injection of 5 mol% (Panel-b), 15 mol% (Panel-c), 30 mol% (Panel-d). Symbols represent experimental data from AlHammadi et al [35] and lines represent results from all the three models.

Models dependency upon amount of SARA fractions

Since SARA analysis may vary from lab to lab and can be significantly different depending on the method applied, it is important to study the models dependency upon amount of SARA fractions. Arya et al [20] have shown that the CPA approach used in this study is not dependent upon SARA fractions. The PC-SAFT (WA) approach is similar to the CPA approach and is also independent of SARA fractions. Panuganti el al [31] mentioned that their PC-SAFT (WOA) approach, which is used in this study, needs accurate value of SARA fractions. Therefore, Fluid-1 is studied with PC-SAFT (WOA) by changing the SARA analysis, in order to check the sensitivity of the model with respect to SARA fractions. Three different sets of SARA analysis are selected as shown in Table 5.11. Panel (b) of Fig. 5.5 shows that the PC-SAFT (WOA) model with all three sets of SARA fractions can correlate the experimental data of 5 mol% gas injection scenario. Panels (a), (c) and (d) of Fig. 5.5 show that the predictions of the model for all the three sets do not differ much. In other words, there are many sets of SARA fractions, which would predict the same results. Model parameters for SARA1, SARA2 and SARA3 sets are mentioned in in Table 5.9. Since all the models used in this work do not depend upon SARA analysis, assumed value of SARA fractions in Table 5.6 will not affect the results of onset conditions. It should be noted that amount of precipitated asphaltene is dependent upon the amount of asphaltene present in the oil.

Sat	Saturates	Aromatics	Resins	Asphaltenes				
501	(wt%)	(wt%)	(wt%)	(wt%)				
SARA1	66.26	25.59	5.35	2.8				
SARA2	57.4	30.8	10.4	1.4				
SARA3	53.75	28.50	14.10	3.65				

Table 5.11. Different sets of SARA analysis used to study Fluid-1.



Fig. 5.5. Fluid-1: Sensitivity of the model results with respect to three different sets of SARA analysis. Upper onset and bubble pressure boundaries for reservoir fluid without gas injection (Panel-a) and with gas injection of 5 mol% (Panel-b), 15 mol% (Panel-c), 30 mol% (Panel-d). Symbols represent experimental data from AlHammadi et al [35] and lines represent results from the PC-SAFT (WOA) model using three different sets of SARA analysis.

Fluid-2

Fluid-2 has been studied by Jamaluddin et al [14] and it is also used by other researchers [12,29,30,32] for asphaltene modeling study. Panel (a) of Fig. 5.6 shows that all the three models are able to correlate the UOP and BP experimental data. The models are also able to predict the LOP data. Panel (b) of Fig. 5.6 shows that predictions of UOP and BP for different amounts of N_2 injection at 419K are also in agreement with the experimental data. The PC-SAFT (WOA) model has larger deviations from the experimental data, shown in panel (b) of Fig. 5.6, compared to the CPA and PC-SAFT (WA) models since the correlation of UOP in panel (a) of Fig. 5.6 by the PC-SAFT (WOA) is not accurate compared to the other two models at around 419K. Panels (c) and (d) of Fig. 5.6 show the predictions of the effect of 10 and 20 mol% of CO_2 injection respectively. There are no experimental data available for CO2 injection for this fluid. There are only minor deviations between the CPA and PC-SAFT (WA) models as we increase the CO2 injection. However, the PC-SAFT (WOA) deviates more from the other two models, especially at higher temperatures, as we increase the CO_2 injection (due to the same reason of different correlation of UOP by the PC-SAFT model in panel (a) of Fig. 5.6). Gonzalez et al [34] have also studied fluid-2 with the PC-SAFT (WOA) and showed that there is a cross-over temperature with CO2 injection below which asphaltene solubility increases with amount of CO_2 injection. We have not seen this behavior since CO_2 -asphaltene binary interaction parameter used in this work is different for the PC-SAFT (WOA) model. If we use CO2-asphaltene binary interaction parameter of the value 0.11, which was used by Gonzalez et al [34], both models (PC-SAFT (WOA) and PC-SAFT (WA)) predict increase in asphaltene solubility with CO_2 injection at low temperatures (results are shown in Supplementary Information) or in other words there is a crossover temperature. However, unlike Gonzalez et al [34], we have not observed single cross-over temperature but the cross-over temperature (with respect to $0 \mod CO_2$ injection scenario) is different for different amount of CO_2 injection. We have fixed the CO_2 -asphaltene binary interaction parameters based on our experience by studying different fluids with CO2 injection. Fluid-3 and Fluid-4 represent the results with CO_2 injection in this article while one more fluid (Fluid-7) from Punnapala and Vargas [8] is also studied and the results are shown in Supplementary Information.



Fig. 5.6. Fluid-2: Upper/lower onset and bubble pressure boundaries for reservoir fluid without gas injection (Panel-a) and with CO_2 injection of 10 mol% (Panel-c), 20 mol% (Panel-d). (Plot-b) Effect of N_2 injection on upper/lower onset and bubble pressure boundaries at 419K. Symbols represent experimental data from Jamaluddin et al [14] and lines represent results from all the three models.

Fluid-3

Fluid-3 is a model oil prepared by dissolving 0.04 wt% of n-heptane insoluble asphaltene (from Furrial field in the Eastern Venezuelan Basin) into the solution of toluene (60 mol%) and n-heptane (40 mol%). Marcano et al [44] studied the asphaltene flocculation onset of solutions with 10, 15 and 20 wt% of CO_2 injection. Experimental results show the critical temperature of 353K where the asphaltene solubility in the solution is maximum. In this work, we calculated the model parameters for all the three models using the 20 wt% of CO_2 injection scenario and models correlations can be

seen in panel (c) of Fig. 5.7. Panel (c) of Fig. 5.7 also shows that the experimental UOP at 423K is not consistent with the trend predicted by any of the models. The three models are then used to predict 10 and 15 wt% of CO_2 injection scenarios. If we assume that experimental data are accurate, the models' prediction is poor especially at 10 wt% of CO_2 injection. More experimental data of this kind should be used to check the reliability of the three models. It should be noted that if we use the CO_2 -asphaltene binary interaction parameter reported by Panuganti et al [31], both PC-SAFT (WOA) and PC-SAFT (WA) predict the cross-over temperature, which contradicts the experimental data. Supplementary Information gives more details. Panel (d) of Fig. 5.7 shows that ε^{AH}/R increases with temperature for both the CPA and PC-SAFT (WA) models, however change in ε^{AH}/R is relatively small over the temperature range (from 250 K to 500K) for the PC-SAFT (WA).



Fig. 5.7. Fluid-3: Upper onset and bubble pressure boundaries with CO_2 injection of 10 wt% (Panel-a), 15 wt% (Panel-b) and 20 wt% (Panel-c). Symbols represent experimental data from Marcano et al [44] and lines represent results from all the three models. (Panel-d) Temperature dependency of ε^{AH}/R for CPA and PC-SAFT (WA) models.

<u>Fluid-4</u>

This fluid is from a Kuwait reservoir and it was studied by Memon et al [45] to check the feasibility of miscible gas injection. In this work, all model parameters are calculated from the experimental data shown in panel (a) and one UOP point (with 10 mol%) CO_2 rich gas injection shown in panel (b) of Fig. 5.8. After calculation of model parameters, results for different amount of CO_2 rich gas injections are predicted and compared with experimental data at 363K in panel (b) of Fig. 5.8. Panel (b) of Fig. 5.8 shows that all the three model are able to predict the gas injection effect on UOP and BP in agreement with experimental data. Panel (a) of Fig. 5.8 shows that the CPA correlations for BP are different to the PC-SAFT (WOA) and PC-SAFT (WA) correlations at low temperature. Please note that we have assumed SARA analysis for this fluid due to lack of experimental data. Fluid-4 SARA data is assumed same as that of for Fluid-2 based on molar mass and SG of C_{6+} /STO. The composition of the injected CO_2 rich gas is shown in Table 5.10.



Fig. 5.8. Fluid-4: Upper/lower onset and bubble pressure boundaries for reservoir fluid without gas injection (Panel-a). (Plot-b) Effect of CO_2 rich gas injection on upper/lower onset and bubble pressure boundaries at 363K. Symbols represent experimental data from Memon et al [45] and lines represent results from all the three models.

<u>Fluid-5</u>

Kabir & Jamaluddin [46] measured both asphaltene phase envelope and asphaltene amount in the reservoir oil during depressurization at 322K and 389K for fluid-5. Panel (a) of Fig. 5.9 shows the correlations for UOP and BP after calculating the model parameters for all the models from the respective experimental data. It can be seen from panel (a) of Fig. 5.9 that PC-SAFT (WOA) cannot correlate well the UOP data whereas the PC-SAFT (WA) and CPA are in good agreement with the experimental data. The LOP lines from the models are predictions. Interestingly, LOP predictions from the CPA are close to those from the PC-SAFT (WOA) but are different to those from the PC-SAFT (WA). Panels (b) and (c) of Fig. 5.9 show the prediction of relative amount of asphaltene in

oil phase (ratio of asphaltene wt% in oil phase at given pressure to asphaltene wt% in oil phase at UOP) at 322K and 389K respectively. Predictions from the CPA and PC-SAFT (WA) are in agreement with the experimental data at 322K. Since the PC-SAFT (WOA) cannot correlate the UOP data, predictions of relative amount of asphaltene in oil phase have considerable deviations from the experimental data. However, we also noticed that when the PC-SAFT (WOA) correlates the UOP at 322K (but unable to correlate the UOP data at other temperatures), it can also predict the relative amount of asphaltene in oil phase at 322K (results are not shown here). We believe that the experimental data at 389K are not sufficient to compare the models predictions shown in Fig. 5.9c. Since model parameters are calculated from correlating UOP & BP data and asphaltene mass is constant, models predictions in panels (b) and (c) of Fig. 5.9 can be seen in terms of the values of LOP and relative asphaltene amount at BP. In other words, UOP, BP and relative asphaltene amount at BP decide the positive slope whereas LOP, GOR at LOP, BP and relative asphaltene amount at BP decide the negative slope in panels (b) and (c) of Fig. 5.9 within APE. It should be noted that we have shown relative amount of asphaltene in oil phase but not absolute value of asphaltene amount. The reason for considering relative amount of asphaltene is that Asphaltene fraction may be different in the reservoir oil than that in STO. In addition, n-pentane and n-heptane insoluble asphaltene fractions are also different. For this reason, the models considered in this work cannot predict the absolute value of asphaltene amount during depressurization. However, the models can predict the relative amount of asphaltene, which is also independent of the amount of asphaltene in STO (models input parameter). Panel (d) of Fig. 5.9 shows that ε^{AH}/R increases with temperature for the CPA model while it decreases for the PC-SAFT (WA) model. The increase in ε^{AH}/R with temperature helps to increase the solubility of asphaltene in the fluid at higher temperatures while decrease in ε^{AH}/R with temperature helps to decrease the solubility of asphaltene. In other words, increase in ε^{AH}/R at fixed temperature decreases the UOP at that temperature. Fig. 5.10 shows that the CPA model predicts same values of relative amount of asphaltene when we consider 0.5, 5 and 15 wt% of asphaltene in STO. The model parameters (not shown here) are different for the three cases of different amounts of asphaltene in STO and are calculated from the same experimental data of UOP and BP shown in panel (a) of Fig. 5.9. It can be seen from Fig. 5.10 that all three cases predict the same results and therefore relative asphaltene amount in the oil phase is independent of asphaltene in STO (model input). Same behavior, like that of the CPA model in Fig. 5.10, is also observed by the PC-SAFT (WA) and PC-SAFT (WOA) but results are not shown here.



(c)

(d)

Fig. 5.9. Fluid-5: Asphaltene phase envelope (Panel-a) and relative amount of asphaltene in oil phase during depressurization at 322K (Panel-b) & 389K (Panel-c). Symbols represent experimental data from Kabir & Jamaluddin [46] and lines represent results from all the three models. (Panel-d) Temperature dependency of ε^{AH}/R for CPA and PC-SAFT (WA) models.



Fig. 5.10. Fluid-5: Relative amount of asphaltene in oil phase during depressurization at 322 K. Symbols represent experimental data from Kabir & Jamaluddin [46] and lines represent results from the CPA model for three different amounts (0.5/5/15 wt%) of asphaltene in STO.

<u>Fluid-6</u>

Fluid-6 is from the Maracaibo basin of western Venezuela. Gonzalez et al [47] studied this fluid with respect to asphaltene precipitation as part of a formation damage investigation. Panel (a) of Fig. 5.11 shows that fluid-6 has unusual asphaltene phase behavior, where asphaltenes are more soluble at lower temperature. Gonzalez et al [47] also modeled this fluid with CPA (but with a different modeling approach than ours) and concluded that the CPA model cannot predict asphaltene phase envelope for fluid-6. Panel (a) of Fig. 5.11 shows that the CPA and PC-SAFT (WA) can correlate both the UOP and BP data after calculating model parameters from the data while the PC-SAFT (WOA) is unable to correlate the UOP data but only the BP data. In addition, BP correlations by the CPA is quite different to those by the PC-SAFT (WA) and PC-SAFT (WOA). The PC-SAFT (WA) model also shows decrease in asphaltene solubility at low temperatures (around <300K), which contradicts the CPA and PC-SAFT (WA) models. Since ε^{AH}/R increases as temperature decreases, it helps to increase the asphaltene solubility as temperature drops. Note that asphaltene solubility depends upon the interactions between asphaltene-HC and asphaltene-asphaltene molecules.



Fig. 5.11. Fluid-6: Upper onset and bubble pressure boundaries for reservoir fluid without gas injection (Panel-a). Symbols represent experimental data from Gonzalez et al [47] and lines represent results from all the three models. (Panel-b) Temperature dependency of ε^{AH}/R for CPA and PC-SAFT (WA) models.

Relative Deviations between Modeling Results and Experimental Data

Table 5.12 shows average relative deviation in bubble pressure, upper onset pressure and lower onset pressure for all fluids studied in this work. It can be seen that the CPA based modeling approach has lower deviations in bubble pressure and upper onset pressure than other two models used in this study. The PC-SAFT (WA) based modeling approach has lower deviations in lower onset pressure, however, the CPA based modeling approach has lower deviations for one fluid out of two (for which experimental data are available). In general, it is analyzed that incorporating the association term in PC-SAFT significantly improves the results of upper onset pressure boundary. Supplementary Information shows the detailed results of deviation from experimental data of each figure.

		Avg. Relative Deviation		Avg. Relative Deviation in		Avg. Relative Deviation					
			in BP (%)		UOP (%)		in LOP (%)				
Fluid	Figure	Panel		PC-	PC-		PC-	DC SAFT		PC-	PC-
			CPA	SAFT	SAFT	CPA	SAFT	(WOA)	CPA	SAFT	SAFT
				(WA)	(WOA)		(WA)	(WOA)		(WA)	(WOA)
Fluid-1	Fig. 5.4	a,b,c,d	4.41	5.35	6.69	12.99	11.71	12.51	NA	NA	NA
Fluid-2	Fig. 5.6	А	1.21	2.28	1.86	2.05	2.54	21.35	11.47	13.45	13.37
Fluid-2	Fig. 5.6	В	1.71	2.72	4.03	6.72	5.90	12.60	NA	NA	NA
Fluid-3	Fig. 5.7	a,b,c	13.26	16.44	17.21	19.02	24.80	21.49	NA	NA	NA
Fluid-4	Fig. 5.8	А	2.54	4.00	3.44	6.60	6.62	5.64	NA	NA	NA
Fluid-4	Fig. 5.8	В	3.95	1.95	2.73	3.10	3.24	5.46	NA	NA	NA
Fluid-5	Fig. 5.9	А	1.62	4.72	4.06	2.05	2.54	21.35	22.39	15.03	29.60
Fluid-6	Fig. 5.11	А	1.00	9.50	8.16	0.90	1.24	14.59	NA	NA	NA
		Avg	3.71	5.87	6.02	6.68	7.32	14.37	16.93	14.24	21.48

Table 5.12. Average relative deviation in BP, UOP and LOP for all fluids.

5.5 Conclusions

Studying a total of seven fluids for which different kinds of experimental data were available, we can conclude that if any of the three models considered in this work can correlate the upper onset pressure and bubble pressure data, it can also predict the lower onset pressure, gas injection effect on upper onset pressure and relative asphaltene amount in the oil during depressurization compared with experimental data. It is shown that the PC-SAFT (without association) is unable to correlate the upper onset pressure boundary for fluid-5 and 6. On the other hand, the PC-SAFT (with association) and CPA can correlate the upper onset boundary for all fluids. This demonstrates that the asphaltene modeling approach with the PC-SAFT (without association) from Panuganti et al [31] has some limitations. It also raises the questions about whether only van der Waals interactions are responsible for asphaltene precipitation or association forces also contribute to asphaltene precipitation. If only van der Waals interaction are responsible then we need to modify the modeling approach for the PC-SAFT (without association) to characterize the stock tank oil components. It is shown that the modeling approach with the PC-SAFT (without association) does not depend upon the SARA analysis and there could be multiple sets of SARA which would give the same asphaltene phase envelope. Asphaltene phase envelopes obtained from all the three models are also different outside of experimental temperature range since the asphaltene phase envelope depends upon the parameters of the stock tank oil components (heavy component and asphaltene for CPA/PC-SAFT (WA); saturates, aromatics+resins, asphaltene for PC-SAFT (WOA); k_{ij} values for all models). It is also observed that as the composition changes from the composition of correlated case (e.g. correlated case is 0% gas injection and predicted case is 30% gas injection), asphaltene phase envelope from the three models deviate more from each other. It is shown that relative asphaltene amount is independent of asphaltene amount in the stock tank oil (as a model input) and can be used to study asphaltene precipitation during reservoir depressurization. We believe more studies related to reservoir depressurization are required to check the reliability of the concept of prediction of the relative asphaltene amount. It was shown that the CO_2 -asphaltene binary interaction parameter (k_{ij}) values used by Gonzalez et al [34] and Panuganti et al [31] predict the increase in asphaltene solubility at lower temperatures for fluid-2 and 3. The CO_2 -asphaltene binary interaction parameter (k_{ij}) value proposed in this work does not predict an increase in asphaltene solubility at lower temperatures for fluid-2 and 3. The experimental data for fluid-3 also confirms that there is no increase in asphaltene solubility with CO_2 injection at low temperatures. For all the fluids studied here, the CPA model accurately correlates bubble pressure data while PC-SAFT (with association) and PC-SAFT (without association) have minor deviations (e.g. Fluid-6). None of the models depends upon the molecular weight of asphaltene and SARA analysis. At least three upper onset pressures and one bubble pressure experimental point are required for all models studied in this work. Most important observation is that model results outside of experimental temperature range may not be reliable due to temperature dependency of the models.

5.6 Supplementary Information

Fluid-2

Fluid-2 is also studied with PC-SAFT (WA) and PC-SAFT (WOA) by changing CO_2 -asphaltene binary interaction parameter (k_{ij}) to the value of 0.11 reported by Gonzalez et al [34]. Fig. 5.12 shows the APE for reservoir fluid without gas injection and UOP boundaries for 10 & 20 mol% CO_2 injection. Both models show that asphaltene solubility increases at lower temperatures with amount of injected CO_2 .



Fig. 5.12. Asphaltene phase envelope using the PC-SAFT (WA) (Panel-a) and PC-SAFT (WOA) (Panel-b) for different amounts of CO_2 gas injection. Symbols represent experimental data from Jamaluddin et al [14] and lines represent results from the respective model. k_{ii} for CO_2 -asphaltene is 0.11.

Fluid-7

Fluid-7 was studied by Punnapala and Vargas [8] using the PC-SAFT (WOA) EoS by slightly modifying the approach from Panuganti et al [31] but keeping the same binary interaction parameters for all components. In this work, we use the same PC-SAFT (WOA) parameters used by Punnapala and Vargas [8] but CO_2 -asphaltene binary interaction parameter (k_{ij}) mentioned in this work is used. The model parameters are calculated from BP data for 0 mol% GI and UOP data for 20 mol% GI. Fig. 5.13 shows that the PC-SAFT (WOA) model is able to correlate the BP and then can predict the UOP for 30 mol% GI. Therefore, we can conclude that CO_2 - asphaltene binary interaction parameter (k_{ij}) used in this work are correct. We also checked the results using CO_2 - asphaltene binary interaction parameter (k_{ij}) equals to 0.10, reported by Panuganti et al [19], but could not reproduce the results shown by Punnapala and Vargas [8]. All information of fluid-7 can be found in Tables 5.13-5.14.

	Fluid-7 ^[8]
Saturates (wt%)	73.42
Aromatics (wt%)	19.32
Resins (wt%)	7.05
Asphaltenes (wt%)	0.17
C_{6+} MW	199.1
STO MW	212.9
STO SG	0.846
MW of reservoir fluid (MW)	75.4
GOR (m^3/m^3)	152

Table 5.13. Properties of Fluids used in Supplementary Information.

the PC-SAFT (WOA) model. Fluid-7^[8] Comp. mol% 0.1 N_2 H_2S 3.7 5.3 CO_2 methane 46.3 ethane 5.4 4.2 propane Heavy Gas 10.3 Saturates 18.0A+R 6.6 0.004 Asp

1	
Heavy Gas	
MW	74.7
m	2.76
σ (Å)	3.77
ϵ/k (K)	232.6
Saturates	
MW	193.2
m	5.84
σ (Å)	4.09
$\epsilon/k(K)$	345.7
A+R	
MW	264.6
m	5.84
σ (Å)	4.09
ϵ/k (K)	345.7
Asp	
MW	2183.9
m	45.09
σ (Å)	4.22
ϵ/k (K)	349.9

Table 5.14. Composition and PC-SAFT parameters of heavy gas, saturates, A+R and asphaltene required for


Fig. 5.13. Asphaltene phase envelope for reservoir fluid without gas injection (Panel-a) and with CO_2 injection of 20 mol% (Panel-b), 30 mol% (Panel-c). Symbols (triangle for UOP, circles for bubble points) represent experimental data from Punnapala & Vargas [8] and lines represent results from the PC-SAFT (WOA) model.

Fluid-3

Fluid-3 is studied with the PC-SAFT (WOA) by changing CO_2 - asphaltene binary interaction parameter (k_{ij}) to the value of 0.10 reported by Panuganti et al [31]. Fig. 5.14 shows that asphaltene solubility increases with amount of CO_2 injection, which contradicts the experimental data.



