Asphaltene Precipitation Models: A Review

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1   ABSTRACT

Asphaltenes are the heaviest and the most polar fraction of crude oil and are defined as a solubility class (typically soluble in toluene but insoluble in n-alkanes like n-heptane). Precipitation and deposition of asphaltenes during production, processing and transportation of oil is a major challenge faced by oil industry. Over the last thirty years, a number of different models have been proposed for predicting the onset of asphaltene precipitation and also the amount of precipitated asphaltenes. This article reviews the different models that have been proposed for predicting asphaltene precipitation either at atmospheric pressure or under depressurization. A brief summary of the different modeling approaches is presented followed by description of work done by different research groups. Our focus will be on the description of the basic assumptions underlying different models and also the ability/performance of the model to match the experimental data. Finally, a comparison of models is presented and discussed along with suggestions for improvement.

Keywords:

Asphaltene precipitation, Thermodynamic models, Solubility models, Equation of state models, Colloidal models

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3   INTRODUCTION

Asphaltenes are considered to represent the most polar and the heaviest components in crude oil.[1] They are a solubility class and defined as the fraction that is insoluble in n-alkane (like n-heptane) but soluble in aromatic solvents (like toluene).[2-3] The precipitation and deposition of asphaltenes during production and transport of crude oil is recognized as a serious problem in the oil industry since it can lead to formation damage, plugging of wellbores and production facilities.[4-5] Asphaltene precipitation can be encountered during primary recovery of oil as well as during enhanced oil recovery operations like miscible flooding with CO_2 or natural gas.[6]

The precipitation of asphaltenes occurs due to a number of reasons. These include changes in pressure, temperature, chemical composition of crude oils, acid stimulation, mixing of oil with diluents, other oil and gas components like CO_2.[4] Heavy crudes usually have a lower tendency to give asphaltene deposition problems inspite of their higher asphaltene content. This observation is normally attributed to their higher resin content and lower saturate content.[7]

Asphaltenes are generally assumed to be composed of fused ring aromaticity, small aliphatic side chains and heteroatom functional groups.[8] The molecular weight of asphaltenes has been a source of controversy for a very long time.[9] It is now recognized to be close to 750 g/mol with a factor of 2 in the width of the molecular weight distribution.[10-11] Asphaltenes have a tendency to self-associate both in model organic solvents and crude oils. Some of the models proposed to explain the self-association are peptization model[12], fractal model[13], Yen model[14] and the modified Yen model[15]. Reviews about asphaltene structure and self-association properties have been recently published.[16-17]

4 ASPHALTENE MODELING APPROACHES

Prediction and modeling of asphaltene precipitation is based on either solubility theory or colloidal theory. The solubility approach assumes that the asphaltenes are dissolved in crude oil and the precipitation occurs if the solubility falls below a certain threshold level.[18] Regular solution theory and equation of state (EoS) are two main solubility theory approaches. The colloidal theory assumes that the asphaltenes exist as colloidal particles stabilized by resins adsorbed onto their surfaces.[19] The partitioning of resins between the colloidal surface and the surrounding medium controls the asphaltene solubility. If sufficient amount of resins desorb, the asphaltenes will be destabilized and precipitate.[20]

4.1 Solubility Approach

The solubility models are most commonly used for predicting asphaltene precipitation. These models make use of the concept of solubility parameter and assume that petroleum crude consists of two phases – asphaltenes and the deasphalted oils. Asphaltene solubility parameters are calculated either using the Scatchard[21] or Hildebrand[22] equations or by calculating the interaction parameters between the asphaltene and the remaining oil constituents. The properties of deasphalted oil are generally calculated using cubic equations of state. Solubility models consider that any change in the solubility parameter to either of the two phases results in change of their phase equilibria. Addition of liquid alkane or uptakes of gas in deasphalted oil phase are examples of ways in which changes can be introduced. The difference between the asphaltene present in the oil and the solubility under given conditions is used for calculating the amount of asphaltene precipitated.[23] Models based on Regular Solution theory, Flory-Huggins theory and Scott-Magat theory fall under this category. Models based on Solution theory and Flory-Huggins theory assume that asphaltenes have homogenous structure and properties while models based on Scott-Magat theory assume that

asphaltenes have a heterogenous structure. The polydisperity of asphaltenes is accounted based on the variation in molecular weight.

4.1.1   Regular Solution Theory

The simplest of solution theories is based on the concept of regular solution. A regular solution has ideal entropy of formation inspite of having a non-ideal enthalpy of formation. Hence a random distribution of molecules in a solution is necessary even in presence of specific solvent-solute interactions.[24] The regular solution theory is based on the assumption that the enthalpic and entropic part of the Gibbs free energy of formation can be treated separately and are additive.[25]

The regular solution theory is best explained using the lattice model. The lattice model assumes that the molecules can be placed on the lattice as show in figure 1. The molecules are represented as black and white balls (corresponding to solvent and solute respectively) of equal size. The molecules constantly switch positions when the system is in liquid state.

The entropy of mixing (ΔS_m) is given by

$$\Delta S_m = -R(n_A ln x_A + n_B ln x_B) \tag{1}$$

Where, R is the gas constant, n_A and n_B are number of moles of component A and B respectively, x_A and x_B are the mole fractions of component A and B respectively.

In order to account for the interaction between the molecules, a parameter known as cohesive energy density (C) was defined. The change in interaction energy on mixing is proportional to

$$C_{AA} + C_{BB} - 2C_{AB} \qquad (2)$$

The cohesive energy density between A-A molecules (C_{AA}) and B-B molecules (C_{BB}) can be found using the heat of vaporization. However, for interactions between molecules A and B, Hildebrand[22] and Scatchard[21] used a geometric mean assumption.

$$C_{AB} = (C_{AA})^{1/2}(C_{BB})^{1/2} \qquad (3)$$

The enthalpy of mixing (ΔH_m) is given by

$$\Delta H_m = v_m \phi_A \phi_B (n_A + n_B)\left[(C_{AA})^{1/2} - (C_{BB})^{1/2}\right] \qquad (4)$$

Where, v_m is the molar volume of the mixture, ϕ_A and ϕ_B are the volume fractions of A and B respectively.

The term 'solubility parameter' was defined by Hildebrand[22]. The solubility parameter of component A is given by

$$\delta_A = (C_{AA})^{1/2} = \left(\frac{\Delta u_A^v}{v_A}\right)^{1/2} \qquad (5)$$

Where δ_A, Δu_A^v and v_A are the solubility parameter, heat of vaporization and molar volume of component A respectively.

The Gibbs free energy change of mixing (ΔG_{mix}) is then given by

$$\frac{\Delta G_{mix}}{RT}\left[\frac{1}{n_A + n_B}\right] = x_A \ln x_A + x_B \ln x_B + \frac{v_m}{RT}\phi_A \phi_B (\delta_A - \delta_B)^2 \qquad (6)$$

It must however be noted that the Hildebrand solubility parameter does not take into account the contribution of polarity of the molecule and the specific interactions like hydrogen bonding.[24] Hence the geometric mean assumption in equation 3 works better for non-polar molecules.

4.1.2 Flory-Huggins Theory

Flory[26] and Huggins[27] had independently developed an equation for Gibbs free energy of polymer mixing using many of the assumptions used in the regular solution theory. Flory and Huggins assumed that polymer is in the form of a flexible chain of segments (of any total size) and each of these segments is equal in size to a solvent molecule.

The Gibbs free energy change on mixing proposed by Flory-Huggins is given by

$$\frac{\Delta G_m}{RT} = x_A ln\phi_A + x_B ln\phi_B + x_A \phi_B \chi_{AB} \tag{7}$$

Where x_A and x_B are the mole fractions of A (solvent) and B (polymer), ϕ_A and ϕ_B are the volume fraction of A and B respectively. χ_{AB} is an interaction parameter and is given by

$$\chi_{AB} = \frac{v_r}{RT}(\delta_A - \delta_B)^2 \tag{8}$$

Where v_r is the molar volume of either component A or B

The Flory Huggins interaction parameter does not take into account the contribution of free volume (non-combinatorial entropy change). An additional term (a constant 0.34 known as fudge factor) was later added to equation 8.[25]

4.1.3 Scott-Magat Theory

The equation developed by Flory and Huggins was for the case of homogeneous chain polymer of uniform molecular weight in a single uniform solvent. Scott and Magat[28] extended the theory of Huggins to a polymer mixture of varying chain lengths. The expression for partial molal free energy of mixing of the solvent $\overline{(\Delta F_0)}$ is given by

$$\frac{\overline{\Delta F_0}}{RT} = ln\phi_0 + (1 - \phi_0)\left(1 - \frac{1}{\overline{m}_N}\right) + \mu(1 - \phi_0)^2 \tag{9}$$

Where, ϕ_0 represents the volume fraction of the solvent, $\overline{m}_N$ is a function of the number average molecular weight and μ is a characteristic constant of the polymer-solvent mixture. The constant μ consists of heat of mixing term and co-ordination number of the rubber segments.

4.1.4   Equation of State (EoS) Models

4.1.4.1 Cubic Equation of State

Cubic equations of state like Soave-Redlich-Kwong and Peng-Robinson EoS are popular in oil industry for calculation of phase equilibria values since they have good accuracy and relatively low mathematical complexity.[29]

Soave-Redlich-Kwong (SRK) EoS[30]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{10}$$

Peng-Robinson (PR) EoS[31]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{11}$$

Where, a and b are the constants of the corresponding EoS and v is the molar volume.

Solid models fall under the category of models utilizing cubic EoS approach. In solid models, precipitated asphaltenes are represented in the form of a pure dense phase (solid phase) while the oil and gas phases are modelled using cubic EoS. The limitation of the cubic EoS is its inability to take into account the effect of polar or association effects like hydrogen bonding.