Fig. 5.14. Fluid-3: Upper onset and bubble pressure boundaries for different amounts of CO_2 injection. Symbols represent experimental data from Marcano et al [44] and lines represent results from the PC-SAFT (WOA) model using $m = 33.3, \sigma = 4.3 \text{ Å}, \in /k = 450.5 K$ of Asp. k_{ij} for CO_2 -asphaltene is 0.10.

References

- 1 J. G. Speight, Petroleum Asphaltenes-Part 1: Asphaltenes, resins and the structure of petroleum, Oil & gas science and technology 59-5 (2004) 467-477.
- 2 Hirschberg, A., DeJong, L. N. J., Schipper, B. A., & Meijer, J. G. (1984). Influence of temperature and pressure on asphaltene flocculation. Society of Petroleum Engineers Journal, 24(03), 283-293.
- 3 F. Vargas, M. Garcia-Bermudes, M. Boggara, S. Punnapala, M.I. Abutaqiya, N.T. Mathew, H.Y. Al Asafen, On the Development of an Enhanced Method to Predict Asphaltene Precipitation, In Offshore Technology Conference held in Houston, Texas, USA, May-(2014).
- 4 E. Buenrostro-Gonzalez, C. Lira-Galeana, A. Gil-Villegas, J. Wu, Asphaltene precipitation in crude oils: Theory and experiments, AIChE Journal 50-10 (2004) 2552-2570.
- 5 Nagel, R. G., Hunter, B. E., Peggs, J. K., Fong, D. K., & Mazzocchi, E. (1990). Tertiary Application of a Hydrocarbon Miscible Flood: Rainbow Keg River" B" Pool. SPE Reservoir Engineering, 5(03), 301-308.
- 6 Srivastava, R. K., Huang, S. S., & Dong, M. (1999). Asphaltene deposition during CO2 flooding. SPE production & facilities, 14(04), 235-245.
- 7 Leontaritis, K. J., Amaefule, J. O., & Charles, R. E. (1994). A systematic approach for the prevention and treatment of formation damage caused by asphaltene deposition. SPE Production & Facilities, 9(03), 157-164.
- 8 Punnapala, S., & Vargas, F. M. (2013). Revisiting the PC-SAFT characterization procedure for an improved asphaltene precipitation prediction. Fuel, 108, 417-429.
- 9 Tharanivasan, A. K., Svrcek, W. Y., Yarranton, H. W., Taylor, S. D., Merino-Garcia, D., & Rahimi, P. M. (2009). Measurement and modeling of asphaltene precipitation from crude oil blends. Energy & Fuels, 23(8), 3971-3980.
- 10 Burke, N. E., Hobbs, R. E., & Kashou, S. F. (1990). Measurement and Modeling of Asphaltene Precipitation (includes associated paper 23831). Journal of Petroleum Technology, 42(11), 1-440.
- 11 Akbarzadeh, K., Ayatollahi, S., Moshfeghian, M., Alboudwarej, H., & Yarranton, H. W. (2004). Estimation of SARA fraction properties with the SRK EOS. Journal of Canadian Petroleum Technology, 43(9), 31-39.
- 12 Arya, A., von Solms, N., & Kontogeorgis, G. M. (2015). Determination of asphaltene onset conditions using the cubic plus association equation of state. Fluid Phase Equilibria, 400, 8-19.
- 13 Ting, D.P., Hirasaki, G. J., & Chapman, W. G. (2003). Modeling of asphaltene phase behavior with the SAFT equation of state. Petroleum Science and Technology, 21(3-4), 647-661.
- 14 Jamaluddin, A. K. M., Joshi, N., Iwere, F., & Gurpinar, O. (2002, January). An investigation of asphaltene instability under nitrogen injection. In SPE International Petroleum Conference and Exhibition in Mexico. Society of Petroleum Engineers.
- 15 Leontaritis, K. J., & Mansoori, G. A. (1987, January). Asphaltene flocculation during oil production and processing: A thermodynamic collodial model. InSPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers.
- 16 Pan, H., & Firoozabadi, A. (1997, January). Thermodynamic micellization model for asphaltene precipitation from reservoir crudes at high pressures and temperatures. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.
- 17 Wu, J., Prausnitz, J. M., & Firoozabadi, A. (2000). Molecular thermodynamics of asphaltene precipitation in reservoir fluids. AIChE journal, 46(1), 197-209.
- 18 P.D. Ting, Thermodynamic Stability and Phase Behavior of Asphaltenes in Oil and of Other Highly Asymmetric Mixtures, PhD Thesis, Rice University May (2003).
- 19 Wiehe, I. A. (2012). Asphaltene solubility and fluid compatibility. Energy & Fuels, 26(7), 4004-4016.
- 20 Arya, A., von Solms, N., & Kontogeorgis, G. M. (2015). Investigation of the Gas Injection Effect on Asphaltene Onset Precipitation Using the Cubic-Plus-Association Equation of State. Energy & Fuels.
- 21 Buenrostro-Gonzalez, E., Groenzin, H., Lira-Galeana, C., & Mullins, O. C. (2001). The overriding chemical principles that define asphaltenes. Energy & fuels, 15(4), 972-978.
- 22 L. Buch, H. Groenzin, E. Buenrostro-Gonzalez, S.I. Andersen, C. Lira-Galeana, O.C. Mullins, Molecular size of asphaltene fractions obtained from residuum hydrotreatment, Fuel 82-9 (2003) 1075-1084.

- 23 S. Badre, C.C. Goncalves, K. Norinaga, G. Gustavson, O.C. Mullins, Molecular size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils and bitumen, Fuel 85-1 (2006) 1-11.
- 24 Mullins, O. C., Martínez-Haya, B., & Marshall, A. G. (2008). Contrasting perspective on asphaltene molecular weight. This comment vs the overview of AA Herod, KD Bartle, and R. Kandiyoti. Energy & Fuels, 22(3), 1765-1773.
- 25 Hortal, A. R., Hurtado, P., Martínez-Haya, B., & Mullins, O. C. (2007). Molecular-weight distributions of coal and petroleum asphaltenes from laser desorption/ionization experiments. Energy & Fuels, 21(5), 2863-2868.
- 26 Herod, A. A., Bartle, K. D., & Kandiyoti, R. (2007). Characterization of heavy hydrocarbons by chromatographic and mass spectrometric methods: An overview. Energy & Fuels, 21(4), 2176-2203.
- 27 Barrera, D. M., Ortiz, D. P., & Yarranton, H. W. (2013). Molecular weight and density distributions of asphaltenes from crude oils. Energy & Fuels, 27(5), 2474-2487.
- 28 B. Shirani, M. Nikazar, S.A Mousavi-Dehghani, Prediction of asphaltene phase behavior in live oil with CPA equation of state, Fuel 97 (2012) 89-96.
- 29 Zhang, X., Pedrosa, N., & Moorwood, T. (2012). Modeling asphaltene phase behavior: comparison of methods for flow assurance studies. Energy & Fuels,26(5), 2611-2620.
- 30 Li, Z., & Firoozabadi, A. (2010). Cubic-plus-association equation of state for asphaltene precipitation in live oils. Energy & Fuels, 24(5), 2956-2963.
- 31 Panuganti, S. R., Vargas, F. M., Gonzalez, D. L., Kurup, A. S., & Chapman, W. G. (2012). PC-SAFT characterization of crude oils and modeling of asphaltene phase behavior. Fuel, 93, 658-669.
- 32 Gonzalez, D. L., Ting, P. D., Hirasaki, G. J., & Chapman, W. G. (2005). Prediction of asphaltene instability under gas injection with the PC-SAFT equation of state. Energy & fuels, 19(4), 1230-1234.
- 33 Gonzalez, D. L., Hirasaki, G. J., Creek, J., & Chapman, W. G. (2007). Modeling of asphaltene precipitation due to changes in composition using the perturbed chain statistical associating fluid theory equation of state. Energy & fuels, 21(3), 1231-1242.
- 34 Gonzalez, D. L., Vargas, F. M., Hirasaki, G. J., & Chapman, W. G. (2007). Modeling Study of CO2-Induced Asphaltene Precipitation[†]. Energy & Fuels, 22(2), 757-762.
- 35 AlHammadi, A. A., Vargas, F. M., & Chapman, W. G. (2015). Comparison of Cubic-Plus-Association and Perturbed-Chain Statistical Associating Fluid Theory Methods for Modeling Asphaltene Phase Behavior and Pressure–Volume–Temperature Properties. Energy & Fuels.
- 36 Sirota, E. B. (2005). Physical structure of asphaltenes. Energy & fuels, 19(4), 1290-1296.
- 37 Sutherland, J. A Proposed Model of Asphaltene Solution Behavior. Diss. MS thesis, Imperial College, University of London, London, England, 1982.
- 38 Wang, J. X., & Buckley, J. S. (2001). A two-component solubility model of the onset of asphaltene flocculation in crude oils. Energy & Fuels, 15(5), 1004-1012.
- 39 Acevedo, S., Castro, A., Vásquez, E., Marcano, F., & Ranaudo, M. A. (2010). Investigation of physical chemistry properties of asphaltenes using solubility parameters of asphaltenes and their fractions A1 and A2. Energy & Fuels, 24(11), 5921-5933.
- 40 Wu, J., Prausnitz, J. M., & Firoozabadi, A. (1998). Molecular-thermodynamic framework for asphaltene-oil equilibria. AIChE journal, 44(5), 1188-1199.
- 41 Pedersen, K. S., Christensen, P. L., & Shaikh, J. A. (2014). Phase behavior of petroleum reservoir fluids. CRC Press.
- 42 Kesler, M. G., & Lee, B. I. (1976). Improve prediction of enthalpy of fractions. Hydrocarbon processing, 55(3), 153-158.
- 43 Liang, X., & Kontogeorgis, G. M. (2015). New Variant of the Universal Constants in the Perturbed Chain-Statistical Associating Fluid Theory Equation of State. Industrial & Engineering Chemistry Research, 54(4), 1373-1384.

- 44 Marcano, F., Antonieta Ranaudo, M., Chirinos, J., Castillo, J., Daridon, J. L., & Carrier, H. (2013). Study of Asphaltenes Aggregation in Toluene/n-Heptane/CO2 Mixtures under High-Pressure Conditions. Energy & Fuels, 27(8), 4598-4603.
- 45 Memon, A. I., Qassim, B., Al-ajmi, M. F., Tharanivasan, A. K., Gao, J., Ratulowski, J., ... & Khan, R. A. (2012, January). Miscible Gas Injection and Asphaltene Flow Assurance Fluid Characterization: A Laboratory Case Study for Black Oil Reservoir. In SPE EOR Conference at Oil and Gas West Asia. Society of Petroleum Engineers.
- 46 Kabir, C. S., & Jamaluddin, A. K. M. (2002). Asphaltene characterization and mitigation in south Kuwait's Marrat reservoir. SPE production & facilities,17(04), 251-258.
- 47 Gonzalez, D. L., Garcia, M. E., & Diaz, O. (2012, January). Unusual asphaltene phase behavior of fluids from Lake Maracaibo, Venezuela. InSPE Latin America and Caribbean Petroleum Engineering Conference. Society of Petroleum Engineers.
- 48 Gonzalez, D. L., Mahmoodaghdam, E., Lim, F. H., & Joshi, N. B. (2012, January). Effects of Gas Additions to Deepwater Gulf of Mexico Reservoir Oil: Experimental Investigation of Asphaltene Precipitation and Deposition. In SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers.

Chapter 6. Modeling of Asphaltene Onset Condition using the CPA, SRK, and SRK+HV Equations of State

Entire content of this chapter is from our journal article "Alay Arya; Xiaodong Liang; Nicolas von Solms; Georgios M. Kontogeorgis. Prediction of Gas Injection Effect on Asphaltene Precipitation Onset using the Cubic and Cubic-Plus-Association Equations of State. Submitted to Energy & Fuels".

Abstract

Gas injection is a proven enhanced oil recovery technique. The gas injection changes the reservoir oil composition, temperature and pressure conditions, which may result in asphaltene precipitation. In this work, we have used a modeling approach from the literature in order to predict asphaltene precipitation onset condition during gas injection. The modeling approach is used with the Soave-Redlich-Kwong (SRK), Soave-Redlich-Kwong-Plus-Huron-Vidal mixing rule (SRK+HV) and Cubic-Plus-Association (CPA) equations of state (EoS). Six different reservoir fluids are studied with respect to asphaltene onset precipitation during nitrogen, hydrocarbon gas mixture and carbon dioxide injection. It is also shown how to extend the modeling approach when the reservoir fluid is split into multiple pseudo-components. It is observed that the modeling approach using any of the three models can predict the gas injection effect on asphaltene onset conditions. The CPA EoS is more reliable than the other two models, which are sensitive to asphaltene molecular weight and sometimes predict highly non-linear behavior outside the experimental temperature range used for fitting the model parameters.

6.1 Introduction

Asphaltenes are the solubility fraction of oil, which are insoluble in *n*-heptane and soluble in aromatic solvents such as toluene [1-3]. They form the heaviest, highly polarizable and polydisperse fraction of oil. Their actual chemical structures are very difficult to identify due to their extremely low volatility, the complex and continuous variation in their chemical structures and self-aggregation [4]. Their mass fraction in oil at ambient conditions is generally measured using the Saturates-Aromatics-Resins-Asphaltenes (SARA) analysis. They may precipitate out of oil depending upon the oil temperature, pressure and composition. Thus, they generally create flow assurance problems in the oil industry by reducing the permeability of reservoirs, forming scale, and plugging the wellbore. The asphaltene flow assurance problem is analyzed by Pressure-Temperature (PT) plots as shown in Fig. 6.5. There are two PT boundaries, the upper onset pressure (UOP) boundary, above which only one (liquid) phase exists, and the lower onset pressure (LOP) boundary, above which three phases (gas,

asphaltene-lean liquid, and asphaltene-rich liquid) exist. Asphaltene precipitation occurs between these two boundaries. Maximum asphaltene precipitation occurs at bubble pressure.

Generally, gas is injected into the reservoir, after water flooding, in order to maintain its pressure and recover more oil. Miscible flooding with carbon dioxide (CO_2) or hydrocarbon (H/C) solvents is considered one of the most effective enhanced oil recovery processes applicable to light and medium oil reservoirs [5]. Miscible CO_2 displacement results in approximately 22% additional recovery, while immiscible displacement achieves approximately 10% additional recovery [6]. In addition, CO_2 has a considerably lower minimum miscibility pressure (MMP) compared to nitrogen (N_2) and methane [7,8]. The MMP is the minimum pressure at which around 95% of contacted oil is recovered for a given temperature. The MMP depends upon the reservoir temperature and oil composition [8,9]. With new technology in horizontal drilling and stimulation, the oil production from tight reservoirs is increasing. Although the initial production rates are high, the recovery factors are low (around 5-10%). Water flooding is not a feasible option for these tight reservoirs due to low permeability; however, gas injection may be a good alternative option based on recent analysis [10]. The asphaltene solubility in oil usually decreases with the amount of injected gas, which increases the upper onset pressure for a given temperature. Therefore, there is a need to develop a model to predict asphaltene onset conditions during gas injection.

There are different models in the literature to study asphaltene precipitation but only a few researchers have studied the effect of gas injection into reservoir fluid using cubic equations of state (EoS). EoS based compositional reservoir simulations use almost exclusively cubic EoS such as the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations [11]. A logical option is therefore to develop a modeling approach based on these EoS to predict the gas injection effect on asphaltene onset conditions. Jamaluddin et al [12] studied the SRK EoS to describe two reservoir fluids. They could correlate the asphaltene UOP boundary by tuning the model parameters and predict the lower onset pressure boundary. Pedersen et al [13] studied both SRK and PR EoS and could also correlate the UOP boundary and predict the lower onset pressure boundary. Panuganti et al [14] studied the SRK and Perturbed-Chain-Statistical-Associating-Fluid-Theory (PC-SAFT) EoS for one reservoir fluid and concluded that the SRK EoS was not able to predict the hydrocarbon gas injection effect on the UOP boundary with the same set of binary interaction parameters. They did not study the SRK EoS for CO₂ and N₂ injections. On the other hand, Hustad et al [15] also used SRK and PC-SAFT for one reservoir fluid and concluded that both models performed well in predicting the asphaltene UOP during N₂ injection at constant temperature. There was no discussion about how their model would work at different temperatures. Zhang et al [16] and Arya et al [17-19] studied the CPA EoS using different modeling approaches and concluded that the CPA EoS can predict the gas injection effect. Given the mixed results of these studies for modeling asphaltene precipitation during gas injection using cubic EoS, more investigations are needed.

In this work, we study the CPA, SRK and SRK+HV models with respect to asphaltene precipitation onset condition during gas injection. To the best of our knowledge, the SRK+HV model has never

been used before for such studies. We first describe the modeling approach and parameters used for all three models. Then we study six different reservoir fluids to check the reliability of the models for the prediction of the gas injection effect. We also study how to extend the modeling approach when the plus fraction (e.g. hexane plus fraction) needs to be split into multiple pseudo-components in order to predict PVT properties.

6.2 Modeling Approach

In this work we take the same modeling approach as presented by Arya et al [17-19] and shown in Fig. 6.1. The reservoir fluid is divided into defined components (shown in Table 6.5) and C_{6+} fraction. The C_{6+} fraction is further divided into heavy component (HC) and asphaltene. The heavy component can be also divided into multiple components: this approach is studied and discussed in the Results & Discussion section. Once the temperature dependent non-ideality between the heavy component and asphaltene pair is appropriately modeled, the gas injection effect can be predicted. The literature shows that the asphaltene solubility parameter varies from 19 to 23 $MPa^{1/2}$ depending upon the source [2,22]. The asphaltene component critical temperature, pressure and acentric factor are fixed based on its solubility parameter of 19 $MPa^{1/2}$ at 298 K and 1 atm. One can also choose the different value of asphaltene solubility parameter (for example $21 MPa^{1/2}$). It should be noted that the binary interaction parameters between gas/alkane-asphaltene pairs are dependent upon the asphaltene pure compound parameters; however this study is not presented here. The asphaltene rich phase is modeled as a liquid phase [23]. The normal boiling point of the heavy component is calculated from the Pedersen relationship [13]. The heavy component critical temperature (T_c) , pressure (P_c) and acentric factor (ω) are calculated from the Kesler-Lee correlation [24] using the information of molecular weight (MW) and specific gravity (SG) of stock tank oil (STO). The critical pressure (P_c) of the heavy component is then tuned with respect to experimental data of bubble point of the reservoir fluid. The binary interaction parameters for gas/alkane-heavy component (k_{12}) pairs are fixed and obtained from the literature [15,28] assuming the heavy component as a heavy n-alkane for which binary parameters are available with respective gas/n-alkane components. For the CPA and SRK models, gas/ alkaneasphaltene binary interaction parameters (k_{13}) are fitted in this study and kept constant for all reservoir fluids. For the SRK+HV model, Huron-Vidal parameters (G_{13}, G_{31}) are fitted in this work and kept constant for all reservoir fluids. It should be noted that for the SRK+HV model, the Huron-Vidal parameters (G_{12}, G_{21}) for gas/*n*-alkane-heavy component binaries are calculated from k_{12} to reduce the Huron-Vidal mixing rule to van der Waal's one fluid (classical) mixing rule for those binaries. If the heavy component is divided into multiple components, they each have the same values of k_{12} , k_{13} and Huron Vidal parameters (G_{12} , G_{21} , G_{13} and G_{31} for the SRK+HV model).



Fig. 6.1. Modeling approach used in this work for the CPA, SRK and SRK-HV equations of state.

The CPA EoS is described by Kontogeorgis and Folas [25]. For the CPA model, the asphaltene fraction is considered as a monodisperse and associating component. The self-associating energy (ε^{33}/R) and volume (β^{33}) between asphaltene molecules are fixed to 3000 K and 0.05 (dimensionless) respectively. The solubility parameter of asphaltene is 21.51 MPa^{1/2} at 298K and 1 atm when these association parameters are used. The heavy component is not self-associating but can cross-associate with the asphaltene component. The asphaltene molecule is treated as having two positive and two negative association sites (four sites in total). The heavy component molecule is treated as having one site, which can associate with all asphaltene molecule sites i.e. regardless of polarity. The cross-association energy (ε^{23}/R) between the heavy component and asphaltene molecules is temperature dependent, as shown in Fig. 6.1, and is fitted to experimental asphaltene precipitation onset data. The cross-association volume (β^{23}) is kept constant to a value of 0.05 (dimensionless). If the heavy component is divided into multiple components, these components will each have the same value of cross-association energy (ε^{23}/R) and volume (β^{23}) with asphaltene. The fitted value of (ε^{23}/R) in the case of a single heavy component will be different from that in the case of multiple heavy components.

The SRK EoS is described by Soave [26]. For the SRK model, the asphaltene fraction is treated as a monodisperse and non-associating component. The binary interaction parameter (k_{23}) for the heavy component-asphaltene pair is assumed to be temperature dependent, as shown in Fig. 6.1, and is fitted to experimental asphaltene precipitation onset data. If the heavy component is divided into multiple components, they each have the same value of k_{23} . The fitted value of k_{23} in case of a single heavy component will be different from that in the case of multiple heavy components.

The SRK+HV model is described by Huron and Vidal [27]. For the SRK+HV model, the asphaltene fraction is treated as a monodisperse and non-associating component. The Huron-Vidal mixing rule for energy parameter (*a*) is defined in equation-2.37to 2.40. The Huron Vidal parameters (G_{23}, G_{32})

of the heavy component-asphaltene pair are assumed to be temperature dependent, as shown in Fig. 6.1, and are fitted to experimental asphaltene precipitation onset data. If the heavy component is divided into multiple components, they each have the same value of G_{23} and G_{32} . The calculated values of G_{23} and G_{32} in case of a single heavy component will be different from those in the case of multiple heavy components.

The binary interaction parameters for the CPA and SRK models are shown in Tables 6.1 and 6.2 respectively. The binary interaction parameters and Huron Vidal Parameters for the SRK+HV model are shown in Table 6.3. For all models, the k_{ij} parameters for all binary pairs (except those with asphaltene) are obtained from the literature [15,28]. The pure component parameters for all models are listed in Table 6.9 in Supplementary Information section.