4.1.4.2 Statistical Association Fluid Theory

Statistical Association fluid Theory (SAFT) was developed by Chapman et al.[32-33] by applying Wertheim's thermodynamic perturbation theory[34-39] and extending it to mixtures. Gross and Sadowski[40] extended the SAFT theory by using Perturbed Chain as the reference fluid and hence the model proposed by Gross and Sadowski is called as PC-SAFT. The details of PC-SAFT theory can be found in literature[40].

4.1.4.3 Cubic-Plus-Association Equation of State

Cubic-plus-association (CPA) equation of state was initially developed by Kontogeorgis et al.[41] to describe the thermodynamic properties of the associating fluids. CPA consists of two terms: a physical term (to describe the non-associating molecular interactions like short range repulsion and dispersion attractions) and an association part (to describe the polar interactions like self-association). The physical term is normally represented using a cubic equation of state (Peng-Robinson EoS or Soave-Redlich-Kwong EoS) while the association term is based on thermodynamic perturbation theory. Thus, in the absence of any association effects, the CPA EoS reduces to cubic EoS.

4.2   Colloidal Approach

Thermodynamic colloidal models for asphaltene precipitation are based on the assumption that the asphaltenes exist in the colloidal state (in suspension) stabilized by the resin molecules adsorbed at the asphaltene surface. The colloidal theory assumes that the precipitation of asphaltenes is an irreversible phenomenon and that a certain amount of resins is necessary for asphaltenes to be completely peptized in crude oil.

5   SOLUBILITY MODELS

5.1   Hirschberg et al.

In 1984, Hirschberg et al.[6] developed a simple thermodynamic model to describe the flocculation tendency of asphaltenes in light crudes. A vapor-liquid equilibrium calculation using Soave Redlich-Kwong (SRK) EoS was initially performed to split the crude into vapor and liquid phases. The liquid phase was then considered to consist of two phases – the oil rich solvent phase and asphalt phase (containing both asphaltene and resins). Flory-Huggins theory was then used to calculate the amount of asphaltene precipitated from the liquid phase based on the assumption that the precipitated asphaltenes do not change the vapor/liquid equilibrium.

The Flory-Huggins theory is given by[42]

$$\Delta G_{mixing} = RT(\eta_m ln\phi_m + \eta_a ln\phi_a + \eta_m \phi_a \chi) \tag{12}$$

where, ΔG_{mixing} is the change in free energy of mixing, η and ϕ are is the number of moles and volume fraction respectively. The subscripts 'a' and 'm' refers to asphaltenes and oil mixture (excluding asphaltenes).

The Flory-Huggins interaction parameter (χ) is given by

$$\chi = \frac{v_m}{RT}(\delta_a - \delta_m)^2 \tag{13}$$

The solubility parameter (δ) was calculated using Hildebrand's definition

$$\delta^2 = \frac{\Delta u^v}{v} \tag{14}$$

Δu^v is the molar cohesion energy and v represents the molar volume.

Based on the assumptions that the reservoir crude was saturated with asphaltenes and that the precipitated phase was pure asphaltenes, an expression for $(\phi_a)_{max}$ or maximum volume fraction of asphaltenes soluble in crude oil was obtained from equations 12, 13 and 14.

$$ln(\phi_a)_{max} + \left(1 - \frac{v_a}{v_m}\right) + \frac{v_a}{RT}(\delta_a - \delta_m)^2 = 0 \tag{15}$$

The values of asphaltene solubility parameter and molar volume were determined by titration experiments. Hirschberg et al. used $v_a = 4\ m^3/kmol$ for their calculations. Similarly, the temperature dependence on asphaltene solubility parameter obtained was

$$\frac{1}{\delta_a}\left(\frac{d\delta_a}{dT}\right) = 1.07 \times 10^{-3}\ K^{-1} \tag{16}$$

However, the model (equation 15) overestimated the asphaltene solubility at very high dilution ratio. Similarly, the model predicted that asphaltenes are in dissolved state above 200 bar, while experimental data indicated the presence of precipitate at 1000 bar. Separation of resins from asphaltenes was considered to be the reason for the shortcoming of the Hirschberg et al. model.[6] Hence a correction term (a pre-factor) was later introduced to the asphaltene solubility (equation 15) to take into account the aggregation of asphaltenes and interactions with resins present in the crude oil.[7] Another shortcoming of the model is to consider asphaltene to be homogeneous.

The Flory-Huggins theory was also used by Burke et al.[43] to predict asphaltene precipitation on addition of low-molecular weight gas mixture (called HCG-2) to the reservoir oil. Zudkevitch-Joffe-Redlich-Kwong EoS[44] was used for obtaining and tuning the molar volumes and solubility parameters. Decreased asphaltene precipitation was observed when

sufficient gas was added to create gas/reservoir-oil mixture that exhibit dew point behavior. However based on the solubility model, an increased precipitation was expected with increased gas concentration.

Similarly, Novosad and Costain[45] used Hirschberg's model for predicting the stability of asphaltenes in a crude oil with 29°API undergoing tertiary CO_2 injection. Both the asphaltene-asphaltene and asphaltene-resin interactions were taken into account in the model. The model successfully predicted the asphaltene behavior under a variety of wellbore conditions and the operating conditions to be avoided for minimizing the asphaltene precipitation.

However, Rassamdana et al.[46] used the method suggested by Hirschberg et al. for predicting the asphaltene precipitation from Iranian crude (29.7°API crude containing 2.2 wt% n-C_7 asphaltenes) by n-alkane addition. The model predictions were found to be in disagreement with the experiment data. The authors attributed the reasons to assumption of complete asphaltene reversibility during derivation of thermodynamic model and treating C_{7+} components in crude as a single pseudocomponent.

5.2 Thomas et al.

Thomas et al.[47] developed a regular solution theory multicomponent model for predicting asphaltene precipitation based on the solution theory by Won[48-49]. Won's liquid-solid model accounted for the multicomponent solid phase and assumed that a regular solution is defined by $G_E = U_E$, where G_E is the Gibbs free energy and U_E is the internal energy. The solid-liquid equilibrium ratio K_i^S was given by

$$ln\left(K_i^S\right) = ln\left(\frac{x_i^S}{x_i^L}\right)$$

$$= \frac{1}{RT}\left[v_i^L(\delta^L - \delta_i^L)^2 - v_i^S(\delta^S - \delta_i^S)^2\right] + \frac{\Delta H_f}{RT}\left(1 - \frac{T}{T_f}\right) \quad (17)$$

$$+ \frac{\Delta C_p}{R}\left[1 - \frac{T_f}{T} + ln\frac{T_f}{T}\right] + \frac{1}{RT}\int_0^P (v_i^L - v_i^S)dp$$

Where, the superscripts S and L refer to solid and liquid. x_i , v_i and δ_i refer to the mole fraction, molar volume and solubility parameter for i^{th} fraction respectively. δ is the average solubility parameter of the mixture, C_p is the heat capacity, ΔH_f is the heat of fusion and T_f is the temperature of fusion.

The model was then used to successfully predict the incipient asphaltene precipitation from Canadian oil fields - Keg River oil and Nisku oil. The same modified Won's modified solution theory was used by MacMillan et al.[50] by inserting constants before each term (in right hand side of (equation 17) and using an Equation of State (EoS) for obtaining the pressure term instead of numerical integration. The model predictions were found to be in good agreement for predicting asphaltene precipitation under lift gas operating conditions and to evaluate the possible location of tar mat.

5.3   Chung et al.

Chung[51] developed a generalized predictive model for organic solid precipitation based on thermodynamic principle for solid-liquid equilibrium. The model was then tested with experimental data for wax and asphaltene precipitation. The model assumed that asphaltenes are dissolved in oil in true liquid state and not in a colloidal state.

The solid-liquid equilibrium was obtained by equating the fugacity of asphaltenes in solid phase (f_a^S) and liquid phase (f_a^L)

$$f_a^S = f_a^L \tag{18}$$

The fugacities of asphaltene in solid and liquid phases was given by

$$f_a^S = \gamma_a^S x_a^S f_a^{0S} \left[\int_0^P \frac{v_a^S dP}{RT} \right] \tag{19}$$

$$f_a^L = \gamma_a^L x_a^L f_a^{0L} \left[\int_0^P \frac{v_a^L dP}{RT} \right] \tag{20}$$

Where γ_a , x_a , v_a and f_a^0 are the activity co-efficient, mole fraction, molar volume and standard state fugacity of asphaltenes. The superscript S and L stand for solid and liquid respectively.

The solid-liquid equilibrium constant K_a^{SL} was then given by

$$K_a^{SL} = \frac{x_a^S}{x_a^L} = \left(\frac{\gamma_a^L}{\gamma_a^S} \right) \left(\frac{f_a^{0L}}{f_a^{0S}} \right) exp \left[\int_0^P \frac{\Delta v_a dP}{RT} \right] \tag{21}$$

Where,

$$\Delta v_a = v_a^L - v_a^S \tag{22}$$

The relationship between fugacities was given by

$$ln \left(\frac{f_a^{0L}}{f_a^{0S}} \right) = \frac{\Delta h_a^f}{RT} \left[1 - \frac{T}{T_a^f} \right] \tag{23}$$

Where Δh_a^f and T_a^f are the latent heat of melting and melting point temperature of asphaltenes.

The solid phase activity co-efficient (γ_a^S) was taken as unity since in solid phase, all molecules are similar in structure and the interactions among molecules are the same. The liquid phase activity co-efficient was given by the relation

$$ln\gamma_a^L = \frac{v_a^L}{RT}(\delta_m^L - \delta_a^L)^2 + \ln\frac{v_a^L}{V_m} + 1 - \frac{v_a^L}{V_m} \tag{24}$$

Where δ_a is the solubility parameter for asphaltene, δ_m is the average solubility parameter and V_m the average molar volume of the liquid phase.

Asphaltene was treated as a pure component and the model assumed that the solid phase consisted of only pure asphaltenes ($x_a^S = 1$). Therefore, the maximum solubility of asphaltene in liquid phase was given by

$$x_a^L = exp\left[-\frac{\Delta h_a^f}{RT}\left(1 - \frac{T}{T_a^f}\right) - \frac{v_a^L}{RT}(\delta_m^L - \delta_a^L)^2 - \ln\frac{v_a^L}{V_m} - 1 + \frac{v_a^L}{V_m}\right] \tag{25}$$

Where, x_a^L is the mole fraction of asphaltene in solution. The authors compared the asphaltene solubility data obtained using their model (equation 25) with experimental solubility results for n-pentane/toluene, n-heptane/toluene and n-decane/toluene systems. The authors had however considered asphaltenes to be a single component (homogeneous) with a molecular weight of 6359 g/mol. The predictions were in reasonable agreement with asphaltene solubility experiment results. Similarly, the authors also tested the accuracy of their model by predicting the asphaltene solubility in n-heptane/toluene and n-decane/toluene mixtures and once again the predictions agreed well with the experimental data.[51]

Similarly, Nor-Azlan and Adewumi[52] developed an asphaltene phase equilibria predictive model based on Flory-Huggins solution theory. The performance of the model was analyzed for addition of low molecular weight n-alkane solvents (n-pentane, n-heptane and n-decane)

to crude oil from Canadian Middale reservoir at fixed temperature and pressure. Even though the model predicted the correct trend of asphaltene precipitation, the model's performance was unsatisfactory since it under-predicted (by 13% and 18%) the maximum amount of asphaltenes precipitated.

5.4   Cimino et al.

Cimino et al.[53] developed a model based on the hypothesis that phase separation leads to obtaining a heavy liquid phase containing both asphaltenes and a fraction of solvent. (Hirschberg et al.[6] had assumed that the asphaltene phase obtained is pure asphaltene). It was also assumed that the light liquid phase does not contain asphaltenes. The Cimino et al. model relies on cloud point measurement for investigating the phase behavior. The model equation obtained by Cimino et al. was

$$ln(1 - \phi_a^*) + \left(1 - \frac{v_m}{v_a}\right)\phi_a^* + \frac{v_m}{RT}(\delta_a - \delta_m)^2\phi_a^{*2} = 0 \qquad (26)$$

Where ϕ_a^* is the asphaltene volume fraction in the nucleating phase at the cloud point/onset of flocculation. Spectrophotometer technique was used for determining the cloud point of oil when antisolvent (n-heptane) was added since the phase nucleation results in scattering of transmitted light.

A comparison between the Cimino et al. and Hirschberg et al.[6] models for fitting tank oil data from Villafortuna-Trecate (VT-FR) field showed better fit using Cimino model.

5.5   De Boer et al.

In 1995, De Boer et al.[7] came up with a simple method to identify crude oils which have a tendency to cause asphalt (asphaltene + resins) precipitation problems. The thermodynamic model of asphaltene solubility (derived from Flory and Higgins) by Hirschberg et al.[6] was the

basis of this method. Experimental data was also used. According to De Boer and co-authors, the tendency of asphalt to precipitate depends on three parameters:

- The extent to which the crude is undersaturated with gas

- Density of crude at reservoir conditions

- Saturation of crude with asphalt at downhole conditions.

De Boer calculated the solubility of asphaltene for different values of in-situ crude oil densities and solubility parameters and defined the maximum supersaturation (($\Delta S/S$) at bubble point as

$$\frac{\Delta S}{S} = \int_{p=p_b}^{p_r} \left(\frac{\partial S}{S\partial p}\right)_T dp \cong \left(\frac{\partial S}{S\partial p}\right)_T (p_r - p_b) \qquad (27)$$

Where p_b and p_r are the bubble-point and reservoir pressures respectively.

In order for asphaltene to precipitate, a certain degree of supersaturation of crude oil is necessary. The maximum degree of supersaturation was shown as a function of difference between the reservoir and bubble point pressures, insitu density of oil and solubility parameter of asphaltene. This is known as the De Boer's plot (figure 2).

According to De Boer, when highly under-saturated light crudes are depressurized, extremely high supersaturation occurs thereby resulting in asphaltene precipitation. Asphaltene precipitation was found to be more common in crude oils with high C_1-C_3 and less C_{7+} content, with high bubble pressure and high compressibility[7]. The De Boer's plot assumes that oil is saturated with asphaltene at reservoir conditions. As a result, the predictions are conservative and result in prediction of asphaltene precipitation for oils that do not present

precipitation in field.[54] Also, the De Boer plot does not provide any information about the amount of asphaltene precipitation expected.

5.6   Yarranton and co-workers

Yarranton and Masliyah[55] observed that the models by Hirschberg[6] and Cimino[53] were successful in predicting the asphaltene precipitation onset but not the amount of precipitate. This was attributed to lumping of asphaltenes as a single component. Hence, in order to obtain more accurate results, Yarranton and Masliyah treated asphaltenes as a mixture of sub-fractions with different densities and molar masses. The asphaltenes were fractionated by solvent extraction technique (solubility and precipitation) and the molar mass distribution of asphaltenes was determined from interfacial tension measurements. The solubility was modeled by solid-liquid equilibrium calculation with the K-values derived from Scatchard-Hildebrand solubility theory incorporating the Flory-Huggins entropy of mixing.

The equilibrium model proposed by Yarranton and Masliyah was

$$K_i = \frac{x_i^s}{x_i^l} = exp\left\{\frac{\Delta H_i^f}{RT}\left(1 - \frac{T}{T_i^f}\right) + 1 - \frac{v_i^l}{v_m} + ln\left(\frac{v_i^l}{v_m}\right) + \frac{v_i^l}{RT}(\delta_m - \delta_i^l)^2\right\} \quad (28)$$

Where, K_i is the solid-liquid equilibrium ratio of component i,

x_i^s and x_i^l are the solid phase and liquid phase mole fractions of component i,

ΔH_i^f is the enthalpy of fusion and T_i^f is the melting point temperature of component i,

v_i^l and v_m are the molar volumes of component i and solvent respectively

δ_i^l and δ_m are the solubility parameters for component i and solvent respectively

The model (equation 28) successfully predicted the precipitation onset and quantity of precipitated asphaltenes. The work by Alboudwarej et al.[56] was an extension of Yarranton

and Masliyah's model and regular solution theory. A modified solution model was used which included the Flory-Huggins entropic contribution (from difference in molecular sizes) as well as the enthalpy contribution from the regular solution theory. Since the systems investigated were above the bubble point, the precipitated phase was considered to be liquid phase.

The fugacity (f_i) of component i was given by

$$f_i = \gamma_i x_i f_i^0 exp\left[\int_0^P \frac{v_i dP}{RT}\right] \qquad (29)$$

Where, x_i and γ_i are the mole fraction and activity-coefficient of component i, f_i^0 is the standard fugacity and v_i is the molar volume of component i.

Liquid-liquid equilibrium was assumed and the equilibrium ratio, K_i^{hl} was obtained by equating the fugacities of each component in existing phases.

$$K_i^{hl} = \frac{x_i^h}{x_i^l} = \frac{\gamma_i^l}{\gamma_i^h} \qquad (30)$$

Where x_i^h and x_i^l are heavy and light liquid phase mole fractions, γ_i^h and γ_i^l are heavy and light liquid phase activity co-efficients

The activity co-efficients were given by,

$$ln\gamma_i^l = ln\left(\frac{v_i^l}{v_m^l}\right) + 1 - \frac{v_i^l}{v_m^l} + \frac{v_i^l}{RT}\left(\delta_i^l - \delta_m^l\right)^2 \qquad (31)$$

$$ln\gamma_i^h = ln\left(\frac{v_i^h}{v_m^l}\right) + 1 - \frac{v_i^h}{v_m^l} + \frac{v_i^h}{RT}\left(\delta_i^h - \delta_m^h\right)^2 \qquad (32)$$

v_i and δ_i are molar volume and solubility parameter of compound i in light liquid phase (l) or heavy liquid phase (h), v_m and δ_m = molar volume and solubility parameter of either the light liquid phase or the heavy liquid phase.

The author assumed that the dense phase consisted of only asphaltenes (i.e., the activity co-efficients in dense phase is unity) and hence equation 28 reduced to

$$K_i = \gamma_i^l = exp\left\{ ln\left(\frac{v_i^l}{v_m^l}\right) + 1 - \frac{v_i^l}{v_m^l} + \frac{v_i^l}{RT}\left(\delta_i^l - \delta_m^l\right)^2 \right\} \qquad (33)$$

Alboudwarej and co-authors considered asphaltenes to be macromolecular aggregates of monodisperse asphaltene monomers of increasing molar mass. They also assumed that the molar mass distribution of aggregates followed a Schultz-Zimm distribution function and divided the asphaltenes into 30 sub-fractions based on this distribution.

The modified Schultz-Zimm distribution $f(r)$ used was[56]

$$f(r) = \frac{4(r-1)}{(r_m-1)^2} exp\left[-\frac{2(r-1)}{(r_m-1)}\right] \qquad (34)$$

Where, r is the aggregation parameter of each asphaltene molar mass fraction (i.e., the number of monomers in an aggregate molecule) and r_m represents the average aggregation state of asphaltenes.

$$r = \frac{M}{M_m} \qquad (35)$$

$$r_m = \frac{\overline{M}}{M} \qquad (36)$$

Where M is molar mass of asphaltene aggregate, M_m is the asphaltene monomer molar mass and $\overline{M}$ is average asphaltene molar mass of the distribution.