		-)		
Component	N ₂ ^b	CO ₂ ^b	H ₂ S ^b	Asphaltene ^c
N ₂	0	0	0	0.44
CO ₂	-0.0315	0	0	0.10
H ₂ S	0.1696	0.0989	0	0
methane	0.0278	0.12	0.08	0.10
ethane	0.0407	0.12	0.0852	0.10
propane	0.0763	0.12	0.0885	0.10
i-butane	0.0944	0.12	0.0511	0.10
n-butane	0.07	0.12	0.06	0.10
i-pentane	0.0867	0.12	0.06	0.10
n-pentane	0.0878	0.12	0.0685	0.10
heavy comp/s ^a	0.13	0.10	0.05	0

Table 6.1. CPA Model: binary interaction parameters (k_{ij}) .

^a Same binary parameters are used if we split C_{6+} fraction into multiple heavy components.

^b Values are referred from [15,28].

^c Values are fitted in this work.

Component	N ₂ ^b	CO ₂ ^b	H ₂ S ^b	Asphaltene ^c
N ₂	0	0	0	0.33
CO ₂	-0.0315	0	0	0.22
H ₂ S	0.1696	0.0989	0	0
methane	0.0278	0.12	0.08	0.165
ethane	0.0407	0.12	0.0852	0.165
propane	0.0763	0.12	0.0885	0.165
i-butane	0.0944	0.12	0.0511	0.165
n-butane	0.07	0.12	0.06	0.165
i-pentane	0.0867	0.12	0.06	0.165
n-pentane	0.0878	0.12	0.068	0.165
heavy comp/s ^a	0.13	0.10	0.05	MAP ^d

Table 6.2. SRK Model: binary interaction parameters (k_{ij}) .

^a Same binary parameters are used if we split C_{6+} fraction into multiple heavy components.

^b Values are referred from [15,28].

^c Values are fitted in this work.

^d Model Adjustable Parameter: calculated value shown in Table 6.6.

Table 6.3. SRK+HV Model:	binary	interaction ((k _{ij}) a	and Huron	Vidal	parameters.
--------------------------	--------	---------------	----------------------	-----------	-------	-------------

G	$N_2^{\ b}$	CO ₂ ^b	H_2S^b	S ^b Asphaltene Huron Vidal Parameters ^c										
Component		\mathbf{k}_{ij}		$G0_{ij}$	GO_{ji}	GT _{ij}	GT _{ji}	$\alpha_{ij}=\alpha_{ji}$						
N ₂	0	0	0	-545.50	530.50	0	0	0.2						
CO ₂	-0.0315	0	0	-722.20	464.80	0	0	0.2						
H ₂ S ^d	0.1696	0.0989	0	11082.74	-648.02	0	0	0						
methane	0.0278	0.12	0.08	344.59	-141.79	-0.5838	0.5963	0.2						
ethane	0.0407	0.12	0.0852	569.03	-56.47	-1.3984	0.7299	0.2						
propane	0.0763	0.12	0.0885	618.02	697.27	-1.6996	-0.3379	0.2						
i-butane	0.0944	0.12	0.0511	661.20	2077.35	-1.2871	-3.0500	0.2						
n-butane	0.07	0.12	0.06	661.20	2077.35	-1.2871	-3.0500	0.2						
i-pentane	0.0867	0.12	0.06	4585.06	-2949.16	-10.4904	12.0512	0.2						
n-pentane	0.0878	0.12	0.0685	4585.06	-2949.16	-10.4904	12.0512	0.2						
heavy comp/s ^a	0.13	0.10	0.05	MAP ^e	MAP ^e	0	0	0.2						

^a Same binary parameters are used if we split C₆₊ fraction into multiple heavy components.

^b Values are referred from [15,28]

^c Values are fitted in this work.

^d Huron-Vidal mixing rule is reduced to classical mixing rule for H₂S-ashaltene pair due to lack of experimental data.

^e Model Adjustable Parameter: calculated value shown in Table 6.6.

6.3 Results and Discussion

In this work, six different reservoir fluids are studied. Tables 6.4 and 6.5 show their fluid properties and compositions. The fluids are selected so that there are at least two fluids each with experimental data of hydrocarbon gas injection (Fluid-1, 2 and 6), N₂ injection (Fluid-2 and 4) and CO₂ injection (Fluid-2, 3 and 5) in order to check the reliability of the models in a wide range of conditions. As discussed in the previous section, each model has three adjustable parameters (see Fig. 6.1) for the heavy component-asphaltene pair to be fitted to experimental data of asphaltene onset condition at three different temperatures within the range of interest. When experimental data are available at only two temperatures, the third adjustable parameter is set to zero. The calculated parameters of each model are shown in Table 6.6. The binary parameters for gas (N_2,CO_2) -asphaltene and light alkanes (methane to n-pentane)-asphaltene pairs are optimized with respect to UOP data and assuming an asphaltene fraction of 0.1 mol% of the C_{6+} fraction for all fluids. One can also optimize the binary parameters and study the models considering different amount of asphaltene (for example 0.3 mol% in the C₆₊ fraction); however, the results are not shown in this work. The calculated parameters $(T_c,$ P_{C}, ω) of the heavy component, after tuning the critical pressure with respect to bubble pressure of reservoir fluid, are listed in Table 6.10 in Supplementary Information section. For all fluids, there are sufficient experimental data so that the model can be correlated with experimental data for a single gas injection amount, and then the model reliability can be evaluated by comparing the model predictions with experimental data for different amounts of gas injection. For example, as shown in Fig. 6.2, the model can be fitted to the 5 mol% gas injection scenario and then the model predictions can be validated against the 0, 15 and 30 mol% gas injection scenarios.

	Fluid-1	Fluid-2	Fluid-3	Fluid-4	Fluid-5	Fluid-6
Saturates (wt%)	66.26	39.2	a	57.4	b	73.42
Aromatics (wt%)	25.59	35.9	а	30.8	b	19.32
Resins (wt%)	5.35	9.0	а	10.4	b	7.05
Asphaltenes (wt%)	2.8	15.5	0.17	1.4	1.4 ^c	0.17
C ₆₊ MW (Da)	208.6	250.6	-	225.7	223.2	191.1
STO MW (Da)	193	289.9	212.9	229.2	-	182
STO SG (-)	0.823	0.919	0.846	0.865	0.863	0.817
MW of reservoir fluid (Da)	97.8	132.9	75.4	102.0	102.6	92.8
GOR (m^3/m^3)	140	160	-	160	140	152

Table 6.4. Properties of all fluids used in this work.

^a SARA values for fluid-3 are not mentioned since there is a mismatch between Tables 5 and A3 of reference [30]. ^b SARA values for fluid-5 are not available. ^c asphaltene amount is assumed.

Chapter 6. Modeling of Asphaltene Onset Condition using the CPA, SRK and SRK+HV EoS

	Fluid-1	Fluid-2	Fluid-3	Fluid-4	Fluid-5	Fluid-6
	[14]	[29]	[30]	[31]	[32]	[30]
Comp.	mol%	mol%	mol%	mol%	mol%	mol%
N ₂	0.163	0.340	0.090	0.496	0.390	0.147
CO ₂	1.944	0.160	3.679	11.374	0.840	1.711
H ₂ S	0.000	0.000	5.267	3.218	0.000	0.000
methane	33.600	32.900	45.840	27.350	36.630	32.508
ethane	7.674	8.150	5.350	9.445	8.630	7.966
propane	7.283	6.280	4.214	7.053	6.660	7.700
<i>i</i> -butane	1.886	0.000	5.163	0.948	1.210	1.930
<i>n</i> -butane	5.671	1.130	2.792	3.675	3.690	4.661
<i>i</i> -pentane	2.194	0.000	1.393	1.388	1.550	2.076
<i>n</i> -pentane	2.981	3.500	1.802	2.061	2.250	2.749
C ₆₊	36.604	47.540	24.410	32.993	38.150	38.553

Table 6.5. Composition of reservoir fluids used in this work for the evaluation of the CPA, SRK and SRK-HV models *.

* C_{6+} mol % is the sum of mol % of heavy component/s and asphaltene.

Table 6.6. Calculated values of the model parameters (see Fig. 6.1) for the CPA, SRK and SRK+HV for all fluids.

			Model A	djustable Param	eters (see Fig.	6.1) for heav	y compone	nt/s (2)-asphalt	ene(3) pair/s		
Fluid	Asp MW (Da)	ε^{23}/F	CPA = A + BT +	C/T (in K)	k ₂₃ =	$\frac{\text{SRK}}{A+BT+C}$	/T	$SRK+HV$ $g0_{23} = g0_{32} = A + BT + CT^{2}(in K)$			
		А	В	С	А	В	С	А	В	С	
	6165	3232	-2.0513	-233132	-0.7908	0.0015	102.63	0.0499	-27.90	7558	
Fluid-1	750	2674	-0.5998	-142291	-0.6408	0.0010	84.50	0.0204	-12.77	4847	
	10000	3341	-2.3771	-247603	-0.8488	0.0016	110.82	0.0799	-45.73	10475	
	38500	3606	-3.5623	-284768	-0.5081	0.0011	60.46	0.0001	-0.1063	31.97	
Fluid-2	750	3048	-1.3732	-181089	-0.3991	0.0007	46.97	0.0001	-0.0922	26.71	
	372	1770	0.1749	0	-0.2654	0.0008	0.00	8.3278	256.05	0.00	
Fluid-3	10000	2246	-2.1483	0	-0.3830	0.0014	0.00	NA ^b	NA ^b	NA ^b	
	3450	8097	-8.6298	-1210194	-1.1939	0.0020	189.23	0.1097	-72.79	16059	
Fluid-4	750	6680	-6.1582	-963365	-1.1186	0.0018	183.19	0.0434	-29.04	8082	
	10000	9599	-11.1237	-1469333	-1.2612	0.0022	196.13	NA ^b	NA ^b	NA ^b	
	3100	1475	0.6444	0	-0.1376	0.0005	0.00	4.1084	2461.10	0.00	
Fluid-5	750	1406	1.2351	0	-0.0921	0.0003	0.00	-0.2775	3267.62	0.00	
	10000	1538	0.1227	0	-0.1742	0.0007	0.00	NA ^b	NA ^b	NA ^b	
	330	2962	-1.7953	-195514	-0.7345	0.0014	94.77	0.0397	-20.95	6063	
Fluid-6	10000	5834	-7.3187	-644148	-1.0292	0.0022	131.70	NA^b	NA ^b	NA^b	
Fluid-1ª (9 HC)	6165	2861	-1.3244	-185970	-0.7524	0.0014	98.47	0.0416	-23.66	6853	

^a Fluid-1 C_{6+} is divided into nine heavy components and asphaltene. ^b SRK+HV model parameters could not be calculated for this case.

Components	Fluid-1	Fluid-5	Fluid-6
- F	[14]	[32]	[30]
N ₂	0.398	0.000	0.462
CO ₂	3.891	60.320	4.510
H ₂ S	0.000	0.000	0.000
methane	71.312	10.730	87.449
ethane	11.912	7.550	7.192
propane	7.224	9.090	0.370
isobutane	1.189	0.000	0.006
nbutane	2.254	6.470	0.005
isopentane	0.567	0.030	0.001
npentane	0.616	5.820	0.001
C ₆₊	0.637	0.000	0.003

Table 6.7. Injected gas composition in mol% for Fluids-1, 5 and 6.

Fig. 6.2 shows that all three models can correlate the 5 mol% gas injection scenario for Fluid-1 with 0.1 mol% of asphaltene in C_{6+} fraction. The composition of the injected hydrocarbon (H/C) gas is given in Table 6.7. Fig. 6.2 shows that there is considerable deviation for the 0 mol% H/C gas injection scenario while deviations for the 15 and 30 mol% scenarios are smaller. The CPA predictions are very different to those of the SRK and SRK+HV outside of the experimental temperature range used in the parameters fitting. The bubble pressure predictions are almost identical for all three models. Table 6.8 shows the relative deviation in UOP for fluid-1 for three different asphaltene molecular weights (750, 6165 and 10000 Da) at 347 K. The asphaltene molecular weight of 6165 Da corresponds to 0.1 mol% of asphaltene in C_{6+} fraction. Table 6.8 shows that the relative deviations for the CPA model are almost the same for all three cases of asphaltene molecular weights and therefore the CPA model is not very sensitive to the asphaltene molecular weight. The relative deviations for the SRK and SRK+HV models are different for all three cases of asphaltene molecular weights and therefore these models are sensitive to the asphaltene molecular weight in case of H/C gas injection. Panuganti et al [14] also studied Fluid-1 with the SRK EoS using the PVT-Sim software from Calsep [33] and concluded that the SRK EoS is unable to predict the gas injection effect correctly. They [14] characterized Fluid-1 and fitted the parameters to match the saturation pressures and asphaltene onset pressures for different temperatures with the 5 mol% gas injection scenario. Since our modeling approach with the SRK EoS can predict the gas injection effect correctly, we believe this shows that the modeling assumptions and model parameters are very important.



(c)

Fig. 6.2. Fluid-1: Upper onset and bubble pressure boundaries for reservoir fluid without gas injection (Fig. 6.2a) and with gas injection of 5 mol% (Fig. 6.2b), 15 mol% (Fig. 6.2c), 30 mol% (Fig. 6.2d). Symbols represent experimental data from Panuganti et al [14] and lines represent results from all the three models. Asphaltene amount in C_{6+} fraction is 0.1 mol%.

	Temp.	Gas Inj.	MW	Re	lative Deviation (%	(o) ^b
Fluid	K	mol%	Da	CPA	SRK	SRK+HV
		30	750	6	-16	-9
1	347	(H/C gas)	6165 ^a	6	-3	-1
			10000	6	2	7
			AAD^{c}	6	7	6
		10	750	14	13	8
		(N ₂)	38500 ^a	10	7	5
		10	750	9	-10	-36
2	311	(CO ₂)	38500 ^a	6	0	-3
		10	750	11	-6	-17
		(methane)	38500 ª	8	-6	-67
			AAD^{c}	10	7	22
		30	372 ^A	-4	-4	-6
3	355	(CO ₂)	10000	-3	17	NA^d
			AAD ^c	3	10	6
		20	750	2	-1	-27
4	419	(N_2)	3450 ª	0	0	1
		. 27	10000	-2	1	NAu
			AAD	1	1	14
		25	750	-4	-15	-28
5	2(2	$(CO_2 \text{ rich gas})$	3100 ª	-5	-1	-8
5	303	(002 8)	10000	-4	12	NA ^d
			AAD^{c}	4	9	18
		30	330 ^a	0	-8	-13
6	348	(H/C gas)	10000	1	19	$\mathbf{N}\mathbf{A}^{d}$
			AAD^{c}	0	13	6
1 (with 9 HC)	347	30 (H/C gas)	6165	7	-3	-1
			AAD^{c}	5	7	15

Table 6.8. Fluid-1: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amounts of gas injection and considering different asphaltene molecular weights.

^a Molecular weight corresponds to 0.1 mol% of asphaltene amount in C_{6+} fraction.

^b Relative Deviation (RD) = $\frac{UOP^{exp} - UOP^{calc}}{UOP^{exp}} \times 100$

^c Average Absolute Deviation (AAD) = $\sum_{i}^{N} |RD_i|$, where $|RD_i|$ is the absolute value of RD of point *i*, *N* is a total number points.

^d SRK+HV model parameters could not be calculated for this case.

Fluid-2 contains the most asphaltene of the fluids studied, 15.5 wt% in stock tank oil, making it possible to check the effect of asphaltene concentration on the models. Fig. 6.3 shows that all three models can correlate the experimental data of reservoir fluid without gas injection with 0.1 mol% of asphaltene in C_{6+} fraction. The models' predictions are very different at higher temperature beyond the experimental range used in the parameters' estimation. It can be observed that the SRK+HV model gives highly non-linear behavior at high temperatures outside of the experimental temperature range. Fig. 6.3 shows that all three models have minor deviations when 10 mol% of N_2 or CO_2 gas are added. The CPA and SRK models have minor deviations when 10 mol% of methane gas is added, whereas the SRK+HV has considerable deviations. Table 6.8 shows relative deviations in UOP prediction for fluid-2 using two different asphaltene molecular weights (750 and 38500 Da) at 311 K.

The asphaltene molecular weight of 38500 Da corresponds to 0.1 mol% of asphaltene in C_{6+} fraction. Like Fluid-1, the relative deviations for the CPA model are almost same for the two cases of asphaltene molecular weights. The relative deviations for the SRK model are not very sensitive to asphaltene molecular weight when 10 mol% N_2 or methane is added but they are relatively sensitive when 10 mol% CO_2 is added. Similarly, the relative deviations for the SRK+HV model are not very sensitive to asphaltene molecular weight when 10 mol% N_2 is added but they are relatively sensitive when 10 mol% CO_2 or methane is added. These results show that the difference between relative deviations, for the SRK or SRK+HV, would increase with the amount of injected gas for different asphaltene molecular weights.



Fig. 6.3. Fluid-2: Upper onset and bubble pressure boundaries for reservoir fluid without gas injection (Fig. 6.3a) and with gas injection of 10 mol% methane (Fig. 6.3b), 10 mol% CO_2 (Fig. 6.3c) and 10 mol% N_2 (Fig. 6.3d). Symbols represent experimental data from Gonzalez et al [29] and lines represent results from all the three models. Asphaltene amount in C_{6+} fraction is 0.1 mol%.

Fig. 6.4 shows that all three models can correlate the experimental data of Fluid-3 with 20 mol% CO_2 gas injection but the correlations are very different at temperatures beyond the experimental range used in the parameters' estimation. It can be observed that the SRK model gives highly non-linear behavior at temperatures (around 250-260 K) beyond the experimental range. Fig. 6.4 shows that all three models have minor deviations when 30 mol% of CO_2 gas is added. Table 6.8 shows the relative deviations in UOP predictions for fluid-3 using two different asphaltene molecular weights (372 and 10000 Da) at 355 K. The asphaltene molecular weight of 372 Da corresponds to 0.1 mol% of asphaltene in C_{6+} fraction. Like the previously mentioned fluids, the relative deviations for the CPA model are almost the same for the two cases of asphaltene molecular weights. The relative deviation for the SRK model is very sensitive to asphaltene molecular weight. The SRK+HV model could not correlate the data when an asphaltene molecular weight of 10000 Da was used. The critical pressure of the heavy component was tuned to the bubble point pressure of Fluid-3 without gas injection.



Fig. 6.4. Fluid-3: Upper onset and bubble pressure for the reservoir fluid with CO_2 injection of 20 mol% (Fig. 6.4a) and 30 mol% (Fig. 6.4b). Symbols represent experimental data from Punnapala et al [30] and lines represent results from all three models. Asphaltene amount in C_{6+} fraction is 0.1 mol%.

Fig. 6.5 shows that all three models can correlate the experimental data of Fluid-4 when there is no gas injection but the correlations are very different at temperatures (around 420-500 K) above the experimental range used in the parameters' estimation. The lower onset pressure results are predictions. For the SRK and SRK+HV models, lower onset pressure predictions are not shown at higher temperature (around 425-500 K) since these models predict asphaltene precipitation at ambient pressure, possibly due to incorrect convergence. The same behavior was also observed for Fluid-1

(with SRK+HV), Fluids-2 and 5 (with SRK and SRK+HV) but is not shown here. Fig. 6.5 shows that all three models have minor deviations when N_2 gas is added at 419 K. Table 6.8 shows relative deviations in UOP prediction for Fluid-4 for three different asphaltene molecular weights (750, 3450 and 10000 Da) at 419 K. The asphaltene molecular weight of 3450 Da corresponds to 0.1 mol% of asphaltene in C_{6+} fraction. The relative deviations for the CPA and SRK models are almost the same for all three cases of asphaltene molecular weights. The relative deviation for the SRK+HV is relatively sensitive to the asphaltene molecular weight. The SRK+HV model could not correlate the data when an asphaltene molecular weight of 10000 Da was used.



Fig. 6.5. Fluid-4: Upper onset, lower onset and bubble pressure boundaries for reservoir fluid without gas injection (Fig. 6.5a). (Fig. 6.5b) Effect of N_2 injection on upper onset, lower onset and bubble pressure boundaries at 419K. Symbols represent experimental data from Jamaluddin et al [31] and lines represent results from all the three models. Asphaltene amount in C_{6+} fraction is 0.1 mol%.

Fig. 6.6 shows that all three models can correlate the experimental data of Fluid-5 when there is no gas injection and 10 mol% CO_2 rich gas injection. It shows that all three models have minor deviations when 15 and 25 mol% CO_2 rich gas is added at 363 K. The composition of injected gas is given in Table 6.7. Table 6.8 shows the relative deviation in UOP for Fluid-5 using three different asphaltene molecular weights (750, 3100 and 10000 Da) at 363 K. The asphaltene molecular weight of 3100 Da corresponds to 0.1 mol% of asphaltene in C_{6+} fraction. Similarly to other previously mentioned fluids, the relative deviations for the CPA model are almost the same for the three cases of asphaltene molecular weights. The relative deviations for the SRK and SRK+HV models are very sensitive to the asphaltene molecular weight. The SRK+HV model could not correlate the data when the asphaltene molecular weight of 10000 Da was used.



Fig. 6.6. Fluid-5: Upper onset and bubble pressure boundaries for reservoir fluid without gas injection (Fig. 6.6a). (Fig. 6.6b) Effect of CO_2 rich gas injection on upper onset, lower onset and bubble pressure boundaries at 363K. Symbols represent experimental data from Memon et al [32] and lines represent results from all the three models. Asphaltene amount in C_{6+} fraction is 0.1 mol%.

Fig. 6.7 shows that all three models can correlate the experimental data of Fluid-6 when 10 mol% H/C gas is injected. It shows that all three models have minor deviations when 15 and 30 mol% H/C gas are added. The composition of injected H/C gas is mentioned in Table 6.7. Table 6.8 shows the relative deviation in UOP for fluid-6 using two different asphaltene molecular weights (330 and 10000 Da) at 348 K. The asphaltene molecular weight of 330 Da corresponds to 0.1 mol% of asphaltene in C₆₊ fraction. Similarly to other previously mentioned fluids, the relative deviations for the CPA model are almost the same for the two cases of asphaltene molecular weights. The relative deviation for the SRK model is once again very sensitive to the asphaltene molecular weight. The SRK+HV model could not correlate the data when the asphaltene molecular weight of 10000 Da was used, which was the case for several of the previously studied fluids.