The molar mass of asphaltene monomer and the largest asphaltene aggregate were assumed to be 1800 g/mol and 30,000 g/mol respectively. The results of modeling were also not sensitive for asphaltene aggregates with molar mass greater than 30,000 g/mol or beyond 30 asphaltene fractions.

The molar volume of asphaltene sub-fraction was determined using the relation

$$v = 1.493M^{0.936} \tag{37}$$

Where v and M are the molar volume and molar mass of the asphaltene sub-subfraction respectively. Similarly, the solubility parameter of asphaltene subfraction (δ_a) was determined using the relation

$$\delta_a = \left(\frac{1000A(T)M}{v}\right)^{1/2} \tag{38}$$

Where, A is the heat of vaporization of asphaltene. The heat of vaporization (J/kg) at any temperature A(T) is given by

$$A(T) = 0.579 - 0.00075T \tag{39}$$

Where, T is the absolute temperature in Kelvin.

The Alboudwarej et al. model (equation 33) was reasonably successful in predicting the onset and amount of asphaltene precipitation of West Canadian heavy oils and bitumens for different amounts of n-alkane added as shown in figure 3. However, the model under-predicted the amount of precipitation at intermediate solvent/bitumen ratios and the authors attributed it to the molar mass of asphaltenes not exactly following the Schultz-Zimm distribution. Subsequently, Akbarzadeh et al.[57-58] used a different gamma distribution function (proposed by Whitson[59]) to describe the molar distribution of asphaltene aggregates.

$$f(M) = \frac{1}{M_m \Gamma(\beta)} \left[\frac{\beta}{(\bar{M} - M_m)} \right]^{\beta} (M - M_m)^{\beta - 1} exp \left[\frac{\beta(M - M_m)}{(\bar{M} - M_m)} \right] \qquad (40)$$

Where M is molar mass of asphaltene aggregate, M_m is the asphaltene monomer molar mass and $\bar{M}$ is average asphaltene molar mass of the distribution. β (=2) is a parameter that governs the shape of the distribution curve.

The model equation used by Akbarzadeh et al. was

$$K_i^{hl} = \frac{x_i^h}{x_i^l} = exp \left\{ \frac{v_i^h}{v_m^h} - \frac{v_i^l}{v_m^l} + ln\left(\frac{v_i^l}{v_m^l}\right) - ln\left(\frac{v_i^h}{v_m^h}\right) + \frac{v_i^l}{RT}\left(\delta_i^l - \delta_m^l\right)^2 \right.$$
$$\left. - \frac{v_i^h}{RT}\left(\delta_i^h - \delta_m^h\right)^2 \right\} \qquad (41)$$

It was assumed that the heavy phase consisted of both asphaltenes and resins. (Note: if the heavy phase is assumed to consist of only asphaltenes, then equation 41 reduces to equation 33). The model (equation 41) was then used for successfully predicting the amount of asphaltene precipitation for Llyodminster bitumen (as shown in figure 4) as well as for heavy oils from Venezuela, Indonesia and Russia. The model also correctly predicted a higher asphaltene precipitation on addition of n-octane (n-C8) than compared to n-heptane (n-C7) addition. The authors also studied the effect of temperature and pressure on asphaltene precipitation from Canadian heavy oil and bitumens.

Figure 5 shows the predictions for Cold Lake bitumen at different temperatures for n-pentane and n-heptane additions. It was observed that the model results do not match well with the experimental data for dilution with n-heptane (C7) at 100°C. Akbarzedeh et al. also had

difficulty in obtaining experimental data at 100°C and hence could not figure out whether the problem is with the model or experimental data.

The model (equation 41) was also found to under-predict the amount of asphaltene precipitation for n-pentane addition at 0°C. The authors attributed this to possible self-association of resins at 0°C and tried dividing resins into 5 sub-fractions. The molar mass of resin monomer was assumed to be 200 g/mol while that of the largest resin aggregate was assumed to 1900 g/mol. The model predictions were found to be better when self-association of resins were taken into account. However, there was lack of evidence to support the phenomena of resin self-association and hence the authors did not incorporate it into the model.[58] Similarly, the model accurately predicted asphaltene precipitation at moderate pressures (around 2.1 MPa) but under-predicted amount of precipitation at high pressures (around 6.9 MPa).

5.7   Refractive Index (RI) Measurements

Buckley and co-workers[60-63] proposed an alternate method for predicting the onset of asphaltene precipitation using refractive index (RI) measurements. The theory was based on the assumption that the aggregation and precipitation of asphaltenes is dominated by differences of London dispersion forces (a type of Van der Waals force) between the crude oil (maltenes) and the asphaltenes. This assumption was supported by the solubility parameter mapping by Wiehe[64] who showed that the aromaticity and molecular weight (and not the polar interactions) dominates asphaltene insolubility.

The interaction energy between asphaltene molecules in a solvent medium with only London dispersion forces is given by the relation

$$w(r) = -\frac{\sqrt{3}hv_e}{4}\frac{(n_a^2 - n_s^2)^2}{(n_a^2 - 2n_s^2)^{3/2}}\frac{a_a^6}{r^6} \tag{42}$$

Where h is Planck's constant, v_e is the absorption frequency in the ultraviolet, n_a and n_s are the refractive indices of asphaltene and the solvent (extrapolated to zero frequency) a_a is the equivalent radius of asphaltene molecule, r is the distance between the centers of the molecules.[60]

The London dispersion interactions between molecules are due to induced polarization. In systems where London dispersion forces dominate, the strength of the interactions is related to the difference in the refractive indices between the two materials (assuming that the materials have same absorption frequency). The relationship between the refractive index (RI) of a medium at visible light frequencies and the electronic polarizability of a medium (α_0) is given by the Lorentz-Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha_0 \rho N_o}{3\varepsilon_0 M} \tag{43}$$

Where N_0 is Avagadro's number, ε_0 is the permittivity in vacuum, n is the refractive index, M is the molecular weight of medium and ρ is the mass density of medium. The term $(\alpha_0 N_0 / 3\varepsilon_0)$ is known as the molar refraction of the material.[42]

The refractive index is a function of density for pure substances. The model proposed by Buckley gives importance to the concept of polarizability (which is measured by the RI). The ability of a hydrocarbon to behave as precipitant or solvent depends on the degree of polarizibility. If the dispersion forces are assumed to play a major role, then the refractive index is an indicator of the extent of molecular attraction between the asphaltene molecules and the solvent.

The function of refractive index (F_{RI}) is defined as

$$F_{RI} = \frac{n^2 - 1}{n^2 + 2} \qquad (44)$$

In case of a mixture in which there is no significant volume change after mixing, F_{RI} of mixture is equal to the sum of the refractive index functions of each component times its volume fraction (φ_i).

$$\left(\frac{n_m^2 - 1}{n_m^2 + 2}\right) = \phi_a \left(\frac{n_a^2 - 1}{n_a^2 + 2}\right) + \phi_s \left(\frac{n_s^2 - 1}{n_s^2 + 2}\right) \qquad (45)$$

Where, ϕ_a and ϕ_s are the volume fractions of asphaltene and solvent respectively, n_m, n_a and n_s are the refractive indices of the mixture, asphaltenes and solvent respectively.[65]

Buckley[61] determined the refractive index at the onset of asphaltene precipitation for several crudes diluted with different precipitants. A plot of F_{RI} and crude oil volume fraction for an asphaltic oil from California is shown in figure 6. If there was no asphaltene precipitation from crude oil, the plot between F_{RI} and crude oil volume fraction is expected to be a straight line (linear relationship). However, if precipitation occurs, a gradual deviation from linearity is observed. As the asphaltene particles flocculate and precipitate out of the solution, they no longer contribute to refractive index of the mixture thereby causing the deviation in mixture refractive index.[65] In case of crude oils which exhibited asphaltene precipitation on addition of precipitant, Buckley[61] observed that the value of refractive index at the onset of precipitation (P$_{RI}$) remained relatively constant for given oil and precipitating agent. Hence P$_{RI}$ was indicated as a horizontal band as shown in figure 6.

It must however be noted that the deviation from linearity depends upon the amount of asphaltene precipitated and hence cannot be modeled. Buckley and Wang[63] later related the RI to the solubility parameter in solutions of non-polar molecules and for crude oils with the following equation,

$$\delta = 52.042 F_{RI} + 2.904 \qquad (46)$$

The themodynamic model based on RI approach was able to predict the onset of asphaltene precipitation. However, it could not predict the amount of asphaltenes that will precipitate at any solubility condition. This was attributed to the fact that molecular distribution (poly-dispersity) of asphaltenes was not taken into account.[42]

Vargas and co-workers[66-67] observed a linear trend with slope equal to 1/3 for a plot between molar refraction (R_m) and molecular weight for several hydrocarbons. This is known as the one-third rule and it implies that the ratio of F_{RI} and mass density ρ is a constant equal to 1/3.

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{\rho} = F_{RI}\frac{M}{\rho} \qquad (47)$$

The molar refraction represents the volume occupied by molecules per unit mole, M/ρ represents the total volume including the free space between molecules. Hence F_{RI} represents the fraction of total volume occupied by the molecules

The 1/3rd rule was validated for several crude oil samples over a wide range of temperatures and pressures and was found to be an alternative for estimating density or refractive index of

hydrocarbons. In absence of refractive index measurements, the solubility parameter can be obtained using mass density (by applying $1/3^{rd}$ rule to equation 46) as

$$\delta = 17.347\rho + 2.904 \qquad (48)$$

This rule does not however hold good for light hydrocarbons like methane, ethane and propane. The model was later extended by deriving the pressure and temperature dependency of solubility parameter.[66]

5.8 Asphaltene Solubility Model (ASM) and Asphaltene Instability Trends (ASIST)

Wang and Buckley[68] developed a two-component asphaltene solubility model (ASM) for prediction of asphaltene precipitation in crude oils. The model was developed based on Flory-Huggins polymer theory but without making any assumptions about the composition of phases formed when asphaltenes separate out from the crude oil (like formation of pure asphaltene phase or pure solvent phase). Instead the correlation between RI and solubility parameters was used for characterizing the oil.

At phase separation, some asphaltenes were considered to remain in the lighter phase (L) while others concentrate in the heavier asphaltene rich phase (H). At phase equilibrium, the chemical potentials for asphaltenes and mixed solvent were considered to be the same and a couple of non-linear equations were obtained which can be solved numerically to give the asphaltene volume fractions in lighter phase (L) and the heavier phase (H) i.e., ϕ_a^L and ϕ_a^H.

$$\ln(1 - \phi_a^L) + \left(1 - \frac{v_m}{v_a}\right)\phi_a^L + \chi(\phi_a^L)^2$$
$$= \ln(1 - \phi_a^H) + \left(1 - \frac{v_m}{v_a}\right)\phi_a^H + \chi(\phi_a^H)^2 \qquad (49)$$

$$ln\phi_a^L + (1 - \phi_a^L)\left(1 - \frac{v_a}{v_m}\right) + (1 - \phi_a^L)^2 \frac{v_a}{v_m}\chi$$
$$= ln\phi_a^H + (1 - \phi_a^H)\left(1 - \frac{v_a}{v_m}\right) + (1 - \phi_a^H)^2 \frac{v_a}{v_m}\chi \tag{50}$$

χ is the Flory-Huggins interaction parameter between asphaltene and solvent mixture given by

$$\chi = \frac{v_m}{RT}(\delta_a - \delta_m)^2 \tag{51}$$

Where, v_m and δ_m are the molar volume and solubility parameter of mixture without asphaltenes while δ_a is the solubility parameter of asphaltenes.

The model represented by equations 49 and 50 needed four input parameters (δ_a, δ_m, v_a and v_m). δ_m was determined based on refractive index measurements while v_m was estimated from measurements of density and average molecular weight of non-asphaltic hydrocarbon mixture. Therefore, the only adjustable parameters of the model are the coupled values of asphaltene solubility parameter δ_a and the molar volume v_a. The model performed reasonably well in predicting asphaltene onset conditions for several crude oils as shown in figure 7.

One of the limitations of the model (ASM) is that since the parameters δ_a and v_a are coupled, a family of solutions to non-linear equations 49 and 50 can be produced. In that case, one of the parameter needs to be fixed and the other parameter varied. Hence proper selection of parameter value is critical. Also, the same solubility parameter can describe conditions under which asphaltenes are precipitated from the crude using pentane and pentadecane. In reality, different precipitants give different amounts and composition of asphaltene precipitated.

Hence the ASM model may be less accurate in predicting the amount of asphaltene precipitated for different n-alkane solvents.[68]

Buckley et al.[42] plotted the experimental onset solubility parameters (δ_{onset}) of several crude oils as a function of $v_p^{1/2}$, where v_p is the molar volume of n-alkane precipitants (from n-pentane to n-pentadecane) and observed a linear relationship between them. This relationship was called as ASphaltene InStability Trend (ASIST).

ASIST can be used to predict the onset of asphaltene precipitation in reservoirs as shown in figure 8. Mars-Pink Stock Tank Oil (STO) was initially titrated with n-alkanes (n-pentane to n-pentadecane) at 20°C. The values of solubility parameter of the STO and n-alkane are known and are represented in the figure as points B and C respectively. Hence if the STO is titrated with undecane (n-C$_{11}$), then the ratio of length of line segments AB/AC gives the volume of n-C$_{11}$ added at onset while the ratio BC/AC gives the volume fraction of STO in the onset mixture.

ASIST can also be used to predict the onset pressure of precipitation as shown in figure 9 for a light oil C-AG3-02 which contains 0.5 wt% asphaltenes. The curves $\delta_{live\ oil}$ and δ_{onset} represent the solubility parameter of the light oil and onset conditions of asphaltenes over the entire pressure range. Asphaltene precipitation is predicted to occur around 8500 psi when the $\delta_{live\ oil}$ curve falls below the δ_{onset} curve during depressurization. However onset measurements done using solids detection system (SDS) indicated the asphaltene onset pressure to be around 6500 psi (This is the point at which the SDS line deviates from linear line). Due to the differences in the two techniques, the asphaltene onset pressure was defined over a range between 6500 and 8500 psi.[42]

It can also be seen that the maximum instability occurs at the bubble point pressure (P_b). Hence for screening purposes, Wang et al.[54] simplified the ASIST procedure by focusing only on asphaltene stability at bubble point pressure. Only a single titration experiment on STO with n-C_7 was necessary to make an assessment of asphaltene stability. The single point ASIST prediction was found to have good agreement with full ASIST predictions. The ASIST method was also found to predict asphaltene problems better than the DeBoer's plot.

The ability to predict asphaltene precipitation by DeBoer method as well as ASIST was tested on seven Iranian crude oils by Shokrlu et al.[69] Modifications were made to both methods to improve the accuracy of predictions. A good conformity was observed in predicting asphaltene precipitation with both De Boer's plot and ASIST method. However, ASIST does not determine the level/intensity of asphaltene precipitation.

5.9 Kawanaka et al. (Scott-Magat Approach)

The asphaltene models based on Scott-Magat theory assume that the asphaltenes have a heterogenous structure and hence a distribution of asphaltene molecular weight is considered.[70] Mansoori and Jiang[71] were the first to apply Scott and Magat theory to formulate a model for predicting asphaltene precipitation. Kawanka et al.[72] used the same model as Mansoori and Jang to predict the phase behavior and deposition of asphaltenes. Kawanka et al. assumed that asphaltene consisted of many components of similar polymeric molecules and hence used a gamma distribution function to relate the properties of asphaltenes with the molecular weight of the asphaltene fraction. They also assumed that the precipitated phase consisted of pure asphaltenes and a phase equilibrium calculation was

done by equating the chemical potential of every asphaltene fraction in the liquid phase and the solid phase.

The volume fraction of asphaltene in liquid phase (ϕ_{fa}^L) in equilibrium with solid phase was given by

$$\phi_{fa}^L = \int d\phi_{fai}^L = \int_0^\infty \left\{ \frac{\left(\frac{M_{ai}}{\overline{M}_a}\right) V_a^C}{V^L + V^S e^{-N_{sai}\theta}} \right\} \times F(M_{ai}) dM_{ai} \tag{52}$$

Where,

$$\theta = \left(\frac{1}{\overline{N}_{sa}^L} - \frac{1}{\overline{N}_{sa}^S}\right) + \left(1 - \frac{1}{\overline{N}_{sa}^L}\right)\phi_{fb}^L - f^L\left(\phi_{fb}^L\right)^2 \tag{53}$$

The subscript 'ai' refers to the ith fraction of asphaltene. ϕ_{fai}, N_{sai} and M_{ai} are the volume fraction, segment number and molecular weight of ith fraction of asphaltene respectively. $\overline{M}_a$ is the average asphaltene aggregate molecular weight. The superscripts S, L and C refer to solid phase, solvent rich liquid phase and original crude oil. ϕ_{fb} represents the volume fraction of asphaltene crude

The parameter f^L in equation 53 consists of two terms - a term resulting from entropy of mixing and a term resulting from heat of mixing and is given by

$$f^L = \frac{1}{N_c} + \frac{V_{Mb}}{RT}[(\delta_a - \delta_b)^2 + 2k_{ab}\delta_a\delta_b] \tag{54}$$

N_c is the co-ordination number between two successive segments in asphaltene molecule (the value of N_c is typically between 3 and 4). δ_a and δ_b are the solubility parameter of asphaltene

and asphaltene free crude (maltenes), V_{Mb} is the molar volume of the solvent and k_{ab} is the molecular interaction parameter between asphaltene molecule and asphaltene free crude oil.

The molecular weight distribution function of asphaltene, $F(M_{Ai})$ in equation 52 was represented by the gamma distribution function

$$F(M_{Ai}) = \left[\frac{(M_{ai} - M_{a0})^{\alpha-1}}{\Gamma(\alpha)\beta^{\alpha}}\right] e^{\left[-\frac{(M_{ai}-M_{A0})}{\beta}\right]} \tag{55}$$

where,

$$\alpha = \frac{\left(\overline{M}_a - M_{a0}\right)^2}{\eta} \tag{56}$$

$$\beta = \frac{\eta}{\overline{M}_a - M_{a0}} \tag{57}$$

$$\Gamma(\alpha) = \int_0^\infty t^{\alpha-1} e^{-t} dt \tag{58}$$

M_{a0} , M_a and η are the initial value, mean value and variance of gamma distribution function. The amount of asphaltene precipitated (W_{Ad}) was given by

$$W_{Ad} = W_{At} - \rho_A V_{fA}^L V^L \tag{59}$$

The total amount of asphaltenes in the crude oil, W_{At} was calculated from the asphaltene composition of the liquid phase at the onset.

$$W_{At} = \rho_A \left(V_{fA}^L V^L\right)^{onset} \tag{60}$$

The model parameters (k_{ab}, W_{At} and η) were calculated by minimizing the differences between the experimental titration data of tank oil with n-pentane and n-decane and the result of the predictive model. The model (equation 52) showed good agreement with experimental data for predicting onset and amount of asphaltene precipitated by different n-alkanes except with n-heptane.