(c)

Fig. 6.7. Fluid-6: Upper onset and bubble pressure boundaries for reservoir fluid with gas injection of 10 mol% (Fig. 6.7a), 15 mol% (Fig. 6.7b) and 30 mol% (Fig. 6.7c). Symbols represent experimental data from Punnapala et al [30] and lines represent results from all the three models. Asphaltene amount in C_{6+} fraction is 0.1 mol%.

Fluid-1 with splitting of C₆₊ fraction into Nine Heavy Components and Asphaltene

Generally reservoir fluids are modeled by dividing them into a few pseudo-components, in addition to defined components, in order to accurately predict PVT (Pressure-Volume-Temperature) properties. The modeling approach described above divides the C₆₊ fraction into two components (heavy component and asphaltene), but here we demonstrate how to extend the modeling approach by dividing the C₆₊ fraction into multiple heavy components and a single asphaltene component. In this study the, C₆₊ fraction of Fluid-1 is divided into nine heavy components and asphaltene. The exponential molar distribution is assumed to divide the C_{6+} fraction into 80 components which then are lumped into nine heavy components having approximately equal mass fractions. An asphaltene molecular weight of 6165 Da, corresponding to 0.1 mol% of asphaltene in C_{6+} fraction, is selected. The critical pressures of all heavy components are multiplied by the same factor in order to match the experimental bubble pressure of Fluid-1. The binary parameters of the nine heavy components with the asphaltene are assumed to be equal and the values are shown in Table 6.6. Figs 6.2 and 6.8 show the upper onset and bubble pressure profiles when one and nine heavy components respectively are considered. These figures show that all three models have the same upper onset and bubble pressure profiles. Table 6.8 shows the relative deviations in the UOP when one and nine heavy components are considered. The relative deviations for all three models are the same in both cases. In other words, all three models are insensitive to the number of heavy components.



Fig. 6.8. Fluid-1 (with 9 HC): Upper onset and bubble pressure boundaries for reservoir fluid with gas injection of 15 mol% (Fig. 6.8a) and 30 mol% (Fig. 6.8b). Symbols represent experimental data from Panuganti et al [14] and lines represent results from all the three models. Asphaltene amount in C_{6+} fraction is 0.1 mol%.

6.4 Conclusions

It has been shown in this work that the CPA, SRK and SRK+HV models can successfully predict the gas (CO₂, N₂, hydrocarbon) injection effect after fitting the model parameters to experimental data of a single gas injection scenario. The temperature dependent cross association energy, the binary interaction parameters (k_{ij}) , and the Huron-Vidal parameters between the heavy component and the asphaltene are used as model parameters for the CPA, SRK and SRK+HV models respectively. However, the three models give very different predictions outside of the experimental temperature range used in parameters estimation. The CPA model is relatively insensitive to the molar amount of asphaltene in C₆₊ fraction, whereas the SRK and SRK+HV models are sensitive to the molar amount of asphaltene in C₆₊ fraction, although the sensitivity is lower for N₂ compared to CO₂ and hydrocarbon gas injection. Therefore, in order to use the SRK and SRK+HV models, the molar amount of asphaltene needs to be fixed at the same value at which the binary parameters for gasasphaltene and light alkanes-asphaltene pairs are regressed. In this work, we assumed the asphaltene molar amount is 0.1 mol% in the C₆₊ fraction. It would be interesting to do the comparison at different asphaltene molar amounts (e.g. 1 mol%). The SRK and SRK+HV models abruptly change the lower onset pressure trend and predict the asphaltene precipitation at ambient pressure (possibly due to incorrect convergence) for certain fluids. This abrupt change can be avoided by changing the asphaltene molar amount (generally by increasing it), requiring regression of a new set of binary parameters. Generally, the SRK+HV model used in this work cannot correlate the data for the upper onset pressures for certain fluids when the asphaltene molar amount used corresponds to an asphaltene molecular weight of 10000 Da. Thus the SRK+HV model has no apparent advantages over the SRK model. In contrast to the SRK and SRK+HV models, the CPA model has not encountered any problems, and appears to be more reliable. It has also been shown that a modeling approach can be used in which the C₆₊ fraction is divided into multiple heavy components and a single asphaltene component. With this approach, the results from all three model are insensitive to the number of heavy components. Therefore, the modeling approach using the CPA EoS can easily be implemented into PVT simulations for reservoir fluids, since it can adequately model such systems using only a few components.

6.5 Supplementary Information

Table 6.9 shows the pure component parameters used in this work for all three models. Table 6.10shows the calculated properties and mol% of heavy component/s for all fluids studied in this work. All calculated properties of the heavy component are the same for all three models when only one heavy component is considered as shown in Table 6.10. Tables 6.11 to 6.17 show the relative deviations in upper onset pressure at experimental temperatures considering different molecular weights.

	1	5	,		1 5		
	Т	р		Mathias	-Copeman Par	ameters	
Component	IC	Г _С	ω	c_1	<i>C</i> ₂	<i>C</i> ₃	Reference
	Κ	bar	-	-	-	-	
N ₂	126.2	34.00	0.0377	0.5867	-0.4459	0.8926	[34]
CO_2	304.2	73.83	0.2236	0.8679	-0.7135	2.6563	[34]
H_2S	373.5	89.63	0.0942	0.6267	0	0	[34]
methane	190.6	45.99	0.0115	0.5857	-0.7206	1.2899	[34]
ethane	305.3	48.72	0.0995	0.7178	-0.7644	1.6396	[34]
propane	369.8	42.48	0.1523	0.7863	-0.7459	1.8454	[34]
<i>i</i> -butane	408.1	36.48	0.1808	0.8284	-0.8285	2.3201	[34]
<i>n</i> -butane	425.2	37.96	0.2002	0.8787	-0.9399	2.2666	[34]
<i>i</i> -pentane	460.4	33.81	0.2275	0.8290	0	0	[34]
<i>n</i> -pentane	469.7	33.70	0.2515	0.8647	0	0	[34]
Heavy Comp	Table 6.10	Table 6.10	Table 6.10	Table 6.10	0	0	Table 6.10
asphaltene ^A	1040.1	15.44	1.535	2.4814	0	0	[17-19]

Table 6.9. Pure Component Parameters used for the CPA, SRK and SRK-HV equations of state.

^A For the CPA model, asphaltene reduced self-association energy and volume are 3000K and 0.05 respectively.

HC Asp Fluid T_C P_C Asp MW Component ω Composition Composition K Da mol% mol% bar Fluid-1 6165 HC-1 735.6 0.7407 14.33 36.567 0.037 38500 Fluid-2 HC-1 47.492 0.048 775.2 0.6428 18.28 Fluid-3 372 HC-1 24.386 0.025 753.0 0.7491 17.34 Fluid-4 3450 HC-1 32.960 775.9 0.7914 16.25 0.033 Fluid-5 3100 HC-1 16.22 38.112 0.038 760.1 0.7331 Fluid-6 330 HC-1 0.039 726.2 0.7181 16.55 38.514 22.31 HC-1 10.831 533.6 0.4843 HC-2 7.625 0.6388 15.62 612.7 HC-3 5.369 673.6 0.7835 13.22 HC-4 3.780 725.5 0.9160 12.13 Fluid-1 6165 HC-5 2.661 0.040 771.9 1.0345 11.57 (with 9 HC) HC-6 2.248 819.4 1.1479 11.26 HC-7 1.874 877.2 1.2636 11.11 HC-8 1.291 952.1 11.12 1.3539 HC-9 0.886 1091.8 1.2249 11.47

Table 6.10. Properties and Composition of Heavy Component/s for all fluids studied in this work for a given asphaltene MW. These values are the same for all three models.

	H	/C Gas II	njectior	n=0 mol	%	H/	C Gas I	njectior	=5 mol	%	H/C Gas Injection=15 mol%				H/C Gas Injection=30 mol%					
Asp MW	Exp	Exp	RD	in calcu UOP (%)	ılated	Exp	Exp	RD	in calcu UOP (%)	ılated	Exp	Exp	RD	in calcu UOP (%)	ılated	Exp Temp (K)	Exp	RD	in calcu UOP (%)	lated
(Da)	Temp (K)	UOP (bar)	СРА	SRK	SRK + HV	UOP (bar)	UOP (bar)	СРА	SRK	SRK + HV	Temp (K)	UOP (bar)	СРА	SRK	SRK + HV		UOP (bar)	СРА	SRK	SRK + HV
	328	107	-69	-61	-60	328	238	-1	0	-1										
6165	347	126	-14	-12	-12	347	193	0	-1	-1	347	296	-7	-11	-12	347	630	6	-3	-1
	394	152	2	3	3	394	168	0	0	2	394	257	-1	2	3	394	481	5	12	13
		AAD	28	25	25			0	0	1			4	6	7			5	7	7
	328	107	-69	-57	-56	328	238	0	-1	1										
750	347	126	-15	-8	-9	347	193	0	0	-1	347	296	-7	-16	-15	347	630	6	-16	-9
	394	152	2	2	1	394	168	0	0	1	394	257	-1	-4	-4	394	481	4	-2	-2
		AAD	28	22	22			0	0	1			4	10	10			5	9	6
	328	107	-69	-63	-63	328	238	0	-1	0										
10000	347	126	-15	-13	-15	347	193	-1	0	-1	347	296	-7	-9	-8	347	630	6	2	7
10000	394	152	3	3	3	394	168	-1	0	1	394	257	-1	4	8	394	481	5	16	23
		AAD	29	26	27			1	0	1			4	7	8			5	9	15

Table 6.11. Fluid-1: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amounts of gas injection and considering different asphaltene molecular weights.

Table 6.12. Fluid-2: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amounts of gas injection and considering different asphaltene molecular weights.

		Gas Inje	ction=0	mol%		l	V ₂ Inject	ion=10	mol%		CO ₂ Injection=10 mol%				Methane Injection=10 mol%					
Asp MW	Exp	Exp	RD	in calcu UOP (%)	lated	Exp	Exp	RD	in calcu UOP (%)	lated	Exp	Exp	RD	in calcu UOP (%)	lated	Exp	Exp	RD	in calcu UOP (%)	lated
(Da)	(K)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)	СРА	SRK	SRK + HV
	371	317	0	-1	0	371	669	-1	-4	-9	371	428	-3	6	7	371	566	7	5	-27
	339	348	0	0	0	339	841	2	-2	-4	339	490	1	2	1	339	724	16	10	-26
20500						325	931	-3	-7	-11										
38500	311	462	-2	-1	-6	311	1352	10	7	5	311	676	6	0	-3	311	897	8	-6	-67
	304	552	2	3	1						304	759	6	-3	-3					
	300	593	-1	-1	0															
		AAD	1	1	1			3	3	4			4	3	3			10	7	40
	371	317	0	0	0	371	669	2	1	-9	371	428	-1	-10	-33	371	566	9	0	-5
	339	348	-1	0	0	339	841	5	5	-1	339	490	4	-10	-32	339	724	19	8	3
750						325	931	0	-1	-8										
/30	311	462	-4	-4	-7	311	1352	14	13	8	311	676	9	-10	-36	311	897	11	-6	-17
	304	552	2	2	0						304	759	10	-11	-35					
	300	593	-1	-1	-1															
		AAD	1	1	2			5	5	4			6	10	34			13	5	9

		CO_2 Gas	Injection=20) mol%			CO_2 Gas I	njection=30	mol%		
Asp MW (Da)	Exp Temp	Exp UOP	RD	in calculated (%)	UOP	Exp Temp	Exp UOP	RD in calculated UOP (%)			
(Da)	(K)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)	СРА	mol% in calculated (%) SRK -4 1 2 17 23 20	SRK + HV	
272	355	387	-1	0	0	355	490	-4	-4	-6	
372	394	363	-1	0	0	394	444	-5	1	-5	
		AAD	1	0	0			4	2	6	
10000	355	387	-1	0	NA ^a	355	490	-3	17	NA ^a	
10000	394	363	0	0	NA ^a	394	444	-3	23	NA ^a	
		AAD	0	0	NA ^a			3	20	NA ^a	

Table 6.13. Fluid-3: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amounts of CO_2 injection and considering different asphaltene molecular weights.

^aSRK+HV model parameters could not be calculated for this case.

Table 6.14. Fluid-4: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amounts of N_2 injection and considering different asphaltene molecular weights.

		Gas II	njection=0 m	iol%			N ₂ Inj	ection @419	K	
Asp MW	Exp	Exp	RD	in calculated (%)	UOP	Exp	Exp	RD	in calculated (%)	I UOP
(Da)	(K)	(bar)	СРА	SRK	SRK + HV	(mol%)	(bar)	СРА	SRK	SRK + HV
	361	373	-1	0	-2	5	379	7	8	8
2450	383	280	4	5	3	10	532	12	13	14
3450	400	251	0	0	-3	20	804	0	0	1
	422	262	0	0	1					
		AAD	1	1	2			6	7	8
	361	373	0	0	0	5	379	8	7	3
750	383	280	4	4	1	10	532	13	12	3
/50	400	251	0	0	-2	20	804	2	-1	-27
	422	262	0	0	0					
		AAD	1	1	1			8	7	11
	361	373	-1	-1	NA ^a	5	379	6	8	NA ^a
10000	383	280	5	5	NA^{a}	10	532	11	13	NA ^a
10000	400	251	-1	0	NA ^a	20	804	-2	1	NA ^a
	422	262	0	0	NA ^a					
		AAD	2	1				7	7	

^aSRK+HV model parameters could not be calculated for this case.

		Gas Ir	ijection=0 m	iol%			CO2 rich ga	s Injection @	i)363 K		
Asp MW	Exp	Exp	RD	in calculated (%)	UOP	Exp	Exp	RD	RD in calculated UOP (%)		
(Da)	(Da) (K) (bar) CPA		SRK	SRK + HV	gas inj. (mol%)	(bar)	СРА	SRK	SRK + HV		
	336	302	-1	-1	0	10	247	-1	-1	1	
3100	350	189	0	-1	1	15	323	4	5	4	
						25	440	-5	-1	-8	
		AAD	1	1	0			3	3	4	
	336	302	-1	-1	0	10	247	0	-2	1	
750	350	189	-1	0	1	15	323	5	1	-2	
						25	440	-4	-15	-28	
		AAD	1	0	0			3	6	10	
	336	302	-1	-1	NA ^a	10	247	-1	-1	NA ^a	
10000	350	189	0	0	NA^{a}	15	323	5	10	NA^{a}	
						25	440	-4	12	NA^{a}	
		AAD	1	1	NA ^a			3	8	NA ^a	

Table 6.15. Fluid-5: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amounts of CO_2 injection and considering different asphaltene molecular weights.

^aSRK+HV model parameters could not be calculated for this case.

Table 6.16. Fluid-6: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amounts of H/C gas injection and considering different asphaltene molecular weights.

		H/C Gas I	njection=	10 mol%			<i>H/C</i> Gas Ir	njection=1	5 mol%			H/C Gas I	njection=		
Asp MW (Da)	Exp Temp	Exp UOP	RD in	calculate (%)	d UOP	Exp Temp	Exp UOP	RD in	calculate (%)	d UOP	Exp Temp	Exp UOP	RD in	RD in calculated UO (%)	
(Da)	(K)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)	СРА	-8 -8 -8 5	SRK + HV
	328	233	-1	-1	0	328	323	1	-3	-4					
330	348	203	0	0	0	348	280	2	0	-2	348	583	0	-8	-13
	392	190	-1	-1	0	392	254	3	4	2	392	427	-12	-8	-15
			1	1	0			2	2	3			4	5	9
	328	233	-1	0	NA ^a	328	323	2	5	NA ^a					
10000	348	203	0	0	NA ^a	348	280	3	8	NA ^a	348	583	1	19	NA ^a
	392	190	-1	0	NA ^a	392	254	3	14	NA ^a	392	427	-11	25	NA ^a
		AAD	1	0	NA ^a			2	9	NA ^a			4	15	NA ^a

^aSRK+HV model parameters could not be calculated for this case.

Table 6.17. Fluid-1 (with 9 HC): Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experimental data for different amount of gas injections and considering different asphaltene molecular weight.

	Н	/C Gas Ir	njection	=0 mol%	6	H/	C Gas I	njection	=5 mol	%	H/	C Gas Ir	jection	=15 mol	%	H/	C Gas Ir	ijection=	=30 mol	%
Asp MW	Exp	Exp	RD	in calcu UOP (%)	lated	Exp	Exp	RD	in calcu UOP (%)	lated	Exp	Exp	RD	in calcu UOP (%)	lated	Exp	Exp	RD in calcu UOP (%) CPA SRK	n calcul UOP (%)	ated
(Da)	(K)	(bar)	СРА	SRK	SRK + HV	(bar)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)	СРА	SRK	SRK + HV	(K)	(bar)		SRK	SRK + HV
	328	107	-69	-60	-59	328	238	0	0	0										
6165	347	126	-15	-13	-10	347	193	0	0	0	347	296	-6	-11	-11	347	630	7	-3	-1
	394	152	2	2	2	394	168	0	0	3	394	257	0	2	3	394	481	7	12	11
		AAD	29	25	24			0	0	1			3	6	7			7	7	6

References

- 1 J. G. Speight, Petroleum Asphaltenes-Part 1: Asphaltenes, resins and the structure of petroleum, Oil and gas science and technology 59-5 (2004) 467-477.
- 2 Hirschberg, A., DeJong, L. N. J., Schipper, B. A., and Meijer, J. G. (1984). Influence of temperature and pressure on asphaltene flocculation. Society of Petroleum Engineers Journal, 24(03), 283-293.
- 3 F. Vargas, M. Garcia-Bermudes, M. Boggara, S. Punnapala, M.I. Abutaqiya, N.T. Mathew, H.Y. Al Asafen, On the Development of an Enhanced Method to Predict Asphaltene Precipitation, In Offshore Technology Conference held in Houston, Texas, USA, 05-08 May-(2014).
- 4 Pedrosa, N., Szczepanski, R., & Zhang, X. (2013). Integrated equation of state modelling for flow assurance. *Fluid Phase Equilibria*, 359, 24-37.
- 5 Malik, Q. M., & Islam, M. R. (2000, January). CO2 Injection in the Weyburn field of Canada: optimization of enhanced oil recovery and greenhouse gas storage with horizontal wells. In SPE/DOE improved oil recovery symposium. Society of Petroleum Engineers.
- 6 Taber, J. J. (1994). A study of technical feasibility for the utilization of CO2 for enhanced oil recovery. *The Utilization of Carbon Dioxide from Fossil Fuel Fired Power Stations*, 134-204.
- 7 Stalkup, F. I. (1987, January). Displacement behavior of the condensing/vaporizing gas drive process. In *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers.
- 8 Holm, W. L. (1987). Evolution of the carbon dioxide flooding processes. *Journal of petroleum technology*, *39*(11), 1-337.
- 9 Holm, L. W. (1986). Miscibility and miscible displacement. *Journal of Petroleum Technology*, *38*(08), 817-818.
- 10 Hoffman, B. T. (2012, January). Comparison of various gases for enhanced recovery from shale oil reservoirs. SPE Improved Oil Recovery Symposium, 14-18 April, Tulsa, Oklahoma, USA.
- 11 Yan, W., Michelsen, M. L., & Stenby, E. H. (2011, January). On application of non-cubic EoS to compositional reservoir simulation. In SPE EUROPEC/EAGE Annual Conference and Exhibition, 23-26 May, Vienna, Austria.
- 12 Jamaluddin, A. K. M., Creek, J., Kabir, C. S., McFadden, J. D., D'Cruz, D., Manakalathil, J., & Ross, B. (2002). Laboratory techniques to measure thermodynamic asphaltene instability. Journal of Canadian Petroleum Technology, 41(07).
- 13 Pedersen, K. S., Christensen, P. L., & Shaikh, J. A. (2014). Phase behavior of petroleum reservoir fluids. CRC Press.
- 14 Panuganti, S. R., Vargas, F. M., Gonzalez, D. L., Kurup, A. S., & Chapman, W. G. (2012). PC-SAFT characterization of crude oils and modeling of asphaltene phase behavior. Fuel, 93, 658-669.
- 15 Hustad, O. S., Jia, N., Pedersen, K. S., Memon, A. I., & Leekumjorn, S. (2013, September). High pressure data and modeling results for phase behavior and asphaltene onsets of GoM Oil mixed with nitrogen. In SPE Annual Technical Conference and Exhibition, 30 September-2 October, New Orleans, Louisiana, USA.
- 16 Zhang, X., Pedrosa, N., & Moorwood, T. (2012). Modeling asphaltene phase behavior: comparison of methods for flow assurance studies. Energy & Fuels, 26(5), 2611-2620.
- 17 Arya, A., von Solms, N., & Kontogeorgis, G. M. (2015). Determination of asphaltene onset conditions using the cubic plus association equation of state. *Fluid Phase Equilibria*, 400, 8-19.
- 18 Arya, A., von Solms, N., & Kontogeorgis, G. M. (2015). Investigation of the Gas Injection Effect on Asphaltene Onset Precipitation Using the Cubic-Plus-Association Equation of State. *Energy & Fuels*.
- 19 Arya, A., Liang, X., von Solms, N., & Kontogeorgis, G. M. (2016). Modeling of Asphaltene Onset Precipitation Conditions with Cubic Plus Association (CPA) and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) Equations of State. *Energy & Fuels*, 30(8), 6835-6852.
- 20 Sutherland, J. A Proposed Model of Asphaltene Solution Behavior. Diss. MS thesis, Imperial College, University of London, London, England, 1982.

- 21 Wang, J. X., & Buckley, J. S. (2001). A two-component solubility model of the onset of asphaltene flocculation in crude oils. *Energy & Fuels*, 15(5), 1004-1012.
- 22 Acevedo, S., Castro, A., Vásquez, E., Marcano, F., & Ranaudo, M. A. (2010). Investigation of physical chemistry properties of asphaltenes using solubility parameters of asphaltenes and their fractions A1 and A2. *Energy & Fuels*, 24(11), 5921-5933.
- 23 Sirota, E. B. (2005). Physical structure of asphaltenes. Energy & fuels, 19(4), 1290-1296.
- 24 Kesler, M. G., & Lee, B. I. (1976). Improve prediction of enthalpy of fractions. Hydrocarbon processing, 55(3), 153-158.
- 25 G.M. Kontogeorgis, G.K. Folas, Thermodynamic models for industrial applications: from classical and advanced mixing rules to association theories. John Wiley & Sons (2009).
- 26 Soave, G. (1972). Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, 27(6), 1197-1203.
- 27 Huron, M. J., & Vidal, J. (1979). New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilibria*, *3*(4), 255-271.
- 28 Chueh, P. L., Prausnitz, J. M., & Knapp, H. (1982). Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances. In *Chem. Data Series* (Vol. 6). DECHEMA Frankfurt/Main.
- 29 Gonzalez, D. L., Mahmoodaghdam, E., Lim, F. H., & Joshi, N. B. (2012, January). Effects of Gas Additions to Deepwater Gulf of Mexico Reservoir Oil: Experimental Investigation of Asphaltene Precipitation and Deposition. In SPE Annual Technical Conference and Exhibition, 8-10 October, San Antonio, Texas, USA.
- 30 Punnapala, S., & Vargas, F. M. (2013). Revisiting the PC-SAFT characterization procedure for an improved asphaltene precipitation prediction.Fuel, 108, 417-429.
- 31 Jamaluddin, A. K. M., Joshi, N., Iwere, F., & Gurpinar, O. (2002, January). An investigation of asphaltene instability under nitrogen injection. In SPE International Petroleum Conference and Exhibition in Mexico, 10-12 February, Villahermosa, Mexico.
- 32 Memon, A. I., Qassim, B., Al-ajmi, M. F., Tharanivasan, A. K., Gao, J., Ratulowski, J., ... & Khan, R. A. (2012, January). Miscible Gas Injection and Asphaltene Flow Assurance Fluid Characterization: A Laboratory Case Study for Black Oil Reservoir. In SPE EOR Conference at Oil and Gas West Asia, 16-18 April, Muscat, Oman.
- 33 <u>http://www.calsep.com/</u> (Date: 12th Dec 2016)
- 34 Nasrifar, K., & Moshfeghian, M. (1998). A saturated liquid density equation in conjunction with the Predictive-Soave–Redlich–Kwong equation of state for pure refrigerants and LNG multicomponent systems. *Fluid phase* equilibria, 153(2), 231-242.

Chapter 7. Modeling of Asphaltene Precipitation from Crude (Degassed) Oil

Entire content of this chapter is from our journal article "Alay Arya; Xiaodong Liang; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Precipitation from Crude Oil with the Cubic Plus Association Equation of State. Submitted to Energy & Fuels".

Abstract

In this study, different modeling approaches using the Cubic Plus Association (CPA) equation of state (EoS) are developed to calculate asphaltene precipitation onset condition and asphaltene yield from degassed crude oil during the addition of *n*-paraffin. A single model parameter is fitted to calculate asphaltene onset condition during the addition of different *n*-paraffin precipitants (*n*-pentane to *n*-hexadecane). Three parameters per precipitant are fitted to calculate the asphaltene yield during the addition of the precipitant. The results obtained from the model are compared with experimental data for eight different crude oils. Results were also obtained for seven crudes using the Perturbed Chain Statistical Association Fluid Theory (PC-SAFT) EoS based approach described in the literature. The CPA EoS based approaches treat the asphaltene fraction as an associating component whereas the PC-SAFT EoS based approach does not. A comparison between the approaches shows that the CPA EoS based approaches, developed in this work, give more reliable results. The predictions from the PC-SAFT EoS based approach result in behavior that is unphysical: mole fraction of *n*-paraffin (at the precipitation onset) and the asphaltene yield do not decrease with the carbon number of *n*-paraffin. Furthermore, it is shown that the approach, developed in this work, can predict the onset conditions of asphaltene precipitation resulting from a blend of two or more crudes.

7.1 Introduction

A crude oil at room temperature can be divided into maltene (deasphalted fraction) and asphaltene fractions. The maltene fraction can be further divided into saturates, aromatics and resins fractions. The SARA (saturates, aromatics, resins, asphaltenes) analysis is used to measure the amount (on weight basis) of these four solubility fractions. All of these fractions are polydisperse in the oil and contain a large number of components. Asphaltenes are defined as the heaviest fraction of the oil, which is not soluble in *n*-pentane/*n*-heptane but soluble in aromatic solvents such as toluene [1-3]. Resins are the fraction of the oil, which is soluble in *n*-pentane/*n*-heptane, toluene and benzene but insoluble in ethyl acetate at room temperature [2,4]. It is believed that resins are cross-associating (form hydrogen bonds) with asphaltenes to keep asphaltenes soluble in the oil [5]. The asphaltene fraction may precipitate out of the crude oil during the addition of a paraffinic solvent. As the carbon

number of *n*-paraffin increases, the solubility of the asphaltene fraction increases and the amount of precipitated asphaltenes decreases. At higher *n*-paraffin carbon number, the amount of precipitated asphaltenes remains almost constant [5]. Asphaltenes containing crude is generally blended with one or more crudes to maintain the properties of feedstock (blended crude) to the refinery. In certain cases, the blending of incompatible crudes results in the asphaltene precipitation. The asphaltene precipitation can result in fouling and coking of preheat trains, heat exchangers and pipestill furnace tubes in the refinery [6]. Therefore, it is important to understand the asphaltene precipitation in order to avoid complications during the processing of crude oil.

There are several studies on the modeling of the asphaltene precipitation from crude oil. Some of them consider the asphaltene fraction as polydisperse while others consider it as monodisperse. These studies can also be classified according to whether the asphaltene fraction is treated as a non-associating or an associating molecule. When the asphaltene molecule is considered not to associate with other asphaltene molecules, it is assumed that the asphaltene component already exists in a pre-aggregated form where only van der Waals forces are included in the asphaltene precipitation model. On the other hand, when the asphaltene molecule is allowed to associate with other asphaltene molecules, it is assumed that the asphaltene molecule exists as a monomer. The association between asphaltene molecules is an important criteria for precipitation, along with the van der Waals forces. This association is a way to account for strong polar forces such as hydrogen bonding. The framework for both PC-SAFT and CPA allows for the modelling of both van der Waals and association forces. However we note here that the aspociation term is not considered in this work for the PC-SAFT based model, where we follow the approach used previously in the literature [7].

Asphaltene as a Non-associating and Pre-aggregated Component

The asphaltene precipitation from crude oil has been modeled by several researchers. Hirschberg et al [2] used the Flory-Huggins theory in order to study the effect of miscible gas flooding on the asphaltene precipitation. They used the Soave-Redlich-Kwong (SRK) EoS for vapor-liquid equilibrium considering no asphaltene precipitation. They then used the Flory-Huggins model to calculate the asphaltene precipitation from the liquid phase, calculated from the SRK EoS. The asphaltene fraction was considered as a monodisperse component. Alboudwarej et al [8] used the regular Flory-Huggins model dividing the asphaltene fraction into multiple components of different molar mass, volume and solubility parameters. They assumed that the precipitated phase is ideal and consists of only the asphaltene components. Akbarzadeh et al [9] used the same approach developed by Alboudwarej et al [8] and showed the temperature and pressure effect on the model predictions. They used a temperature dependent gamma distribution function to describe the temperature dependent molar mass distribution of the asphaltene fraction. Pazuki and Nikookar [10] modified the Flory-Huggins model and compared the asphaltene precipitation results with the original Flory-Huggins model and experimental data. They concluded that the modified model is better than the original one. Wiehe et al [6] developed the oil compatibility model in order to check whether the blending of two or more crudes is compatible with respect to the asphaltene precipitation. Wiehe et

al [11] compared the oil compatibility model with the regular Flory-Huggins theory based model from Yarranton and co-workers [8, 9]. They concluded that both models can calculate the asphaltene onset condition as well as the maximum in volume of *n*-paraffin, as a function of the carbon number of *n*-paraffin at the onset of asphaltene precipitation. They also mentioned that the basic assumption of the oil compatibility model, that the solubility parameter of mixture at the onset is constant, contradicts the physical behavior. Tharanivasan et al [12] used the regular Flory-Huggins theory based model, developed by Yarranton and co-workers [8, 9], to calculate the asphaltene yield (ratio of mass of precipitated asphaltenes to mass of oil before addition of precipitant) as well as the onset condition of the blend of different crudes. They considered the asphaltene fraction as polydisperse components. Sabbagh et al [13] used the Peng-Robinson (PR) EoS. They divided the asphaltene fraction into multiple components of different molar mass based on the gamma distribution function. The precipitated phase was assumed to contain only the asphaltene components. They concluded that the PR model is not a universal predictor and not better than the previously developed regular solution model. Panuganti et al [14] and Tavakkoli et al [7] used a model, based on the PC-SAFT EoS, considering the asphaltene fraction as polydisperse components. They studied both light and heavy crudes. They used interaction parameters for the asphaltene-n-paraffin binary pairs in order to correlate both the onset conditions and asphaltene yield from the light crude. They kept the binary interaction parameters for asphaltene-n-paraffin binary pairs to zero value in order to predict the asphaltene yield from the heavy crude, however, they used non-zero values of binary interaction parameter for the asphaltene-saturates binary pair to correlate the onset conditions. Their model predictions contradict the general experimental observation [2,15,4], where the amount of precipitated asphaltenes decreases or remains constant with the carbon number of n-paraffin precipitant. This contradiction is discussed in detail in the "Results and Discussion" section of this work.

Asphaltene as an Associating and Monomeric Component

Wu et al [16,17] used the SAFT EoS in the framework of McMillan-Mayer theory. In their model, asphaltenes and resins are considered as monodisperse pure pseudo-components and the interactions between them are screened through the continuous medium of solution containing other components. They applied their model to calculate the asphaltene yield from the crude oil and the onset conditions from the reservoir oil. However, they did not study the onset conditions for crudes during the addition of *n*-paraffin. Buenrostro-Gonzalez et al [15] modified the modeling approach of Wu et al [16,17] by using the SAFT-VR instead of the SAFT EoS. They applied their model to calculate both the onset conditions and asphaltene yields from the crude. However, they could not match both types of experimental data with the single set of parameters. Li and Firoozabadi [18] developed a modeling approach based on the CPA EoS considering the asphaltene fraction as a monodisperse component. They studied the asphaltene precipitation from the heavy oil. They did not study their modeling approach with respect to the asphaltene onset condition from the crude oil.

To our knowledge, nobody has so far studied the CPA equation of state for the asphaltene precipitation from the crude considering the asphaltene fraction as polydisperse. There is also no study on the blending of crudes with the CPA and PC-SAFT equations of state. In this study, different CPA approaches are developed to study the asphaltene yield and onset conditions. The PC-SAFT approach is referred from Tavakkoli et al [7]. Both CPA and PC-SAFT approaches are studied and compared with the experimental data. A total of eight crudes are studied. Crude-1 is studied with respect to both the asphaltene yield and onset conditions considering the asphaltene fraction as a polydisperse fraction. Crude-2 to 4 are studied with respect to 8 are studied with respect to onset conditions considering the asphaltene fraction as a polydisperse fraction, while Crude-5 to 8 are studied with respect to onset conditions considering the asphaltene fraction as a monodisperse fraction.

7.2 Modeling Approaches

Approach-1

Approach-1 is based on the CPA EoS and is the same approach as was proposed by Arya et al [20-22]. As shown in Table 7.1, the modeling approach-1 has a single component for the maltene fraction and six components for the asphaltene fraction. The asphaltene components are considered selfassociating with two positive and two negative sites on each asphaltene molecules. The maltene component's molecule has one association site and can cross-associate with both positive and negative sites of the asphaltene components. The maltene component is not self-associating. The critical temperature and pressure (T_c, P_c) and acentric factor (ω) of maltene component are calculated from the Kesler-Lee correlations [23] based on the information of normal boiling point, molecular weight (MW) and specific gravity (SG). The MW and SG of maltene component are calculated from the experimental information of MW and SG of the crude and asphaltenes MW (750 Da) and SG (1.2 g/cc). The normal boiling point is calculated from the Pedersen correlation [24]. The critical temperature and pressure (T_c, P_c) , acentric factor (ω) and self-association volume are constant for all six asphaltene components and are referred from Arya et al [20-22]. The self-association energies of asphaltene components (Asp-4 to Asp6) are also kept constant to reduce the number of model parameters. In addition the self-association energies of asphaltene components (Asp1 to Asp3) are assumed to be same. The cross-association volume between the asphaltenes and maltene is also fixed to the value of 0.05.

Mitchell and Speight [4] mentioned that the asphaltene yield decreases with the carbon number of *n*-paraffin. However, approach-1 cannot predict this physical behavior and precipitate all asphaltene components (Asp1 to 6) irrespective of the carbon number of *n*-paraffin. To overcome this issue, one more model parameter is incorporated, which is the cross-association energy between the *n*-paraffin and asphaltene components (except Asp6). It means that Asp1 to Asp5 have the same cross-association energy with a given *n*-paraffin. By doing this, the solubility of Asp1 in *n*-paraffin is more compared to that of other asphaltene components (Asp2 to Asp5) in *n*-paraffin since the self-association energy of Asp1 is less compared to those of other asphaltene components. If the cross-

association energy for a given *n*-paraffin increases, the solubility of all asphaltene components (with fixed self-association energies) in a given *n*-paraffin increases. Therefore, we can assign the higher value of the cross-association energy for *n*-paraffin precipitant as the carbon number increases and can correlate the asphaltene yield data. Li and Firoozabadi [18] also studied the CPA EoS for the calculations of asphaltene yield from the crude and they suggested that the cross-association energy between (A+R) and asphaltenes is different for different *n*-paraffin. They have not considered any cross-association between *n*-paraffin and asphaltenes. However, in our approach, the crossassociation energy between aromatics+resins (A+R)/maltene and asphaltenes is the same for different *n*-paraffin and the cross-association energy between *n*-paraffin and asphaltenes is different for different *n*-paraffin. Speight [25] mentioned that the asphaltene yield is almost constant for *n*-paraffin of higher carbon number (around >11). Therefore, Asp6 component is treated as an *n*-paraffin undissolved asphaltene fraction and does not cross-associate with the *n*-paraffin precipitant. Thus, approach-1 needs two additional model parameters (the cross-association energy between the precipitant and asphaltene components and amount of Asp6). It should be noted that the binary interaction parameter (k_{ij}) between the *n*-paraffin and asphaltenes pair could also be used instead of the cross-association energy between them. However, it needs some modification of the modeling approach and is not shown in this work. In addition, one could also fix the amount of Asp6 for all crudes, for example 30% of asphaltenes amount from SARA analysis, which would result in minor deviations from the experimental data. Table 7.2 shows that there are total three model adjustable parameters (MAP1, MAP2, and MAP3). The model parameter MAP3 is different for different nparaffin.

Comp	Amount	MW	T _c	P _c	ω	Self-association energy (ε^{AA}/R)	Self- association volume (β^{AA})	No. Of Sites
	wt%	g/mol	K	bar	-	(K)	-	-
Maltene	X a	Calc ^d	Calc ^d	Calc ^d	Calc ^d	0	0	1^{f}
Asp1	Y ^b	750	1040.1	15.44	1.535	MAP1 ^e	0.05	2+,2-
Asp2	Y ^b	750	1040.1	15.44	1.535	MAP1 ^e	0.05	2+,2-
Asp3	Y ^b	750	1040.1	15.44	1.535	MAP1 ^e	0.05	2+,2-
Asp4	Y ^b	750	1040.1	15.44	1.535	6500	0.05	2+,2-
Asp5	Y ^b	750	1040.1	15.44	1.535	6600	0.05	2+,2-
Asp6	Z ^c (MAP) ^e	750	1040.1	15.44	1.535	7000	0.05	2+.2-

Table 7.1. Approach-1: Crude oil characterization and components parameters.

^a X is the sum of wt% of saturates, aromatics and resins from SARA analysis.

^b Y = (Asp wt% from SARA - Z)/5.

^c Z is the amount of asphaltene sub-fraction (Asp6), which is not dissolved in *n*-paraffin.

^d Calculated (Calc) from the Kesler-Lee correlations as mentioned in the text.

^e Model Adjustable Parameter (MAP) determined from the experimental data.

^f Maltene molecule has one site, which can cross-associate with both positive and negative sites of asphaltene molecule.

	Asp1	Asp2	Asp3	Asp4	Asp5	Asp6	Maltene	<i>n</i> -paraffin
Asp1	MAP1 ^a	Elliott	Elliott	Elliott	Elliott	Elliott	MAP2 ^a	MAP3 ^a
Asp2	Elliott	MAP1 ^a	Elliott	Elliott	Elliott	Elliott	MAP2 ^a	MAP3 ^a
Asp3	Elliott	Elliott	MAP1 ^a	Elliott	Elliott	Elliott	MAP2 ^a	MAP3 ^a
Asp4	Elliott	Elliott	Elliott	6500	Elliott	Elliott	MAP2 ^a	MAP3 ^a
Asp5	Elliott	Elliott	Elliott	Elliott	6600	Elliott	MAP2 ^a	MAP3 ^a
Asp6	Elliott	Elliott	Elliott	Elliott	Elliott	7000	MAP2 ^a	0
Maltene	MAP2 ^a	0	0					
<i>n</i> -paraffin	MAP3 ^a	0	0	0				

Table 7.2. Approach-1: Self-association and Cross-association energy parameter in Kelvin.^b

^a Model Adjustable Parameters (MAP1, MAP2 and MAP3) determined from the experimental data of asphaltene yield and onset conditions.

^b Cross-association volume is 0.05 for all pairs where Elliott combining rule is not used.

Approach-2

Approach-2 is based on the CPA EoS and similar to approach-1, except for a few differences, and is shown in Table 7.3. In approach-2, the maltene fraction is divided into saturates and (A+R) components. The critical temperature and pressure (T_c , P_c), acentric factor (ω) and MW are fixed for all components and are taken from Li and Firoozabadi [18]. For asphaltenes MW, the value of 750 Da is used in this study, whereas Li and Firoozabadi [18] used the value of 1800 Da. Sabbagh et al [13] showed the relationship between MW and critical temperature and pressure (T_c , P_c) and acentric factor (ω), which were then used by Li and Firoozabadi [18]. There are two reasons for the development of approach-2 over approach-1. The first reason is to show that the maltene fraction can further be divided into two components (and possibly more) and model can still be fitted to the experimental data. The second reason is to use the different set of component parameters, derived based on the information of experimental MW from the vapor pressure osmometry technique, for the heavy oil from the literature. Table 7.4 shows that there are total three model adjustable parameters (MAP1, MAP2, and MAP3). The model parameter MAP3 is different for different *n*-paraffin.

Comp	Amount	MW	T_c	P_c	ω	Self-association energy (ε^{AA}/R)	Self-association volume (β^{AA})	No. Of Sites
1	wt%	g/mol	Κ	bar	-	(K)	-	-
Saturates	X1 a	460	930	13.4	0.9	0	0	0
A+R	X2 ^b	660	1074	10.85	1.5	0	0.05	1^{f}
Asp1	Y ^c	750	1474	7.07	2	MAP1 ^e	0.05	2+,2-
Asp2	Y ^c	750	1474	7.07	2	MAP1 ^e	0.05	2+,2-
Asp3	Y ^c	750	1474	7.07	2	MAP1 ^e	0.05	2+,2-
Asp4	Y ^c	750	1474	7.07	2	6500	0.05	2+,2-
Asp5	Y ^c	750	1474	7.07	2	6600	0.05	2+,2-
Asp6	Z^{d} (MAP) ^e	750	1474	7.07	2	7000	0.05	2+,2-

 Table 7.3. Approach-2: Crude oil characterization and components parameters.

^a X1 is the wt% of saturates from SARA analysis.

^b X2 is the sum of wt% of aromatics and resins from SARA analysis.

^c Y = (Asp wt% from SARA - Z)/5.

^d Z is the amount of asphaltene sub-fraction (Asp6), which is not dissolved in *n*-paraffin.

^e Model Adjustable Parameter (MAP1) determined from the experimental data.

^f (A+R) molecule has one site, which can cross-associate with both positive and negative sites of asphaltene molecule.

	Asp1	Asp2	Asp3	Asp4	Asp5	Asp6	saturates	A+R	<i>n</i> -paraffin
Asp1	MAP1 ^a	Elliott	Elliott	Elliott	Elliott	Elliott	0	MAP2 ^a	MAP3 ^a
Asp2	Elliott	MAP1 ^a	Elliott	Elliott	Elliott	Elliott	0	MAP2 ^a	MAP3 ^a
Asp3	Elliott	Elliott	MAP1 ^a	Elliott	Elliott	Elliott	0	MAP2 ^a	MAP3 ^a
Asp4	Elliott	Elliott	Elliott	6500	Elliott	Elliott	0	MAP2 ^a	MAP3 ^a
Asp5	Elliott	Elliott	Elliott	Elliott	6600	Elliott	0	MAP2 ^a	MAP3 ^a
Asp6	Elliott	Elliott	Elliott	Elliott	Elliott	7000	0	MAP2 ^a	0
saturates	0	0	0	0	0	0	0	0	0
A+R	MAP2 ^a	0	0	0					
<i>n</i> -paraffin	MAP3 ^a	MAP3	MAP3 ^a	MAP3 ^a	MAP3 ^a	0	0	0	0

Table 7.4. Approach-2: Self-association and Cross-association energy parameters in Kelvin.^b

^a Model Adjustable Parameters (MAP1, MAP2 and MAP3) determined from the experimental data of asphaltene yield and onset conditions.

^b Cross-association volume is 0.05 for all pairs where Elliott combining rule is not used.

Approach-3

If we are only interested in calculating the precipitation onset condition, we can reduce the number of components and therefore the number of model adjustable parameters. Approach-3 is based on the CPA EoS and is similar to approach-2. Approach-3 has only one asphaltene component as shown in Table 7.5. There is no cross-association between the precipitant and asphaltene component but the cross-association between (A+R) and asphaltene components is present. Moreover, the selfassociation energy of asphaltene is fixed to 3000K (instead of 7000K) to show that the relative balance between the asphaltene and solvent is important rather than the absolute values of asphaltene selfassociation energy and cross-association energy of solvent. In other words, there can be multiple pairs of values of the asphaltene self-association energy and cross-association energy (between (A+R) and asphaltene components), which can correlate the experimental data. The experimental values of MW are used, if they are available, without changing the critical temperature and pressure (T_c , P_c), acentric factor (ω) for saturates and (A+R) components. Table 7.6 shows that there is only one model adjustable parameter (MAP1).