6 EQUATION OF STATE MODELS

6.1 Models based on Cubic Equation of State

6.1.1 Gupta et al.

The simplest model for precipitated asphaltenes using cubic equation of state was first proposed by Gupta.[73] The assumption made was that the precipitated phase is a pure solid phase consisting of only asphaltenes. Gupta used a combination of solid phase fugacity correlation and Peng-Robinson (PR) equation (for calculating the phase equilibrium) to fit the experimental data. Similar approach was later used by Thomas et al.[47] to fit titration data of Keg River Oil and Nisku Oil using pure solvents C_2, C_3, n-C_4 and a 54% C_{2+} multicomponent solvent. However, the model did not have predictive capability and significant experimental work was needed for fitting the interaction co-efficients. Any change in solvent composition would alter the model (either the number of parameters or the value of parameters) and then another set of experimental work would be necessary.[47]

6.1.2 Ngheim et al.

Nghiem et al.[74-75] considered the precipitated asphaltenes as a pure dense phase (also called as asphalt phase) and split the heaviest component of crude oil (C_{31+}) into two psuedocomponents: a non-precipitating component and a precipitating component. The precipitating components consisted of asphaltene that dissociate and asphaltene/resin micelle

that precipitate unaltered while the non-precipitating component consisted of asphaltene/resin micelle that do not precipitate or dissociate and heavy paraffins. The precipitating and non-precipitating components had identical critical properties and acentric factors (a measure of non-sphericity of the molecules), but their interaction co-efficient with light components were different.

The fugacity of the asphaltenes in asphalt phase was then given by

$$ln f_a = ln f_a^* + \frac{v_a(p - p^*)}{RT} \tag{61}$$

where, f_a and f_a^* are the fugacities of precipitated asphaltenes at pressure p and p^* respectively. v_a is molar volume of pure asphaltenes.

In order to obtain the vapor/liquid/asphalt equilibrium, the following fugacity (f) relations were considered.

$$f_{iv} = f_{il} \tag{62}$$

$$f_{n_c l} = f_a \tag{63}$$

Where $i = 1, \ldots, n_c$. The subscripts v and l represent vapor and liquid phase respectively.

The authors had considered a mixture of n_c components with asphaltene being the n_c component. The fugacities of components in liquid and vapor phases was calculated using Peng Robinson equation of state (PR-EoS)[31]. The values of f_a^* and v_a were obtained from experimental solubility data. The existence of the asphalt phase was based on the criteria $ln f_{n_c l} \geq ln f_a$.

The interaction co-efficients between the hydrocarbons were calculated using the relationship given below

$$d_{ik} = 1 - \left(\frac{2v_{ci}^{1/6} v_{ck}^{1/6}}{v_{ci}^{1/3} + v_{ck}^{1/3}} \right)^e \qquad (64)$$

Where 'e' is a regression parameter, d_{ik} is the interaction co-efficient between components i and k. v_{ci} and v_{ck} represent the critical values of components i and k respectively

The authors[74] validated the model (equation 61) with experimental data from Hirschberg et al.[6] , Burke et al.[43] and from an industrial fluid. The model showed good agreement with the experimental values. Proper division of heaviest component of oil and characterization of these components is essential in order to apply this model.

Kohse et al.[76] later introduced the effect of temperature and pressure on asphaltene precipitation into the solid model proposed by Nghiem as shown in equation 65.

$$\begin{aligned} lnf_a = lnf_a^* + \frac{v_a}{R}\left[\frac{p - p_{tp}}{T} + \frac{p^* - p_{tp}}{T^*} \right] - \frac{\Delta H_{tp}}{R}\left[\frac{1}{T} - \frac{1}{T^*} \right] \\ - \frac{\Delta C_p}{R}\left[ln\left(\frac{T}{T^*}\right) - T_{tp}\left(\frac{1}{T} - \frac{1}{T^*}\right) \right] \end{aligned} \qquad (65)$$

Where p_{tp} is the triple point pressure, ΔC_p is the heat capacity difference, ΔH_{tp} is the enthalpy of fusion at triple-point. T^* and p^* are the reference temperature and pressure respectively. The parameters needed for the model are v_a , ΔH_{tp} and ΔC_p. These parameters can be tuned using two or three experimentally determined asphaltene onset precipitation pressures.

Thus equation 65 can be considered to be the generalized form for obtaining the fugacity values of asphaltene precipitation at any pressure and temperature. This model was compared with experimental asphaltene precipitation onset data for a South American fluid and showed

good agreement with the experiment data.[76] Another work extending Ngheim's model is by Lindeloff et al.[77], where the precipitated solid was treated as a multi-component mixture. The model was then used for predicting the experimental data of Burke et al.[43] However, the model was not able to predict the precipitation behavior at high solvent dilution ratios.

6.1.3 Sabbagh et al.

Cubic EoS only describes the physical interaction between molecules in crude. However, they do not take into account the self-association of asphaltenes and the cross-association between asphaltenes and resins. Du et al.[78] developed a predictive model by combining a chemical contribution term to the cubic EoS for describing asphaltene association with reasonable success. Similarly, Sabbagh et al.[2] used PR-EoS to model the asphaltene precipitation from heavy oils and bitumens by taking into account the asphaltene self-association. They assumed a liquid-liquid equilibrium between dense liquid phase (asphaltene rich phase) and light liquid phase. The values of parameters a and b of PR-EoS were obtained by using

$$a_i = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} \left[1 + c_i \left(1 - T_{ri}^{0.5} \right) \right]^2 \tag{66}$$

$$b_i = 0.07780 \frac{R T_{ci}}{P_{ci}} \tag{67}$$

where

$$c_i = 0.3796 + 1.485 \omega_i - 0.1644 \omega_i^2 + 0.01667 \omega_i^3 \tag{68}$$

T_r, T_c, P_c and ω represent the reduced temperature, critical temperature, critical pressure and acentric factor of the pure component i.

A mixing rule was applied to calculate the PR-EoS parameters for the mixtures

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{69}$$

$$b = \sum_i x_i b_i \tag{70}$$

Where

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{0.5} \tag{71}$$

k_{ij} represents the binary interaction parameter between the components i and j.

The model needed temperature, pressure, mole fractions, parameters a and b for each component or pseudocomponent, and interaction parameters between each component and/or pseudo component as input. The authors divided the crude into pseudo components based on SARA fractions. Saturates, Aromatics and Resins were considered as pseudo-components while the asphaltenes were further divided into 30 pseudo-component fractions based on gamma distribution function described by Whitson[59].

The asphaltene EoS parameters were determined using

$$a_i = \left(\frac{M_i}{M_m}\right)^2 a_m \tag{72}$$

$$b_i = \left(\frac{M_i}{M_m}\right) b_m \tag{73}$$

Where, a_i and b_i are the EoS parameters of asphaltene aggregate while a_m and b_m are the EoS parameters of asphaltene monomers. M_i and M_m are the molar mass of asphaltene aggregate and asphaltene monomer respectively.

The PR-EoS model was then used to fit and predict the onset and amount of precipitation for several heavy oils and bitumens from Alberta diluted with n-alkanes for a wide range of temperature and pressure. The model used average molar mass of asphaltenes as a fitting parameter and this was determined by fitting precipitation data for n-heptane diluted bitumens and heavy oils. The model's predictions were poor for n-pentane diluted systems since the model did not account for resin precipitation. Similarly, the model also performed poorly for n-heptane dilution at high temperatures (100°C) at both moderately high pressures (2.1 Pa and 6.9 MPa respectively).

6.2   Statistical Associated Fluid State (SAFT) models

The most widely used EoS model for asphaltene prediction is the Statistical Associated Fluid Theory (SAFT). SAFT was developed by Chapman et al.[32-33] by applying Wertheim's thermodynamic perturbation theory[34-39] and extending it to mixtures. In perturbation theory, a reference fluid is considered and it is assumed that the reference fluid roughly describes the fluid of interest. The properties of the fluid of interest are obtained by expanding/correcting the same properties of the reference fluid.

In SAFT equation of state, the molecules are modeled in the form of chains composed of bonded spherical segments as shown in figure 10. The SAFT EoS is defined in the form of residual Helmholtz Free Energy (A^{res}). The residual free energy consists of 3 terms

- $A^{segment}$ - which represents the segment-segment interaction
- $A^{chain\ formation}$ - which accounts for the covalent chain forming bonds among the segments
- $A^{association}$ - which accounts for the presence of site – site specific interactions among the segments like hydrogen bonding interactions.[32]

$$A^{res} = A^{segment} + A^{chain\ formation} + A^{association} \tag{74}$$

The different variations of SAFT equation are CK-SAFT[79], LJ-SAFT[80-81], SAFT-VR[82], PC-SAFT[40], etc. All these variations differ only in the segment term.

PC-SAFT Equation of State

Gross and Sadowski[40] applied the perturbation theory for chain molecules and derived an expression for the segment term. Since chain molecules were used as reference fluid instead of spherical molecules, the model proposed by Gross and Sadowski was called as Perturbed Chain-SAFT (PC-SAFT). The PC-SAFT EoS requires three parameters as input

- Segment number (m)

- Segment diameter (σ)

- Segment energy parameter (ε/k)

By correlating the liquid volume and vapor pressures, Gross and Sadowski[40] identified the three pure component parameters (m, σ and ε/k) for 78 non-associating molecules.

In order to model asphaltene precipitation using PC-SAFT EoS, it is necessary to divide the reservoir fluid into vapor and liquid phases. The vapor phase is generally represented using 4 pseudo-components nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4) and light pseudo-components (C_2 and heavier gas). The liquid phase is represented using pseudo components saturates, aromatics + resins and asphaltenes. The PC-SAFT parameters (m, σ, ε/k) are then determined for each of the pseudo component based on correlations with corresponding molecular weights.

6.2.1 Ting et al.

Ting et al.[18] modeled the asphaltene phase behavior in model live oil (a mixture of C_7 asphaltenes, toluene and methane) and a recombined oil (stock oil with its separator gas) under reservoir conditions. The authors did not consider the contribution of association term in SAFT EoS since they assumed that the asphaltene phase behavior in crude oil is dominated by molecular size and van der waal interactions. The asphaltenes were also assumed to be pre-aggregated.

The asphaltene SAFT parameters for live model oil were m=80, $\sigma=4.05A^°$ and $\varepsilon/k = 350.8K$. The molecular weight for asphaltenes was taken in the range of 3767-4000 g/mol. The SAFT predictions for onset of asphaltene instability were however found to be inaccurate at higher methane concentrations in model oil system since asphaltene polydispersity was not taken into account. The parameters used for different pseudocomponents in recombined oil are listed in table 1. For the recombined oil, the binary interaction parameters between various subfractions were obtained from binary interaction parameters of representative species of subfractions. The SAFT model predicted accurately the asphaltene instability of recombined oil as shown in figure 11. However, it was tested for only two conditions of Gas-to-oil ratio (GOR).

6.2.2 Gonzalez et al.

Gonzalez et al.[83] predicted the asphaltene instability under gas injection of the same model live oil and recombined oil studied by Ting et al.[18] SAFT EoS was able to adequately predict the onset of asphaltene precipitation when methane, ethane, CO_2 and N_2 were injected to oil mixtures as shown in figure 12.

Gonzalez et al.[84] divided asphaltenes into subfractions (C_5-C_7, C_7-C_{15} and C_{15+}) and tuned the SAFT parameters in order to account for asphaltene polydispersity. The PC-SAFT parameters used are given in table 2. However, the simulations predicted higher asphaltene precipitation than compared to experimental values under gas injection as shown in figure 13. For mono-dispersed asphaltenes (average molecular weight=1700 g/mol) with SAFT parameters m=29.5, $\sigma = 4.30A^{\circ}$ and $\varepsilon/k = 392.3K$ the prediction obtained is shown in figure 14. Similarly, a higher asphaltene precipitation was predicted by PC SAFT simulation when asphaltenes were considered to be polydisperse (from comparison of total asphaltenes precipitated in figures 13 and 14).

6.2.3 Panuganti et al.

Panuganti et al.[85] improved the characterization procedure for crude oil and considered ethane and propane separately instead of lumping it as heavy gas. This led to more flexibility in binary interaction parameter and hence subsequently better estimation of SAFT parameters. The PC-SAFT parameter correlations used were given in table 3.

Panuganti showed that the modeling of asphaltene phase behavior by PC-SAFT was better than that using SRK EoS (a cubic equation of state). The cubic equation of state cannot describe accurately the phase behavior of mixture of molecules with large size differences since they are unable to accurately calculate the liquid density of the precipitated phase. The characterization procedure by Panuganti et al. was further improved by Punnapala and Vargas.[86] Similarly, PC-SAFT EoS was used by Zuniga-Hinojosa et al.[87] for predicting asphaltene precipitation by addition on n-alkane solvents to bitumens and heavy oils. A gamma distribution function was used for representing the molar mass distribution of asphaltenes.

Another approach used for modeling asphaltene is based on McMillan-Mayer theory. In this theory, the asphaltenes are assumed to be large spherical molecules with multiple association sites. The asphaltene molecules can bind with other asphaltenes or with smaller molecules like resins with just one association site per molecule. Asphaltene precipitation work under this approach includes studies by Wu et al.[88-89] based on SAFT model (considering hard spheres repulsive, association and dispersion force interactions) and Buenrostro-Gonzalez et al.[90] based on SAFT-VR EOS model. Even though the model prediction by Wu et al. fitted well with the experiment data, it suffered from inability to explain phenomena related to poly-dispersity since the model considered asphaltenes to be a single psuedocomponent.[91]

6.3   Models based on Cubic-Plus-Association (CPA) Equation of State

6.3.1   Li and Firoozabadi

Li and Firoozabadi[29, 92] applied cubic-plus-association (CPA) EoS to study the asphaltene precipitation. The CPA consisted of two parts: physical part (based on Peng Robinson EoS) and association part (based on Wertheim's thermodynamic perturbation theory).

The physical contribution is represented by

$$\frac{A_{ph}^{ex}}{nRT} = -ln(1 - b\rho) - \frac{a}{2\sqrt{2}RT} ln\left(\frac{1 + (1 + \sqrt{2})b\rho}{1 + (1 - \sqrt{2})b\rho}\right) \qquad (75)$$

Where A_{ph}^{ex} represents the physical contribution to excess Helmholtz free energy, n is the number of moles and ρ is the molar density of the mixture. a and b are the energy and volume parameters of the mixture.

The association contribution is given by

$$\frac{A^{ex}_{assoc}}{nRT} = N_A x_A \left(ln\chi_A + \frac{1 - \chi_A}{2} \right) + N_R \chi_R \left(ln\chi_R + \frac{1 - \chi_R}{2} \right) \qquad (76)$$

Where, A^{ex}_{assoc} represents the association contribution to excess free energy, A and R refer to asphaltene and heavy molecules (resins/aromatics) respectively, x_A and x_R are the mole fractions of asphaltenes and heavy molecules respectively.

The authors assumed that each asphaltene molecule had N_A identical association sites and the each heavy molecule (resins or aromatics) had N_R identical association sites. Similarly, χ_A and χ_R represents the mole fractions of asphaltene and heavy molecules not bonded to one of the association sites. The self-association among heavy molecules was neglected and hence χ_A and χ_R were evaluated using the following equations

$$\chi_A = \frac{1}{1 + \rho N_A x_A \chi_A \Delta^{AA} + \rho N_R x_R \chi_R \Delta^{AR}} \qquad (77)$$

$$\chi_R = \frac{1}{1 + \rho N_R x_R \chi_R \Delta^{AR}} \qquad (78)$$

Where,

$$\Delta^{ij} = g\kappa_{ij}b_{ij} \left[exp\left(\frac{\varepsilon_{ij}}{k_B T} \right) - 1 \right] \qquad (79)$$

Δ^{ij} ($i = A$ and $j = A$ or R) characterizes the association strength.

k_B = Boltzmann constant, κ_{ij} = association volume parameter, ε_{ij} = association energy parameter, g = contact value of the radial distribution of hard sphere mixtures approximated by

$$g \approx \frac{1 - 0.5(b\rho_c/4)}{[1 - (b\rho_c/4)]^3} \qquad (80)$$

The model contains only one adjustable parameter 'ε_{AR}'. The authors tested their model by fitting the experimental data for crude oil from Sabbagh et al.[2] to predict the effect of temperature, pressure and n-alkane addition. Though the model successfully predicted the overall trend in asphaltene precipitation, it could not accurately predict the onset of asphaltene precipitation. The authors considered it possible to reduce the deviation in onset by adjusting the parameter ε_{AR}. However, this may lead to lower performance of the model (equations 75 and 76).[29]

6.3.2 Shirani et al.

The CPA EoS of state was also used by Shirani et al.[93] to predict the asphaltene precipitation from live oils. Asphaltene was considered as molecules with two association sites in the model. The model used for the study was

$$Z = Z^{physical} + Z^{association} \tag{81}$$

Where, Z is the compressibility factor. The physical part of the equation ($Z^{physical}$) was evaluated using both Soave Redlick Kwong (SRK) and Peng Robinson (PR) EoS.

For a mixture of components, the parameters a and b of the PR and SRK EoS were evaluated using the mixing rule given in equations 69, 70 and 71.

The association part ($Z^{association}$) was evaluated using the relation

$$Z^{association} = -\frac{1}{2}\left(1 + \frac{1}{v}\frac{\partial lng}{\partial(1/v)}\right)\sum_i x_i \sum_{A_i}\left(1 - X_{A_i}\right) \tag{82}$$

Where, x_i is the mole fraction of component i, v is the molar volume, X_{A_i} is the mole fraction of molecule i not bonded at site A and g is a radial distribution function given by

$$g = \frac{1}{1 - 1.9(b/4v)} \tag{83}$$

The adjustable parameter in the model is the binary interaction parameter $\left(k_{ij}\right)$ between asphaltenes and other components (heavy components like resin and pseudocomponents, light components – CO_2, N_2, C_1 and H_2S).

The model prediction deviated by 55% from the experimental data. The model's prediction was however better than predictions by colloidal models of Victorov et al.[94] and Pan et al.[95] Also, SRK EoS was found to give a better fit than PR EoS.[93]

7 COLLOIDAL MODEL

The idea of existence of asphaltenes in colloidal form was first proposed by Nellensteyn[96] and then by Pfeiffer and Saal.[12] According to Pfeiffer and Saal, the center of colloid is occupied by the substance with the highest molecular weight and having most aromatic nature (asphaltenes). These asphaltenes are then surrounded by lighter constituents with lower molecular weight and less aromatic nature. Thus when the system consists of sufficient constituents to form the outer regions of structure, asphaltenes are said to be fully peptized. However, if there is a shortage of resins surrounding the asphaltenes, then the colloid will experience mutual attraction and result in formation of flocculated asphaltene aggregates.

7.1 Leontaritis and Mansoori

In 1987, Leontaritis and Mansoori[19] proposed a thermodynamic colloidal model for predicting asphaltene flocculation due to changes in composition or electrical phenomena. The basis for colloidal model is the assumption that asphaltene molecules exist in the oil in

the form of small solid particles in colloidal suspension, stabilized by the resins adsorbed on their surfaces. Addition of miscible solvent to crude oil results in desorption of resins from the surface.