Comp	Amount	MW	T_c	P_c	ω	Self-association energy (ε^{AA}/R)	Self-association volume (β^{AA})	No. Of Sites
	wt%	g/mol	Κ	bar	-	(K)	-	-
Saturates	X1 ^a	460	930	13.4	0.9	0	0	0
A+R	X2 ^b	660	1074	10.85	1.5	0	0.05	1 ^d
Asp	X3 °	750	1474	7.07	2	3000	0.05	2+,2-

Table 7.5. Approach-3: Crude oil characterization and components parameters.

^a X1 is the wt% of saturates from SARA analysis.

^b X2 is the sum of wt% of aromatics and resins from SARA analysis.

^c X3 is the wt% of asphaltene from SARA analysis.

^d (A+R) molecule has one site, which can cross-associate with both positive and negative sites of asphaltene molecule.
	Asp	saturates	A+R	<i>n</i> -paraffin
Asp	3000	0	MAP1 ^a	0
saturates	0	0	0	0
A+R	MAP1 ^a	0	0	0
<i>n</i> -paraffin	0	0	0	0

Table 7.6. Approach-3: Self-association and Cross-association energy parameters in Kelvin.^b

^a Model Adjustable Parameter (MAP1) determined from the experimental data of asphaltene onset condition.

^b Cross-association volume is 0.05 for all pairs.

Approach-4

Approach-4 is based on the PC-SAFT EoS and no association term is used since there is no associating component. Approach-4 is the same approach as was developed by Tavakkoli et al [7]. In approach-4, the crude is divided into saturates, A+R and multiple components of the asphaltene fraction. The number of asphaltene components depends upon the experimental data of different *n*paraffin undissolved asphaltene amounts. For example, if the experimental data of nC5, nC7 and nC10 undissolved asphaltene amounts are available, three asphaltene components (nC5 insoluble but nC7 soluble asphaltene fraction, nC7 insoluble but nC10 soluble asphaltene fraction and nC10insoluble asphaltene fraction) are used. The PC-SAFT parameters of saturates components are calculated from the MW correlations developed from the homologous series of *n*-paraffin. The standard *n*-paraffin PC-SAFT parameters from Gross and Sadowski [26] are used for this approach. The PC-SAFT parameters of the (A+R) and asphaltene components are also calculated from the MW and aromaticity (γ) correlations developed from the polynuclear aromatic components by Gonzalez et al [27]. The zero value of aromaticity (γ) corresponds to benzene derivatives and value of unity corresponds to polynuclear aromatics. Both correlations are mentioned in Table 7.7. The aromaticity value of (A+R) is tuned to match density of the crude. The aromaticity (γ) values of all asphaltene components are assumed to be the same considering they have the same physical nature. The single value of aromaticity (γ) and respective value of MW of all asphaltene components are tuned to match the precipitation data. In addition, binary interaction parameters $(k_{ij}s)$ are also used to match the precipitation data. Tavakkoli et al [7] also tuned the segment diameter σ of asphaltenes to find a good match with the experimental data. However, the segment diameter σ is not used as an adjustable parameter in approach-4 in order to reduce the number of fitting parameters. When we are only interested in onset conditions, one asphaltene component, like approach-3, is used for approach-4 rather than dividing it into multiple components. Also, when the experimental MW of aromatics and resins fractions are available, (A+R) component can be divided into aromatics and resins components with the same value of aromaticity (γ) .

oj i orijimereta ili olitatico (i iki) ana oci	
Correlation for Saturates	(γ) PNA correlation + (1 – γ) benzene derivatives correlation
$m = 0.0257 \times MW + 0.8444$	$m = (1 - \gamma)[0.0223 \times MW + 0.751] + \gamma[0.0101 \times MW + 1.7296]$
$\sigma(\text{\AA}) = 4.047 - \frac{4.8013 \times \ln(MW)}{MW}$	$\sigma(\text{\AA}) = (1 - \gamma) \left[4.1377 - \frac{38.1483}{MW} \right] + \gamma \left[4.6169 - \frac{93.98}{MW} \right]$
$\ln(\epsilon/k)$ in $K = 5.5769 - \frac{9.523}{MW}$	(ϵ/k) in $K = (1 - \gamma)[0.00436 \times MW + 283.93] + \gamma \left[508 - \frac{234100}{(MW)^{1.5}} \right]$

Table 7.7. Approach-4: Empirical correlations for the estimation of the PC-SAFT parameters for saturates and mixture of Polynuclear Aromatics (PNA) and benzene derivative components from Panuganti et al [14].

7.3 Results and Discussion

In this work, a total of eight different crudes are studied. The composition and properties of the crudes are mentioned in Table 7.8. Crudes-1, 2 and 8 are light crudes whereas Crudes-3 to 7 are relatively heavy crudes. The model parameters for the CPA EoS based approaches-1 to 3, calculated from the experimental data, and are shown in Tables 7.9 and 7.10. The model parameters and characterization of the crudes for approach-4 are shown in Tables 7.11 and 7.12. The binary interaction parameters $(k_{ii}s)$ used for approach-4 are shown in Table 7.13. The experimental and calculated density using approach-4, after tuning the aromaticity (γ) of A+R component, are compared in Table 7.14. For approaches-1 to 3, Peneloux volume corrections are used for the *n*-paraffin unless otherwise mentioned. It should be noted that no k_{ii} parameter is used for approaches-1 to 3. For all the crudes (except Crude-2), one of the CPA EoS based approaches-1 to 3 and the PC-SAFT EoS based approach-4 are compared with experimental data. For Crude-2, only approach-1 is studied. For Crudes-1, 3, and 4, the PC-SAFT parameters and oil characterization for approach-4 are referred from Tavakkoli et al [7]. For Crudes-5 to 8, the PC-SAFT parameters for approach-4 are from this work. Table 7.15 shows the comparison of the number of model adjustable parameters between the approaches for all the crudes. Approaches-1 and 2 are used for Crudes-1 and 2 and Crudes-3 and 4 respectively. One can also use either approach-1 or approach-2 for Crudes-1 to 4 but results are not presented here. Since we are only interested in onset conditions, approach-3 (instead of approaches-1 and 2) is used for Crudes-5 to 8.

1	5 1			2 0					
С	rude	1	2	3	4	5	6	7	8
	Volatile	-	-	-	-	-	-	12.6	25.7
	Saturates	_ a	54.67	25	20.5	19.5	16.4	25.3	34.2
Composition	Aromatics	- ^a	28.89	31.1	38	38.2	40.1	40.9	33.5
Composition	Resins	_ a	12.66	37.1	19.6	26.8	28.7	4.9	3.2
	nC5 Asphaltenes	3.9	3.8	6.8	21.8	15.5	14.8	16.3	3.5
	solids	-	-	-	0.1	-	-	-	-
	Volatile	-	-	-	-	-	-	86	86
	Saturates	-	-	361	400	508	524	460	460
MW	Aromatics	-	-	450	508	522	550	522	522
(Da)	Resins	-	-	1108	1090	930	976	1040	1040
	Asphaltenes	-	-	7065	7662	2850	2910	-	-
	Crude	221.5	238.1	-	-	-	-	-	-
	Volatile	-	-	-	-	-	-	0.657	0.657
	Saturates	-	-	0.853	0.882	0.882	0.885	0.880	0.880
Density	Aromatics	-	-	0.972	0.997	0.995	1.003	0.990	0.990
(g/cc)	Resins	-	-	1.066	1.052	1.037	1.040	1.044	1.044
	nC5 Asphaltenes	-	-	1.192	1.193	1.203	1.203	-	-
	Crude	0.873	0.857	0.982	1.016	0.991	0.995	0.924	0.870

Table 7.8. Experimental data of composition, MW and density of all crudes.

^a Molar composition of saturates (50 mol%), aromatics (25 mol%) and hetero-compounds (25 mol%) are given in reference [2].

Table 7.9. The model adjustable parameters for Crudes-1 to 4 for the CPA EoS based approaches-1 and 2.

Crude	Self-association Energy $(\varepsilon^{AA}/R \text{ in K})$			Cross-association Energy (K)								Asp-6	
	Asp-1	Asp-2	Asp-3	Maltene	A+R	nC5	nC7	пС9	nC10	<i>nC</i> 12	nC16	(W170)	
1	6450	6450	6450	3670	-	2400	2970	-	3135	3135	3135	1.2	
2	6000	6000	6000	3480	-	2000	2610	2720	-	2920	-	0.5	
3	6100	6100	6100	-	3440	1950	2380	-	-	-	-	0.5	
4	6430	6430	6430	-	3580	2300	2550	-	-	-	-	2	

Table 7.10. The model adjustable parameters for Crudes-5 to 8 for the CPA EoS based approach-3.

Crude	Self-association Energy (K)	Cross-association Energy (K)				
	Asphaltenes	A+R	Toluene			
5	Default	1810	-			
6	Default	1845	-			
7	Default	1860	1410			
8	2600	1690	1260			

	Cı	rude-1		Cı	rude-3		Crude-4			
Components	MW (Da)	γ	wt%	MW (Da)	γ	wt%	MW (Da)	γ	wt%	
Saturates	207.43	0	46.8	361	0	25	400	0	20.5	
Aromatics	-	-	-	450	0.23	31.1	508	0.3	38	
Resins	-	-	-	1108	0.23	37.1	1090	0.3	19.6	
Aromatic+Resins	219.44	0.38	49.3	-	-	-	-	-	-	
nC5 – nC7 Asphaltenes	2900	0.2	2	4700	0.2	2.2	2500	0.4	4.3	
nC7 – nC10 Asphaltenes	2950	0.2	0.4	-	-	-	-	-	-	
<i>nC</i> 7 Asphaltenes	-	-	-	5600	0.2	4.6	2600	0.4	17.5	
<i>nC</i> 10 Asphaltenes	4307	0.2	1.5	-	-	-	-	-	-	

Table 7.11. Characterization of Crudes-1, 3 and 4 for the PC-SAFT EoS based approach-4 referred from Tavakkoli et al [7].

Table 7.12. The parameters for Crudes-5 to 8 for the PC-SAFT EoS based approach-4 from this work.

		MW (Da)		γ		
Crude	Saturates	A+R	Asp	A+R	Asp	
5	508	637.3	2850	0.32	0.37	
6	524	672.4	2910	0.32	0.37	
7	460	800	6350	0.38	0.18	
8	460	800	5200	0.30	0.25	

Table 7.13. The binary interaction (k_{ij}) parameters used for the PC-SAFT EoS based approach-4 for different crudes. For Crudes 1 and 4, parameters are from Tavakkoli et al [7].

	· •	v					
Crude	Component	nC5	nC7	nC10	nC12	nC16	Saturates
	Aromatic+ Resins	0.007	0.0065	0.006	0.006	0.005	0.007
1	nC5 — nC7 Asphaltenes	0.01 ª	0.007 ^a	0.006	0.005	0.005	0.003
	nC7 – nC10 Asphaltenes	0.01 ª	0.007 ^a	0.006	0.005	0.005	0.003
	nC10 Asphaltenes	0.01 ^a	0.0075 ^a	0.0075 ª	0.006 ^a	0.006 a	0.003
4	nC5 — nC7 Asphaltenes	0	0	0	0	0	-0.009
	nC7 Asphaltenes	0	0	0	0	0	-0.009
5,6,7,8	Asphaltenes	0	0	0	0	0	-0.02

^a Modified in this work to decrease the deviations from the experimental data.

Crude	Experimental Crude density (g/cc)	Calculated Crude density (g/cc)					
1	0.873	0.872					
3	0.982	0.951					
4	1.016	0.997					
5	1.001	1.002					
6	0.995	1.011					
7	0.928	0.927					
8	0.871	0.841					

Table 7.14. The experimental density and calculated density using the PC-SAFT based approach-4, after adjusting aromaticity (γ) of A+R, for Crudes-5 to 8.

Table 7.15. The number of Model Adjustable (MAP) Parameters for all the approaches calculated from experimental data of asphaltene precipitation.

N	umber of Model Adj	ustable (MAP) Para	meters calculated fr	om experimental asp	phaltene precipita	tion data	
МАР	Crude-1	Crude-2	Crude-3	Crude-4	Crude-5	Crude-6	Blend of Crude-7 and 8
		C	PA EoS based appro	paches			
	Approach-1	Approach-1	Approach-2	Approach-2	Approach-3	Approach-3	Approach-3
Self-association energy of asphaltene	1 ^a	1 ^a	1 ^a	1 ^a	0	0	l (Crude-8)
Cross-association energy with maltene/(A+R)	1	1	1	1	1	1	2 (Crude-7 and 8)
Cross-association energy with precipitant	5 (5 precipitants)	4 (4 precipitants)	2 (2 precipitants)	2 (2 precipitants)	0	0	2 (Crude-7 and 8 with Toluene)
Amount of Asp6	1	1	1	1	0	0	0
Total	8	7	5	5	1	1	5
		PC	-SAFT EoS based aj	proach			
	Approach-4	Approach-4	Approach-4	Approach-4	Approach-4	Approach-4	Approach-4
Asphaltene component MW	3 (3 components)	Not studied	2 (2 components)	2 (2 components)	0	0	2 (Crude-7 and 8)
Asphaltene components aromaticity	1 ^b	Not studied	1 ^b	1 ^b	1	1	2 (Crude-7 and 8)
k_{ij} (asphaltene-saturates)	3 (3 components)	Not studied	1	1	1	1	1
k_{ij} (asphaltene- precipitants)	15 (3 components) (5 precipitants)	Not studied	0	0	0	0	0
k_{ij} (saturates-(A+R))	1	Not studied	0	0	0	0	0
Total	23	Not studied	4	4	2	2	5

^a Self-association energy of Asp1, Asp2 and Asp3 components are assumed same.

^b Aromaticity of all asphaltene components of the crude are assumed same.

Asphaltene Precipitation from Light Crudes

Crude-1 is an Iranian crude whose information including the experimental data are referred from Hirschberg et al [2]. It is characterized using the CPA EoS based approach-1 and the PC-SAFT EoS based approach-4. The characterization of the crude and model parameters for approach-4 are referred from the work of Tavakkoli et al [7]. Fig. 7.1a shows the experimental asphaltene yield for nC5, nC7, and nC10 precipitants while Fig. 7.1b shows the experimental concentration of precipitant (nC7, nC10, nC12 and nC16) at the onset of asphaltene precipitation condition. Fig. 7.1a and 7.1b show that both approaches can correlate the data but the accuracy of approach-1 is higher than approach-4. It should be noted that approach-4, with all $k_{ii}=0$, cannot predict the asphaltene precipitation during the addition of *n*-paraffin. However, as shown in Fig. 7.1a, when k_{ij} is used, as shown in Table 7.13, approach-4 can correlate the asphaltene precipitation data. The higher value of k_{ii} (e.g. k_{ii} with nC5 is greater than that with nC7) results in more asphaltene yield. From Fig. 7.1b, one can analyze that the difference between the approaches-1 and 4 fitted results for the nC5 concentration at the onset point is large since the higher value of k_{ii} lowers the precipitant concentration at onset. From the approach-4 results, it can be concluded that it cannot predict both types of the experimental data (the asphaltene yield and onset condition for different *n*-paraffins) qualitatively. The approach-1 results of onset conditions are not very sensitive to the cross-association energy of n-paraffin since the crossassociation between *n*-paraffin undissolved asphaltene (Asp6) component and *n*-paraffin is not considered. Therefore, approach-1 can predict both types of experimental data qualitatively. For approach-1, the difference between the values of cross-association energies for nC5-asphaltenes and *nC7*-asphaltenes pairs is higher than the difference between the values of cross-association energies for the nC7-asphaltenes and nC10-asphaltenes pairs. The two widely different values of the model parameters (cross-association energy in approach-1 and k_{ii} value in approach-4) related to nC5 and nC7 precipitants are due to the widely different values of respective asphaltene yield. From the fitted results using both approaches, as shown in Fig. 7.1a, it is observed that the asphaltene yield decreases at higher dilution of nC7 and nC10. Hirschberg et al [2] did not mention the error margin on the experimental data. Wang and Buckley [28] concluded from their experimental studies that the asphaltene yield increases with the amount of *n*-paraffin, reaches a maximum value, then decreases at higher amount of *n*-paraffin. They observed the maximum in the asphaltene yield at around 30:1 to 40:1 *n*-paraffin:oil volume ratio when *nC6* or *nC7* used. For *nC5*, they observed the maximum at around 80:1 n-paraffin: oil volume ratio. They mentioned that the overall error on asphaltenes amount measurement was around ± 0.02 wt%.



Fig. 7.1. Crude-1: (a) Asphaltene yield during the addition of nC5, nC7 and nC10 paraffins. (b) Amount of different n-paraffin (nC5, nC7, nC10, nC12, nC16) required at the onset of asphaltene precipitation. Experimental data are from Hirschberg et al [2]. All experimental data (Fig. 7.1a and 7.1b) are used for the parameters estimation.

Crude-2 is a Mexican crude whose information including the experimental data are referred from Buenrostro-Gonzalez et al [15]. The experimental data of the asphaltene yield for nC5, nC7, nC9 and nC12 precipitants are available. For this crude, only the CPA EoS based approach-1 is studied. Fig. 7.2 shows that approach-1 is able to correlate the data after calculating the model adjustable parameters. The PC-SAFT EoS based approach-4 could also predict this data but we could not fit the model due to the difficulty of estimation of a large number of model adjustable parameters. Buenrostro-Gonzalez et al [15] used the SAFT-VR EoS in McMillan-Mayer framework developed by Wu et al [16-17] to predict this experimental data (with seven adjustable model parameters), however, their model results are not as accurate as the results of this work. The reader is referred to their work for more detail.



Fig. 7.2. Crude-2: Asphaltene yield during the addition of nC5, nC7, nC9 and nC12 paraffins. Lines represent the correlations using approach-1. Symbols represent the experimental data from Buenrostro-Gonzalez [15].

Asphaltene Precipitation from Heavy Crudes

Crude-3 and 4 are Russian and Venezuelan heavy oils respectively whose information including the experimental data are referred from Sabbagh et al [13]. They mentioned that the asphaltene yield data were repeatable to ± 0.015 (wt/wt). For approach-4, the oil characterization and model parameters are referred from Tavakkoli et al [7]. For these crudes, the experimental data of asphaltene yield for *nC*5 and *nC*7 precipitants are available. As seen from Fig. 7.3a and 7.3b, approach-2 can correlate the data better than approach-4. For approach-4, only one k_{ij} , of negative value, between saturates and asphaltenes is used. The k_{ij} value is used to correlate the onset condition.



Fig. 7.3. (a) Crude-3: Asphaltene yield during the addition of nC5 and nC7 paraffins. (b) Crude-4: Asphaltene yield during the addition of nC5 and nC7 paraffins. Experimental data are from Sabbagh et al [13] for both Crude-3 and 4.

Fig. 7.4 shows the predictions of asphaltene yield for Crude-3 for nC7, nC9, nC10 and nC11 precipitants using approach-4. One can see that for the nC10 precipitant, the asphaltene yield is zero and the asphaltene yield for nC11 is higher than that for nC9, when precipitant concentration is 40 cm³/g of oil. However, it contradicts the general experimental behavior from the literature, where the asphaltene yield always decreases or remains almost constant as the carbon number of paraffinic solvent is increased. Therefore, we hypothesize that approach-4 needs k_{ij} between asphaltenes and precipitant (like Crude-1) before calculating the PC-SAFT parameters of polydisperse asphaltene fraction. In other words, the asphaltene yield of the crude for different *n*-paraffin precipitants cannot be predicted using approach-4 but can be correlated considering k_{ij} between asphaltene yield for different *n*-paraffin and that is why the approach-2 predictions, like Fig. 7.4 for the approach-4 predictions, are not shown. The same behavior of the approach-4 results, like Fig. 7.4 for Crude-3, has been observed for Crude-4 but results are not shown here. Therefore, one must check physical behaviors (mole fraction of *n*-paraffin at the precipitation onset, discussed later, and the asphaltene yield should decrease with the carbon number of *n*-paraffin) while calculating the model parameters.



Fig. 7.4. Crude-3: Predictions of the asphaltene yield during the addition of different n-paraffins using approach-4.

Asphaltene Precipitation Onsets for Heavy Crudes

When the asphaltene precipitation onset conditions are modeled for the reservoir fluid (at high T and P), the asphaltene fraction is usually considered as a monodisperse fraction/component since we are generally interested in calculating the onset conditions. Therefore, it is important to check whether the modeling approaches can predict the onset conditions when the asphaltene fraction is treated as a single component. Crude-5 and 6 are Cold Lake Bitumen and Athabasca heavy oils respectively whose information including the experimental data are referred from Wiehe et al [11]. The experimental data of asphaltene onset conditions for different *n*-paraffin are available for these crudes. Wiehe et al [11] mentioned that the precision of the onset data is within 0.1 vol%. Fig. 7.5a and 7.5b show the experimental onset data and model fitted results on molar and volume basis respectively for Crude-5. Fig. 7.5a shows that the experimental g-moles of *n*-paraffin at the onset condition decreases with the *n*-paraffin carbon number. Fig. 7.5b shows that the experimental data has a maximum at the *n*-paraffin carbon number of 9. Fig. 7.5a and 7.5b show that approach-3 correlates the experimental data qualitatively while approach-4 has major deviations. Approach-4 is studied with respect to scenarios-1 and 2. In scenario-1, the standard n-paraffin PC-SAFT parameters from Gross and Sadowski [26] are used while in scenario-2, the n-paraffin PC-SAFT parameters are calculated from the generalized MW correlations, as shown in Table 7.7. For all other crudes, approach-4 is studied with scenario-1 only. Approach-4 with scenario-1 introduces an inconsistent effect of carbon number that does not seem to exist in the experimental data as shown in Fig. 7.5. On the other hand, approach-4 with scenario-2 gives linear trend as shown in Fig. 7.5. Therefore, the nonlinearity with scenario-1 is due to the inconsistent values of the PC-SAFT parameters for the *n*-paraffin (especially for *nC*7 to nC10). The other model parameters like the PC-SAFT parameters of other components and k_{ij}

values are kept the same for scenarios-1 and 2. The approach-4 with scenario-2 model fitted results on volume basis, as shown in Fig. 7.5b, have considerable deviations due to the poor predictions of the fitted results on mole basis shown in Fig. 7.5a. It should be noted that approach-4 with scenario-2 still gives accurate prediction of the molar volume. Therefore, it can be concluded that the asphaltene onset precipitation is very sensitive to the PC-SAFT parameters and detailed study about it could give us more insight. For approach-4 with scenarios-1 and 2, using k_{ij} value for asphaltenes*n*-paraffin pair could correlate the experimental onset data. The same conclusion, like Crude-5, can be drawn for Crude-6 from Fig. 7.6. From Table 7.8, one can observe that Crudes-5 and 6 have almost similar properties and SARA fractions. For approach-4, a negative k_{ij} value (-0.02) between saturates and asphaltenes is used for both Crudes-5 and 6 to decrease the deviations from the experimental data. Since there are multiple sets of MW and aromaticity values, which give the same modeling results (for approach-4), the experimental MW for the asphaltene component is used to reduce the number of adjustable parameters and the aromaticity value is calculated from the experimental data. The results of mole fraction of *n*-paraffin at the asphaltene onset condition for crudes-1 to 6 are mentioned in Table 7.16.



Fig. 7.5. Crude-5: (a) Amounts of n-paraffin on molar basis at the onset of asphaltene precipitation. (b) Amounts of n-paraffin on volume basis at the onset of asphaltene precipitation. Experimental data are from Wiehe et al [11]. Solid lines are from approach-3, dashed lines are from approach-4 with scenario-1, dotted lines are from approach-4 with scenario-2.



Fig. 7.6. Crude-6: Amounts of n-paraffin on volume basis at the onset of asphaltene precipitation. Experimental data are from Wiehe et al [11].

	Mole Fraction of <i>n</i> -paraffin at Asphaltene Onset											
n paraffin	Crude-1		Crude-2	Crude-3		Cru	de-4	Cru	ude-5	Crude-6		
<i>n</i> -parami	CDA	PC-	CDA	CDA	PC-		PC-	CDA	PC-	CPA	PC-	
	CFA	SAFT	UFA	CFA	SAFT	CFA	SAFT	CFA	SAFT		SAFT	
nC5	0.716	0.633	0.575	0.830	0.809	0.870	0.798	0.892	0.887	0.917	0.890	
nC6	-	-	0.544 ^a	0.827 ^a	0.835	0.874 ^a	0.810	0.889	0.900	0.916	0.901	
nC7	0.681	0.697	0.516	0.818	0.863	0.874	0.824	0.881	0.913	0.909	0.913	
nC8	-	-	0.491 ^a	0.730 ^b	0.846	0.796 ^b	0.801	0.877	0.899	0.904	0.899	
nC9	-	-	0.467	0.724 ^b	0.869	0.779 ^b	0.815	0.866	0.911	0.896	0.910	
nC10	0.616	0.643	0.445 ^a	0.706 ^b	0.914	0.773 ^b	0.830	0.855	0.933	0.887	0.930	
nC11	-	-	0.406 ^a	0.690 ^b	0.793	0.759 ^b	0.747	0.838	0.857	0.874	0.856	
nC12	0.550	0.593	0.387	0.672 ^b	0.774	0.745 ^b	0.721	0.826	0.843	0.865	0.847	
nC13	-	-	0.371 ^b	0.657 ^b	0.701	0.741 ^b	0.666	0.812	0.794	0.854	0.798	
nC14	-	-	0.358 ^b	0.642 ^b	0.701	0.718 ^b	0.655	0.785	0.790	0.831	0.796	
nC15	-	-	0.322 ^b	0.628 ^b	0.639	0.716 ^b	0.605	0.774	0.742	0.822	0.749	
nC16	0.445	0.436	0.291 ^b	0.615 ^b	0.640	0.694 ^b	0.610	0.752	0.738	0.800	0.747	

Table 7.16. Mole fraction of different n-paraffin at the onset of asphaltene precipitation using CPA and PC-SAFT approach.

^a Cross-association energy value between *nCN* -asphaltene is interpolated.

^b Cross-association energy value between nCN -asphaltene is assumed same as that of between maltene/(A+R)asphaltene as a conservative measure to show the mole fraction trend with carbon number of *n*-paraffin.

Asphaltene Precipitation Onsets from Blending of Crudes

In this section, the modeling approach to calculate the asphaltene precipitation onsets from the blends of Crudes-7 and 8 is discussed. Crudes-7 and 8 are from Gulf of Mexico and Middle East respectively whose information including the experimental data are referred from Tharanivasan et al [12]. They

mentioned that the repeatability (in terms of relative standard deviation) of the measured yields was within $\pm 14\%$ and $\pm 5\%$ of the reported yield data at low (*n*-heptane mass fraction <0.6) and high (*n*heptane mass fraction>0.6) dilution ratios respectively of crude oil or blend. The repeatability for the onset measurements was within $\pm 4\%$ of the reported amount of *n*-heptane at the onset. The experimental data of *nC7* precipitant mass fraction at the onset of asphaltene precipitation from the blends of Crude-7 or 8 with three different toluene concentrations are available as shown in Fig. 7.7. Also, the experimental data of *nC*16 mass fraction at the onset of asphaltene precipitation from the blend of Crude-7 with three different concentrations of Crude-8 are available as shown in Fig. 7.8. The approaches-3 and 4 parameters, as shown in Table 7.10 and 7.12 respectively, are calculated from the experimental data of Figs. 7.7 and 7.8 and the model fitted results are also shown in the same figures. As shown in Fig. 7.7, both approaches can correlate the experimental data. Fig. 7.8 shows that only approach-3 can correlate the non-linear behavior whereas approach-4 shows almost a linear trend between two extremes, which represent pure Crude-7 result (left) and pure Crude-8 result (right). For approach-3, this non-linearity increases with the difference between the self-association energies for the Crude-7 and Crude-8 asphaltenes. In other words, a large difference between the solubility parameters of asphaltene component of Crudes-7 and 8 is required. However, for approach-4, the appropriate parameters could not be found, which can show the non-linearity. The minimum in this non-linear behavior is very important to decide the correct order of crudes to prepare the blend. For example, in this case, the minimum is close to the extreme of pure Crude-8 as shown in Fig. 7.8. Therefore, one should always prepare the blend by adding Crude-8 into Curde-7 and not the other way. The experimental data for the blend of Crude-7 and Crude-8 with three different toluene concentrations are also available as shown in Fig. 7.9. This figure shows that the approach-3 predictions have minor deviations while the approach-4 predictions have moderate deviations from the experimental data. One can also analyze that the trend between two extremes becomes more linear as the toluene concentration is increased. It would also be interesting to study the blend of three or more asphaltenic crudes, however, we could not find such experimental data from the literature.



Fig. 7.7. Crude-7 and 8: Amount of n-Heptane at the onset of asphaltene precipitation for the blend of different concentrations of crude oil and toluene. Experimental data are from Tharanivasan et al [12].



Fig. 7.8. Amount of *n*-Hexadecane at the onset of asphaltene precipitation for the blend of different concentrations of Crude-7 and 8. Experimental data are from Tharanivasan et al [12].



Fig. 7.9. Amount of *n*-Heptane at the onset of asphaltene precipitation for the blends of Crude-7, 8 and toluene at three different concentrations of toluene. Symbols represent the experimental data from Tharanivasan et al [12].

7.4 Conclusions

Based on the results found in this work we conclude that the solubility of asphaltene fraction in solvent at precipitation onset condition can be calculated from experimental data of onset composition for different *n*-paraffin precipitants. The solubility of asphaltene fraction is not dependent upon the number of solvent (maltene) components. The asphaltene fraction can be treated as monodisperse (single component) rather than polydisperse (multiple components) to calculate onset composition of the precipitant. The results for Crudes-5 and 6 show that the CPA EoS based approach-3 (with one adjustable parameter) can accurately correlate the onset composition while the PC-SAFT EoS based approach-4 without association term (with two adjustable parameters) has moderate deviations. Approach-4 needs binary interaction parameters to correlate the onset composition. With the modeling approaches used in this work, the asphaltene yield during the addition of a precipitant can only be correlated with given experimental data of asphaltene yield with the same precipitant. The approaches consider the asphaltene fraction as multiple components having different solubility parameters to correlate asphaltene yield. For the CPA EoS based approaches-1 and 2, different selfassociation energies are used to define multiple asphaltene components. For the PC-SAFT EoS based approach-4, different pure component parameters are used to define multiple asphaltene components. In addition, one adjustable parameter linked to the specific precipitant is also used. For approaches-1 to 3, it is the cross-association energy between precipitant and asphaltene. For approach-4, it is the k_{ij} value between precipitant and asphaltenes. It is also shown from the results of Crudes-3 and 4 that when k_{ii} values (for *n*-paraffin- asphaltene pairs) for approach-4 are not used, the model predictions of asphaltene yield for different *n*-paraffin precipitants are not in agreement with the observed physical behavior of asphaltene precipitation: (a) In the first case it has been observed that the asphaltene yield decreases or remains constant with the carbon number of n-paraffin (b) In the second case the mole fraction of *n*-paraffin precipitant at onset condition is known to decrease with the carbon number of *n*-paraffin. A detailed study of the PC-SAFT parameters of *n*-paraffins (especially for *n*heptane to *n*-decane) is required to establish monotonic trend of the mole fraction of *n*-paraffin precipitants at the onset conditions versus the carbon number of *n*-paraffin. It is also observed from the results of Crudes-7 and 8 that approach-3 correlates and predicts the non-linear trend of onset condition for the blend (Fig. 7.8 and 7.9) while approach-4 cannot. It should be noted that similar approach based on the CPA EoS has already been studied with respect to the asphaltene precipitation onset conditions from the reservoir fluid in our previous studies [20-22].

References

- 1 J. G. Speight, Petroleum Asphaltenes-Part 1: Asphaltenes, resins and the structure of petroleum, Oil and gas science and technology 59-5 (2004) 467-477.
- 2 Hirschberg, A., DeJong, L. N. J., Schipper, B. A., and Meijer, J. G. (1984). Influence of temperature and pressure on asphaltene flocculation. Society of Petroleum Engineers Journal, 24(03), 283-293.
- 3 F. Vargas, M. Garcia-Bermudes, M. Boggara, S. Punnapala, M.I. Abutaqiya, N.T. Mathew, H.Y. Al Asafen, On the Development of an Enhanced Method to Predict Asphaltene Precipitation, In Offshore Technology Conference held in Houston, Texas, USA, May-(2014).
- 4 Mitchell, D. L., and Speight, J. G. (1973). The solubility of asphaltenes in hydrocarbon solvents. *Fuel*, *52*(2), 149-152.
- 5 Koots, J. A and Speight, J. G. (1975). Relation of petroleum resins to asphaltenes. Fuel, 54(3), 179-184.
- 6 Wiehe, I. A., and Kennedy, R. J. (2000). The oil compatibility model and crude oil incompatibility. *Energy fuels*, *14*(1), 56-59.
- 7 Tavakkoli, M., Panuganti, S. R., Taghikhani, V., Pishvaie, M. R., and Chapman, W. G. (2014). Understanding the polydisperse behavior of asphaltenes during precipitation. *Fuel*, *117*, 206-217.
- 8 Alboudwarej, H., Akbarzadeh, K., Beck, J., Svrcek, W. Y., and Yarranton, H. W. (2003). Regular solution model for asphaltene precipitation from bitumens and solvents. *AIChE Journal*, *49*(11), 2948-2956.
- 9 Akbarzadeh, K., Alboudwarej, H., Svrcek, W. Y., and Yarranton, H. W. (2005). A generalized regular solution model for asphaltene precipitation from n-alkane diluted heavy oils and bitumens. *Fluid Phase Equilibria*, 232(1), 159-170.
- 10 Pazuki, G. R., and Nikookar, M. (2006). A modified Flory-Huggins model for prediction of asphaltenes precipitation in crude oil. *Fuel*, *85*(7), 1083-1086.
- 11 Wiehe, I. A., Yarranton, H. W., Akbarzadeh, K., Rahimi, P. M., and Teclemariam, A. (2005). The paradox of asphaltene precipitation with normal paraffins. *Energy & Fuels*, *19*(4), 1261-1267.
- 12 Tharanivasan, A. K., Svrcek, W. Y., Yarranton, H. W., Taylor, S. D., Merino-Garcia, D., and Rahimi, P. M. (2009). Measurement and modeling of asphaltene precipitation from crude oil blends. *Energy & Fuels*, 23(8), 3971-3980.
- 13 Sabbagh, O., Akbarzadeh, K., Badamchi-Zadeh, A., Svrcek, W. Y., and Yarranton, H. W. (2006). Applying the PR-EoS to asphaltene precipitation from n-alkane diluted heavy oils and bitumens. *Energy & fuels*, 20(2), 625-634.
- 14 Panuganti, S. R., Tavakkoli, M., Vargas, F. M., Gonzalez, D. L., and Chapman, W. G. (2013). SAFT model for upstream asphaltene applications. *Fluid Phase Equilibria*, *359*, 2-16.
- 15 Buenrostro-Gonzalez, E., Lira-Galeana, C., Gil-Villegas, A., and Wu, J. (2004). Asphaltene precipitation in crude oils: Theory and experiments. *AIChE Journal*, *50*(10), 2552-2570.
- 16 Wu, J., Prausnitz, J. M., and Firoozabadi, A. (1998). Molecular-thermodynamic framework for asphaltene-oil equilibria. *AIChE Journal*, 44(5), 1188-1199.
- 17 Wu, J., Prausnitz, J. M., and Firoozabadi, A. (2000). Molecular thermodynamics of asphaltene precipitation in reservoir fluids. *AIChE journal*, *46*(1), 197-209.
- 18 Li, Z., and Firoozabadi, A. (2010). Modeling asphaltene precipitation by n-alkanes from heavy oils and bitumens using cubic-plus-association equation of state. *Energy & Fuels*, 24(2), 1106-1113.
- 19 G.M. Kontogeorgis, G.K. Folas, Thermodynamic models for industrial applications: from classical and advanced mixing rules to association theories. John Wiley and Sons (2009).
- 20 Arya, A., von Solms, N., and Kontogeorgis, G. M. (2015). Determination of asphaltene onset conditions using the cubic plus association equation of state. *Fluid Phase Equilibria*, 400, 8-19.
- 21 Arya, A., von Solms, N., & Kontogeorgis, G. M. (2015). Investigation of the Gas Injection Effect on Asphaltene Onset Precipitation Using the Cubic-Plus-Association Equation of State. *Energy & Fuels*, *30*(5), 3560-3574.
- 22 Arya, A., Liang, X., von Solms, N., and Kontogeorgis, G. M. (2016). Modeling of Asphaltene Onset Precipitation Conditions with Cubic Plus Association (CPA) and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) Equation of States. Energy & Fuels, 30(8), 6835-6852.

- 23 Kesler, M. G., and Lee, B. I. (1976). Improve prediction of enthalpy of fractions. Hydrocarbon processing, 55(3), 153-158.
- 24 Pedersen, K. S., Christensen, P. L., and Shaikh, J. A. (2014). Phase behavior of petroleum reservoir fluids. CRC Press.
- 25 Speight, J. G., Long, R. B., Trowbridge, T. D., and Linden, N. (1982). On the definition of asphaltenes. *Am. Chem. Soc., Div. Pet. Chem., Prepr.*, 27(3), 268-275.
- 26 Gross, J., and Sadowski, G. (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & engineering chemistry research*, *40*(4), 1244-1260.
- 27 Gonzalez, D. L., Hirasaki, G. J., Creek, J., and Chapman, W. G. (2007). Modeling of asphaltene precipitation due to changes in composition using the perturbed chain statistical associating fluid theory equation of state. *Energy & fuels*, *21*(3), 1231-1242.
- 28 Wang, J., and Buckley, J. (2007). Effect of dilution ratio on amount of asphaltenes separated from stock tank oil. *Journal of dispersion science and technology*, 28(3), 425-430.

Chapter 8. Conclusions and Recommendations

8.1 Conclusions

- ➤ In this project, a modeling approach is developed to model asphaltene precipitation using the Cubic Plus Association (CPA) and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) equations of state (EoS). There are few studies of asphaltene modeling with the CPA and PC-SAFT (without association term) EoS in the literature. The PC-SAFT (including association term) is first applied in this work for asphaltene modeling. The modeling approach is very simple and divides the C_{6+} fraction into only two components (heavy component and asphaltene) in order to calculate asphaltene onset conditions.
- The developed modeling approach (using the CPA/PC-SAFT EoS) can predict the gas injection effect on asphaltene onset condition. It can successfully be used to study the enhanced oil recovery (EOR) by gas injections before implementing it (EOR). The approach is temperature dependent and needs one experimental onset condition for a given temperature. It is believed that around 3-4 experimental onset points are required in the temperature range of interest.
- It is also shown that the CPA/PC-SAFT model with the developed modeling approach is not very sensitive to the molecular weight or molar amount of asphaltenes for the prediction of onset conditions during different amounts of gas injection. However, the model need the correct amount of asphaltene (mass basis) in order to predict amount of precipitated asphaltene during the reservoir oil depressurization. The model does not need the amount of saturates, aromatics and resins fractions.
- The developed modeling approach using both CPA and PC-SAFT EoS are compared with the modeling approach from the literature based on the PC-SAFT (without association term) term EoS. It is found that the PC-SAFT (without association term) model cannot correlate the asphaltene upper onset pressure boundary for certain fluids and needs temperature dependency. The PC-SAFT (without association term) can also predict the gas injection effect after correlating the experimental data for a given temperature.
- ▶ The modeling approach is studied with the Soave-Redlich-Kwong (SRK) EoS using both classical and Huron-Vidal mixing rules. Asphaltenes are considered a non-associating component for these SRK based models. It is found that the SRK based models can also predict the gas injection effect but the molar amount of asphaltene in C_{6+} fraction needs to be

fixed to a certain value at which the binary interaction parameters for gas/light alkanesasphaltenes pairs are regressed.

- > It is shown that the modeling approach is not affected when the C_{6+} fraction is divided into multiple heavy and one asphaltene components instead of one heavy and one asphaltene component. Thus, it can easily be integrated with existing PVT simulators.
- The models presented in this work cannot predict the asphaltene yield from degassed crudes but can correlate the experimental data.
- The models presented in this work can predict the onset conditions when different *n*-alkane precipitants are used. The models can also predict the asphaltene stability when more than two crudes are blended based on the experimental data of each binary system.
- A MATLAB tool is developed to calculate asphaltene phase envelope with or without gas injection and PVT properties of reservoir fluids. It is disseminated and being used by consortium company members.

8.2 Recommendations

- Based on this work, we propose that higher pressure measurement for the asphaltene upper onset point for a given temperature is not required with reservoir oil but relatively simple ambient or near ambient pressure measurement of the amount of *n*-pentane/*n*-heptane precipitant at the onset condition when added into stock tank oil (STO) is sufficient. We need this measurement at different temperatures in the temperature range of interest. Once we have these experimental data for STO, we can add separator gas into STO, with known separator gas composition and GOR, and the model can then predict the asphaltene phase envelope for the given reservoir fluid. This proposed method needs to be validated.
- The modeling approach presented in this work is temperature dependent. The future research should focus to remove this temperature dependency possible by accurately characterizing STO from certain measurements.
- The modeling approach presented in this work is applied to the SRK EoS considering asphaltenes as a non-associating components. One can also study the PC-SAFT (without association term) EoS with this approach.
- We propose a method to calculate asphaltene stability in blends. For example, we need to blend crudes A, B, C and D. Based on the proposed method, asphaltene precipitation data (*n*-heptane amount at the onset of asphaltene precipitation) for binary systems crude-A/B/C/D and reference crude are required. This proposed method needs to be validated.

One can explore the application of density functional theory or Monte-Carlo method to model asphaltene precipitation.

List of Symbols

Parameters

а	=	Energy parameter of mixture (temperature dependent)
<i>a</i> _{0<i>i</i>}	=	Energy parameter of component i (temperature independent)
a _i	=	Energy parameter of component i (temperature dependent)
a _{0i}	=	Universal Constants in the PC-SAFT EoS
a _{1i}	=	Universal Constants in the PC-SAFT EoS
Å	=	Angstrom (unit of length)
A ^{res}	=	Residual Helmholtz Free Energy
A ^{hs}	=	Helmholtz Free Energy for the HS repulsive term
A ^{chain}	=	Helmholtz Free Energy for the chain formation
A ^{disp}	=	Helmholtz Free Energy for dispersion forces between chains
A ^{assoc}	=	Helmholtz Free Energy for association forces between chains
b	=	Co-volume parameter of mixture
b _i	=	Co-volume parameter of component <i>i</i>
b _{0i}	=	Universal Constants in the PC-SAFT EoS
b_{1i}	=	Universal Constants in the PC-SAFT EoS
С	=	Compressibility
$c_{1,i}, c_{2,i}, c_{3,i}$	=	Parameter in the energy term of component <i>i</i> , dimensionless
C ₆₊	=	<i>n</i> -hexane plus fraction
d_i	=	Temperature dependent diameter of spherical segment
g	=	Radial Distribution Function
g^E_∞	=	Excess Gibbs Free Energy at infinite pressure
G^E	=	Excess Gibbs Free Energy
g_{ii}^{hs}	=	Radial Distribution Function for the mixture of hard spheres
$g0_{ij}$	=	Huron-Vidal parameter: Interaction energy for the pair of components <i>i</i> and <i>j</i>
$gT0_{ij}$	=	Huron-Vidal parameter: Temperature correction factor to interaction energy for the pair of components i and j
H^A	=	Hamaker Constant of Asphaltenes
H^R	=	Hamaker Constant of Resins
H^S	=	Hamaker Constant of Solvent
k	=	Boltzmann constant
k _{ij}	=	Binary interaction parameter
Κ	=	Kelvin
m _i	=	Number of segments/spheres per chain/molecule of component <i>i</i>

M _i	=	Number of association sites on molecule of component <i>i</i>
Ν	=	Total number of Points
N _{AV}	=	Avogadro's constant
nC7	=	<i>n</i> -heptane
nCN	=	<i>n</i> -Paraffin of carbon number <i>N</i>
Р	=	Pressure
P_c	=	Critical Pressure
$P_{c,i}$	=	Critical Pressure
P_{calc}	=	Calculated pressure
P_{exp}	=	Experimental pressure
$P^{Assoc,L}$	=	Association term contribution to the upper onset pressure for asphaltene lean phase
$P^{Assoc,R}$	=	Association term contribution to the upper onset pressure for asphaltene rich phase
$P^{SRK,L}$	=	SRK term contribution to the upper onset pressure for asphaltene lean phase
$P^{SRK,R}$	=	SRK term contribution to the upper onset pressure for asphaltene rich phase
P^{UOP}	=	Upper onset pressure
R	=	Gas constant
Т	=	Temperature
T_c	=	Critical Temperature
$T_{c,i}$	=	Critical Temperature
V_m	=	Molar volume
X_{A_i}	=	Mole fraction of site-A in molecule <i>i</i> not bonded to any other site/s
x_i	=	Mole fraction of component <i>i</i>

Greek Letter

α_{ij}	=	Non-randomness factor for the pair of component <i>i</i> and <i>j</i> in Huron-Vidal mixing rule
$\rho A_i B_i$	=	Association volume between site A of molecule of component <i>i</i> and site B of molecule of component
p · ,		j
$\Delta^{A_iB_j}$	=	Association strength between site A of component i and site B of component j
$\mathcal{E}^{A_i B_j}$	=	Association energy between site A of molecule of component i and site B of molecule of component j
ϵ_i	=	Potential energy between spherical segments of component <i>i</i>
η	=	Packing fraction
$\mathcal{K}^{A_iB_j}$	=	Association volume between site A of molecule of component i and site B of molecule of component j
γ	=	Aromaticity (1 means 0% benzene derivative and 100% PNA)
γ1	=	Aromaticity (1 means 100% benzene derivative and 0% saturates)
ω	=	Acentric factor
ρ	=	Molar density
$\hat{ ho}$	=	Number density

 σ_i = Temperature independent diameter of spherical segment of component *i* in the PC-SAFT EoS

 ω = Acentric factor

List of Abbreviations

A	=	Aromatics
	_	Average Absolute Deviation (AAD) = $\sum_{i}^{N} RD_i $, where $ RD_i $ is the absolute value of RD of
AAD	_	point <i>i</i> ,N is a total number points.
ADE	=	Asphaltene Deposition Envelope
AEOS	=	Association Equation of State
APE	=	Asphaltene Phase Envelope
AOE	=	Asphaltene Onset Envelope
A+R	=	Aromatics+Resins
Asp	=	Asphaltene
ASTM	=	American Society for Testing and Materials
Avg	=	Average
BP	=	Bubble Point/ Bubble Pressure
Calc	=	Calculated
CERE	=	Center for Energy Resources and Engineering
CME	=	Constant Mass Expansion
СРА	=	Cubic Plus Association
CR	=	Combining Rule
C1	=	Methane
C2	=	Ethane
C3	=	Propane
Da	=	Dalton
DTU	=	Technical University of Denmark
EOR	=	Enhanced Oil Recovery
EoS	=	Equation of State
Exp	=	Experimental
GI	=	Gas Injection
GOR	=	Gas to Oil ratio
H/HC	=	Heavy Component
HCs	=	Hydrocarbons
H/C	=	Hydrocarbon
HP	=	High Pressure
HPM	=	High Pressure Microscopy
HS-SAFT	=	Hard Sphere SAFT
HT	=	High Temperature
IP	=	Institute of Petroleum
IOR	=	Improved Oil Recovery
LLE	=	Liquid Liquid Equilibrium
LOP	=	Lower Onset Pressure

МАР	=	Model Adjustable Parameter
MMP	=	Minimum Miscibility Pressure
MW	=	Molecular Weight
NA	=	Not available
NIR	=	Near Infrared
OOIP	=	Original Oil in Place
PC	=	Pseudo component
PC-SAFT	=	Perturbed Chain Statistical Association Fluid Theory
PC-SAFT (WA)	=	PC-SAFT with association term
PC-SAFT (WOA)	=	PC-SAFT without association term
PNA	=	Polynuclear Aromatics
PR	=	Peng Robinson
PR-P	=	Peng Robinson with Peneloux volume correction
PSA	=	Particle Size Analysis
РТ	=	Pressure-Temperature
R	=	Resins
RAAOP	=	Relative Amount of Asphaltene in Oil Phase
RD	=	Relative Deviation = $=\frac{x_{exp}-x_{calc}}{x_{exp}} \times 100$, where x is any propertie e.g. pressure
S	=	Saturates
SAFT	=	Statistical Associating Fluid Theory
SAFT-HS	=	Statistical Associating Fluid Theory with Hard Sphere potential
SAFT-VR	=	Statistical Associating Fluid Theory with Variable Range potential
SARA	=	Saturates Aromatics Resins Asphaltenes
SCN	=	Single Carbon Number
SDS	=	Solid Detection System
SG	=	Specific Gravity
SRK	=	Soave Redlich Kwong
SRK+HV	=	Soave Redlich Kwong with Huron-Vidal mixing rule
SRK-P	=	Soave Redlich Kwong with Peneloux volume correction
STO	=	Stock Tank Oil
UOP	=	Upper Onset Pressure
VLE	=	Vapor Liquid Equilibrium
WAG	=	Water Alternating Gas

List of Figures

Fig. 1.1. Oil-Gas Separator System	11
Fig. 1.2. Typical procedure of SARA analysis. STO=Stock Tank Oil (oil at ambient condition)	12
Fig. 1.3. Asphaltene phase envelope (APE).	13
Fig.3.1. Fluid-C1 upper/lower asphaltene onset pressures and bubble points vs temperature. Symbols (s onset, circles for bubble points) represent experimental data from Buenrostro et al [4] and lines for upper pressures are the correlations by CPA with $\varepsilon^{AH} / R = 1594 + 16166/T$ K and P of HC =17.79 bar. Line	quares for upper onset and bubble e for lower onset

Fig. 3.4. Fotland 1997: Upper onset and bubble point pressure vs amount of gas injection at 365 K. Symbols (squares for upper onset and circles for bubble points) represent experimental data from Fotland [34] and lines are correlations by CPA with $\varepsilon^{AH} / R = 1428$ K and P_c of HC = 20.21 bar. (a) with default values of k_{ij} mentioned in Table 3.3 (b) when methane/ethane/propane-asphaltene pairs $k_{ij} = (-0.2)$.

Fig. 3.6. Kabir 1999: (a) upper/lower asphaltene onset pressures and bubble points vs temperature. Symbols (squares for upper onset, circles for bubble points, and triangles for lower onset) represent experimental data from Kabir et al [36]. Lines for upper onset and bubble curves (for oil without gas injection) are the correlations by CPA with ε^{AH} / R =1257+81602/T K and P_c of HC =19.97 bar. Line for lower onset curve and effect of 10 mol% of N_2 , CO_2 and methane (C1) injections on upper onset pressures are the predictions by CPA after determination of ε^{AH} / R and P_c of HC. (b) Asphaltene content in the oil vs pressure at 322 K. Symbols represent experimental data from Kabir et al [36] and the line represents the prediction by CPA.

Fig. 3.7. Jamaluddin 2002: (a) upper/lower asphaltene onset pressures and bubble points vs temperature. Symbols (squares for upper onset, circles for bubble points, triangles for lower onset) represent experimental data from Jamaluddin

Fig. 3.10. Ting 2003: (a) Volume fraction of different n-alkane at the onset of asphaltene precipitation at 293 K and 1 bar vs carbon number of respective n-alkane. Circles represent experimental data from Ting et al [14] and cross marks represent the correlation by CPA with $\varepsilon^{AH} / R = 2132$ K. (b) Upper onset and bubble point pressures vs amount of methane injected in terms of mass fraction. Symbols represent experimental data and lines are the predictions with CPA.

Fig. 4.8. Fluid-3: UOP and bubble points vs temperature for different types of gas injections. Symbols (squares for upper onset, circles for bubble points) represent experimental data from Gonzalez et al [37]. (Plot-a) Lines for upper onset and bubble pressures for 0 mol% gas injection case are the correlations by CPA with $\varepsilon^{AH} / R = 3977-58536/T$ K, P_c of HC =19.13 bar, $\varepsilon^{AA}/R = 7000$ K & $\beta^{AH} = 0.05$ (case-1/solid lines) and $\varepsilon^{AH} / R = 1887-33418/T$ K, P_c of HC =19.13 bar for default values of $\varepsilon^{AA}/R = 3000$ K & $\beta^{AH} = 0.05$ (case-2/dashed lines). Lines for 10 mol% of N_2 (Plot-b), CO_2 (Plot-c), CH_4 (Plot-d) and nC7 (plot-e) injections are the predictions after determination of ε^{AH} / R , ε^{AA}/R and P_c of HC using the 0 mol% gas injection case. (Plot-f) Comparison of UOP boundaries for different types of gas injections using the two parameters approach (case-2).

Fig. 4.11. Fluid-5: Comparison of upper onset pressure boundaries for different types of gas injection at 373 K. ε^{AH} / R =1540 K, P_c of HC =21.5 bar and default value of ε^{AA} / R =3000 K & β^{AH} =0.05 are used. Composition is in mole%.74

Fig. 5.2. Graphical representation of the assumptions made for the modeling approach used in this work from Arya et al [12-20]. (a) Real condition, where asphaltene subfractions are scattered in the medium of heavy component in the heavy oil/STO. (b) All asphaltene subfractions are assumed of having same physical properties. (c) The cross-association energy (ε^{AH}) between asphaltene and heavy component is assumed to be the same everywhere but it is temperature dependent.

Fig. 5.3. Characterization approach for separator gas and STO from Panuganti et al [31]. A=aromatics, R=resins.......90

Fig. 7.3. (a) Crude-3: Asphaltene yield during the addition of nC5 and nC7 paraffins. (b) Crude-4: Asphaltene yield during the addition of nC5 and nC7 paraffins. Experimental data are from Sabbagh et al [13] for both Crude-3 and 4.

Fig. 7.4. Crude-3: Predictions of the asphaltene yield during the addition of different n-paraffins using approach-4...154

Fig. 7.8. Amount of n-Hexadecane at the onset of asphaltene precipitation for the blend of different concentrations of Crude-7 and 8. Experimental data are from Tharanivasan et al [12].

List of Tables

Table 1.1. Equations of state used for different categories of asphaltene modeling study
Table 1.2. Experimental data from the literature used by different groups to compare thier modeling results
Table 2.1. Association Scheme for pure compound molecules as per Huang and Radosz [10] temrminology. 28
Table 3.1. List of models used for asphaltene phase equilibria in the literature. 35
Table 3.2. Comparison of Modeling Approach of this work, Li et al [8] and Zhang et al [9]. 37
Table 3.3. Binary interaction parameter (kij) used by CPA model. T is temperature in K. 38
Table 3.4. Composition and SARA information of reservoir oils required for CPA model. 39
Table 3.5. Injected Gas Composition
Table 3.6. Comparison of lower onset pressure between experimental data and CPA predictions for propane, methane and CO ₂ as precipitants. 49
Table 3.7. Value of cross-association energy ε^{AH} / R (K) and P_c of HC after tuning for all fluids studied
Table 3.8. SARA analysis and cross-association energy ε^{AH} / R (K) at 298 K for five reservoir fluids
Table 4.1. Overview of how this work is different than the available work in the literature, based on asphaltene modeling study with CPA and PC-SAFT. 57
Table 4.2. Binary interaction parameter (kij) used by CPA model from Arya et al [17]. T is temperature in K. A missing value means that the binary interaction parameter is set to zero
Table 4.3. Values of Model Parameters for all fluids studied in this work. 61
Table 4.4. Composition, properties and asphaltene amount (optional) of reservoir fluids required for the CPA model. 61
Table 4.5. Injected Gas Composition in mol% for Fluid-1, Fluid-2 and Fluid-5 from Punnapala & Vargas [20]
Table 4.6. Fluid-1 (Asp MW=750 DA): Pressure contribution due to the association term ($P^{Assoc,R}$) and Asp mol% in the binary mixture of Asp and HC components for the asphaltene rich phase at the upper onset boundary
Table 4.7 . Fluid-1 (Asp MW=750 DA): Pressure contribution due to the association term ($P^{Assoc,R}$), Asp mol% in the mixture of Asp and HC components for asphaltene rich phase and amount of nC7 required at the onset of asphaltene precipitation during nC7 injection into STO at 1.01325 bar

Table 4.11. Fluid-3: Relative Deviation (RD) between experimental data and calculated results for BP and UOP. Experimental data are from Punnapala & Vargas [20]. Model parameters ($\varepsilon^{AH} / R = 3977-58536/T$ K, $\varepsilon^{AA} / R = 7000$ K, P_c of HC =19.13 bar for MW of 750) are calculated from 0% GI case. Data for 10 mol% of N2, CO2, CH4 and nC7 injections are the predictions after determination of ε^{AH} / R , ε^{AA} / R and P_c of HC using the 0 mol% gas injection case.

Table 4.13. Fluid-5: Relative Deviation (RD) between experimental data and calculated results for BP and UOP with
respect to amount of GI at 373 K. Experimental data are from Punnapala & Vargas [20]. Model parameters (\mathcal{E}^{AH} / R
=1540 K & P_c of HC =21.5 bar for \mathcal{E}^{AA}/R =3000K & MW of 750) are calculated from *HCs* GI case. Data
for *HCs* 90% + *N*210% , *HCs* 80% + *CO*220% , *HCs* 96.4% + *H2S* 3.6% , *HCs* 66% + *CO*222% + *N*211% ,
associated gas injections are the predictions after determination of \mathcal{E}^{AH}/R and P_c of HC using *HCs* gas
injection case. Composition is in mole%.79**Table 5.1.** CPA binary interaction parameters (k_{ij}) from Arya et al [12,20]. T is temperature in K.87**Table 5.2.** PC-SAFT (WA) binary interaction parameters (k_{ij}) from Panuganti et al [31].88**Table 5.3.** Empirical correlations for the initial estimation of the PC-SAFT (WA) model parameters for mixture of
saturates and polynuclear aromatics (PNA) derivative components from Punnapala & Vargas [8].89**Table 5.4.** PC-SAFT (WOA) binary interaction parameters (k_{ij}) from Panuganti et al [31].89

Table 5.5. Empirical correlations for the estimation of the PC-SAFT (WOA) model parameters for saturates and mixture of Polynuclear Aromatics (PNA) and benzene derivative components from Panuganti et al [31].

 91

Table 5.6. Properties of fluids used in this work	92
Table 5.7. Calculated values of the model parameters for the CPA and PC-SAFT (WA) for all fluids studied in this	is work. 92
Table 5.8. Composition of reservoir fluids used for the CPA and PC-SAFT (WA) model*.	92
Table 5.9. Composition and PC-SAFT parameters of heavy gas, saturates, A+R and asphaltene required for the PC (WOA) model.	C-SAFT
Table 5.10. Injected Gas Composition in mol% for Fluid-1 [8,31,35] and Fluid-4 [45].	94
Table 5.11. Different sets of SARA analysis used to study Fluid-1.	96
Table 5.12. Average relative deviation in BP, UOP and LOP for all fluids.	105
Table 5.13. Properties of Fluids used in Supplementary Information.	108
Table 5.14. Composition and PC-SAFT parameters of heavy gas, saturates, A+R and asphaltene required for SAFT (WOA) model.	the PC-
Table 6.1. CPA Model: binary interaction parameters (<i>kij</i>).	118
Table 6.2. SRK Model: binary interaction parameters (kij).	119
Table 6.3. SRK+HV Model: binary interaction (kij) and Huron Vidal parameters.	119
Table 6.4. Properties of all fluids used in this work.	120
Table 6.5. Composition of reservoir fluids used in this work for the evaluation of the CPA, SRK and SRK-HV me	odels *. 121
Table 6.6. Calculated values of the model parameters (see Fig. 6.1) for the CPA, SRK and SRK+HV for all fluid	s121
Table 6.7. Injected gas composition in mol% for Fluids-1, 5 and 6	122
Table 6.8. Fluid-1: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experiment for different amounts of gas injection and considering different asphaltene molecular weights.	ıtal data 124
Table 6.9. Pure Component Parameters used for the CPA, SRK and SRK-HV equations of state	132
Table 6.10. Properties and Composition of Heavy Component/s for all fluids studied in this work for a given asp MW. These values are the same for all three models.)haltene 132
Table 6.11. Fluid-1: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to exper data for different amounts of gas injection and considering different asphaltene molecular weights.	imental
Table 6.12. Fluid-2: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to exper data for different amounts of gas injection and considering different asphaltene molecular weights	imental
and a series of the series of	

Table 6.13. Fluid-3: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experime	ental														
data for different amounts of CO2 injection and considering different asphaltene molecular weights.	. 134														
Table 6.14. Fluid-4: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experime	ental														
data for different amounts of N2 injection and considering different asphaltene molecular weights	. 134														
Table 6.15. Fluid-5: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experime	ental														
data for different amounts of CO2 injection and considering different asphaltene molecular weights.	. 135														
Table 6.16 Fluid-6: Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respect to experime	ental														
data for different amounts of H/C gas injection and considering different asphaltene molecular weights	135														
Table 6.17. Fluid-1 (with 9 HC): Relative Deviation (RD) in calculated Upper Onset Pressure (UOP) with respe	ct to														
experimental data for different amount of gas injections and considering different asphaltene molecular weight	. 135														
Table 7.1 Approach 1: Crude oil characterization and components parameters	1/2														
Table 7.1. Approach-1. Crude on characterization and components parameters.	. 142														
Table 7.2. Approach-1: Self-association and Cross-association energy parameter in Kelvin. ^b	. 143														
	1.40														
Table 7.3. Approach-2: Crude oil characterization and components parameters.	. 143														
Table 7.4. Approach-2: Self-association and Cross-association energy parameters in Kelvin. ^b	. 144														
Table 7.5. Approach-3: Crude oil characterization and components parameters.	. 144														
Table 7.6. Approach-3: Self-association and Cross-association energy parameters in Kelvin. ^b	. 145														
Table 7.7. Approach-4 [.] Empirical correlations for the estimation of the PC-SAFT parameters for saturates and mix	xture														
of Polynuclear Aromatics (PNA) and benzene derivative components from Panuganti et al [14].	. 146														
Table 7.8. Experimental data of composition, MW and density of all crudes.	. 147														
Table 7.9. The model adjustable parameters for Crudes-1 to 4 for the CPA EoS based approaches-1 and 2	. 147														
Table 7.10. The model adjustable parameters for Crudes-5 to 8 for the CPA EoS based approach-3.	. 147														
Table 7.11 Characterization of Crudes 1, 3 and 4 for the PC-SAFT FoS based approach 4 referred from Tavakkoli	et al														
[7].	. 148														
Table 7.12. The parameters for Crudes-5 to 8 for the PC-SAFT EoS based approach-4 from this work.	. 148														
Table 7.12 The binary interaction (life) normators used for the DC SAET EaS based envroush 4 for different or	daa														
Frame 7.13. The binary interaction (kij) parameters used for the PC-SAFT EoS based approach-4 for different cit	10es.														
Tor crudes 1 and 4, parameters are noni ravakkon et al [7].	. 170														
Table 7.14. The experimental density and calculated density using the PC-SAFT based approach-4, after adjust	sting														
aromaticity (γ) of A+R, for Crudes-5 to 8	. 149														
Table 7.15 The number of Model Adjustable (MAD) Decemptors for all the approaches calculated from amoring	ontal														
data of asphaltene precipitation.	. 149														
i I I	-														
Table 7.16	. Mole	fraction	of	different	n-paraffin	at	the	onset	of	asphaltene	precipitation	using	CPA	and	PC-SAFT
-------------------	--------	----------	----	-----------	------------	----	-----	-------	----	------------	---------------	-------	-----	-----	---------
approach															156

APPENDICES

Appendix A. Academic activities

Peer reviewed journal articles

- 1. <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Determination of asphaltene onset conditions using the cubic plus association equation of state. Fluid Phase Equilibria 2015, Vol. 400, pp. 8-19.
- 2. <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Investigation of the Gas Injection Effect on Asphaltene Onset Precipitation Using the Cubic-Plus-Association Equation of State. Energy Fuels. 2016, Vol. 30(5), pp.3560-3574.
- 3. <u>Alay Arya</u>; Xiaodong Liang; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Onset Precipitation Conditions with Cubic Plus Association (CPA) and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) Equations of State. Energy Fuels. 2016, Vol. 30(8), pp.6835-6852.
- 4. <u>Alay Arya</u>; Xiaodong Liang; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Precipitation from Crude Oil with the Cubic Plus Association Equation of State. Submitted to Energy & Fuels.
- 5. <u>Alay Arya</u>; Xiaodong Liang; Nicolas von Solms; Georgios M. Kontogeorgis. Prediction of Gas Injection Effect on Asphaltene Precipitation Onset using the Cubic and Cubic-Plus-Association Equations of State. Submitted to Energy & Fuels.

Conference presentations

- Alay Arya; <u>Nicolas von Solms</u>; Georgios M. Kontogeorgis. Modeling of Asphaltene Precipitation Onset using Cubic Plus Association Equation of State, 16th PetroPhase, Mexico, June 7-11, 2015. (*Poster*)
- <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Precipitation Onset using Cubic Plus Association Equation of State, 28th ESAT, Athens, Greece, June 11-14, 2015. (*Poster*)
- <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Precipitation Onset using Cubic Plus Association Equation of State, CERE Annual Discussion Meeting, Denmark, June 17-19, 2015. (*Poster*)
- 4. <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Application of CERE CPA for Modeling of Asphaltenes Onset Precipitation, CERE Annual Discussion Meeting, Denmark, June 17-19, 2015. (*Oral*)
- 5. <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Application of CERE CPA for Modeling of Asphaltene Onset Precipitation, Thermodynamics, Denmark, Sept 16, 2015. (*Oral*)
- 6. <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Onset Precipitation using the CPA Equation of State, Society of Petroleum Engineering, Denmark, Oct

6, 2015. (*Oral*)

- 7. <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Precipitation using CPA & PC-SAFT Equations of State, PPEPPD, Portugal, May 22-26, 2016. (*Poster*)
- 8. <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Precipitation using CPA & PC-SAFT Equations of State, CERE Annual Discussion Meeting, Denmark, June 15-17, 2016. (*Poster*)
- <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Onset Precipitation Conditions using the CPA & PC-SAFT Equations of State, 17th PetroPhase, Denmark, June 19-13, 2016. (*Oral*)
- <u>Alay Arya</u>; Nicolas von Solms; Georgios M. Kontogeorgis. Modeling of Asphaltene Onset Precipitation Conditions using the CPA & PC-SAFT Equations of State, CERE Annual Discussion Meeting, Denmark, June 15-17, 2016. (*Oral*)

Teaching Assistance

- 1. Assistant in Thermodynamic Models Applied Colloid and Surface Chemistry (2014).
- 2. Assistant in Chemical Engineering Thermodynamics (2015 & 2016).
- 3. Assistant in Chemical and Biochemical Product Design (2016)
- 4. Member of organization committee for Research Day (May-2014).