In thermodynamic colloid model, a vapor-liquid equilibrium (VLE) calculation is initially performed for estimating the liquid phase composition at which asphaltenes can flocculate. In order to split the resins between the oil phase and the asphaltene phase, the model equates the chemical potential of resins between the phases at equilibrium. Hence

$$\mu_{resin}^{asphaltene\ phase} = \mu_{resin}^{oil\ phase} \tag{84}$$

The chemical potential of resin was calculated using Flory-Huggins statistical thermodynamics theory using the equation

$$\frac{\Delta\mu_R}{RT} = \frac{\mu_R - (\mu_R)_{reference}}{RT} = ln(\phi_R) + 1 - \frac{v_R}{v_m} + \chi_R \tag{85}$$

Where, ϕ_R is the fraction of resin in the liquid, $\Delta\mu_R$ is the chemical potential of the resins, χ_R is the Flory-Higgins interaction parameter, v_R and v_m are the molar volume of resin and liquid mixture respectively.

The authors defined critical resin concentration $(C_R)_{crit}$ as the concentration of resin in oil phase which is just enough for keeping the colloidal asphaltene particles completely covered with resins. The critical chemical potential of resins in oil phase is then equal to the chemical in solid phase (asphaltene phase). For a given reservoir fluid, the $(C_R)_{crit}$ value was determined using titration experiments. This value was then compared to the oil phase resin concentration, C_R. Flocculation and aggregation problems may occur if

$$C_R < (C_R)_{crit} \tag{86}$$

The authors tested the ability of the model to predict the asphaltene flocculation onset of tank oil 1 of Hischberg et al.[6] using different solvents (hexadecane, heptane and dodecane). The model needed one experimental determined onset data for fitting while the rest was predicted. The model made good predictions for hexadecane and dodecane fitted runs while the predictions for heptane fitted runs were poor. Also, the colloidal model is applicable to solutions where asphaltene dissociation can take place.

7.2 Victorov and Firoozabadi

Victorov and Firoozabadi[94] developed an alternate colloidal model for solubilization of asphaltenes by resins using advanced thermodynamic models. The authors assumed that the asphaltene colloidal particle has a core formed by n_1 aggregated asphaltene molecules with n_2 resin molecules adhered to the surface of core. In the original paper, the authors called aggregates of asphaltenes as "micelles". This term is doubtful as shown by Friberg[97]. For clarity reason we will continue to use micellization in the text though it can be misleading.

The micelle chemical potential,

$$\mu_M^\beta = n_1 \mu_{a1}^\beta + n_2 \mu_{r1}^\beta \tag{87}$$

Where μ_{a1} , μ_{r1} and μ_M are the chemical potential for asphaltenes, resin and micelle in petroleum fluid. The superscript β denotes petroleum fluid.

Applying thermodynamics for dilute solution,

For monomeric asphaltenes and resins

$$\mu_{a1} = \mu_{a1}^* + kTlnX_{a1} \tag{88}$$

$$\mu_{r1} = \mu_{r1}^* + kTlnX_{r1} \tag{89}$$

For micelle

$$\mu_M = G_M^{00} + kTlnX_M \tag{90}$$

Where, X_{a1}, X_{r1} and X_M are the mole fractions of asphaltenes, resins and micelle respectively. μ_{a1}^*, μ_{r1}^* and G_M^{00} are the standard chemical potential of asphaltenes, resin and micelle respectively.

The mole fraction of micelle in the crude was given by

$$X_M = X_{a1}^{n1} X_{r1}^{n2} exp\left\{\frac{\Delta G_M^{00}}{RT}\right\} \tag{91}$$

in which the standard Gibbs energy of formation of micelle (micellization process), ΔG_M^{00} was defined as

$$\Delta G_M^{00} = n_1\mu_{a1}^* + n_2\mu_{r1}^* - G_M^{00} \tag{92}$$

In order to find the expression for Gibbs energy of micellization, the authors considered lyophobic, interfacial and electrostatic contributions and came up with the expression

$$\frac{\Delta G_M^{00}}{RT} = n_2 f(\Theta) - n_1 lnX_{a1}^{ons} \tag{93}$$

where,

$$f(\Theta) = ln(1 - \Theta) + \frac{\Delta U_r}{RT} - \frac{\sigma_0 a(1 - \Theta)}{RT\Theta} \tag{94}$$

$$\Delta U_r = a(\bar{U}_{r-c} - \bar{U}_{r-a}) \tag{95}$$

Θ = the fraction of micellar core covered by resins, a = surface area of a resin molecule polar head, X_{a1}^{ons} = equilibrium concentration of monomeric asphaltenes in crude co-existing with solid asphaltene phase (or) maximum concentration of monomeric asphaltenes in crude at given condition, σ_0 = interfacial tension at zero adsorption of resin onto the micelle, $\overline{U}_{r-c}$ and $\overline{U}_{r-a}$ are the average interaction energies of resin molecule head with crude and with asphaltene molecules (micellar core) respectively.

The model (equation 93) assumed that all micelles are mono-disperse. The most probable composition of micelle Θ was determined using

$$ln\left(\frac{X_{a1}}{X_{r1}X_{a1}^{ons}}\right) - \frac{\Delta U_r}{RT} - \frac{\sigma_0 a}{RT}(1+b) = ln(1-\Theta) - \frac{\Theta}{(1-\Theta)}(1+\Theta b) \qquad (96)$$

Where,

$$b = \frac{v_a}{a}\left(\frac{8\pi}{an_2^s}\right)^{1/2} \qquad (97)$$

n_2^s represents the maximum number of resin molecules that can be accommodated on the flat surface if micellar core. For the titration experiments i.e., titration of crude oil with an n-alkane, the equilibrium concentration was calculated using the equation

$$X_{a1}^{ons}(T,P,ratio) = X_{a1}^{ons}(T,P,ratio=0)\frac{f_{a1}^{\beta}((T,P,ratio=0)}{f_{a1}^{\beta}(T,P,ratio)} \qquad (98)$$

Where f_{a1}^{β} is the fugacity co-efficient of monomeric asphaltenes in petroleum fluid, 'ratio' refers to the dilution ratio (volume of solvent added/amount of original crude), ratio=0 indicates the original state before dilution. The fugacities were calculated using Equation of State (EoS).

Asphaltene precipitation occurs if $X_{a1}^{\beta} > X_{a1}^{ons}$. X_{a1}^{β} refers to the concentration of asphaltene monomers in the petroleum fluid (crude). Due to lack of experimental data on the parameters σ_0, a and $(\overline{U}_{r-c} - \overline{U}_{r-a})$ the authors assigned arbitrary values to them. The plot obtained on dilution of tank oil is shown in figure 15. The precipitation of asphaltene starts when the solid and the curved lines intersect. Similarly, the asphaltene precipitation curves obtained for various precipitant addition is shown in figure 16. The results obtained predicted that the precipitation ability of the n-alkane decreases with their chain length. The predictions were also found to agree well with the experimental data. Similarly, the model was able to predict the effect of resins on the asphaltene precipitation tendency as shown in figure 17.

One of the main drawbacks of the model was its inability to predict accurately the precipitation of asphaltenes under gas titration conditions. The thermodynamic micellization model for gas titration was further improved by Tavakkoli et al.[98-99] by applying the characterization method used by Ngheim et al.[74] for oil characterization. The new model introduced a new matching parameter for representing the interaction co-efficient between the asphaltene and light hydrocarbons thereby improving the prediction capability of thermodynamic micellization model.

7.3   Pan and Firoozabadi

Another thermodynamic model within the framework of colloidal theory was proposed by Pan and Firoozabadi.[95, 100-101] This approach is also known as a reverse micelle approach. In this approach, the precipitated phase was assumed to consist of asphaltenes and resins which do not associate with each other, while the liquid phase was assumed to consist of mixture of asphaltenes and resin monomers, asphaltene-resins micelles and other oil species. The fugacity co-efficient of each species was calculated using an equation of state. The

equilibrium phase compositions were calculated by minimizing the Gibbs energy of system consisting of liquid phase and precipitated phase. The main drawback of the model is the large number of parameters needed. Also, the variation of these parameters with pressure, temperature and oil composition is not clear.[102]

8   COMPARISON OF MODELS

A comparative study of thermodynamic micellization model and the solid model (based on cubic EoS) by Tavakkoli et al.[98] showed that both models predict the asphaltene precipitation reasonably well at atmospheric pressure using precipitants. However, the micellization model was found to be complex and computationally demanding and also showed poor prediction of maximum asphaltene precipitation. The micellization model's predictions did however match well with more experimental point. Similarly, a comparison study of thermodynamic modelling based on solid model, Flory-Huggins model and PC-SAFT EoS model for Iranian crude by Behbahani et al.[103] showed that the PC-SAFT EoS was able to predict more accurately the onset points of asphaltene precipitation for different solvents (n-C_5, n-C_9 and n-C_{12}).

9   CONCLUDING REMARKS

Asphaltenes precipitation and deposition continue to be one of the major challenges faced by the industry. In the last 30 years, several attempts have been made for modeling and predicting asphaltene precipitation. As shown in this review, the various modeling techniques have increased our knowledge of the various models and their limitations in predicting onset and amount of asphaltene precipitation. A comparison of modeling works indicates that precipitation modeling using PC-SAFT EoS is promising. Also, improvements in fluid

characterization technique and the accounting for asphaltene poly-dispersity are seen to play an important role in improving the quality of predictions.

10   ACKNOWLEDGEMENTS

11   REFERENCES

1.   Mullins, O. C. The Asphaltenes. *Annual Review of Analytical Chemistry* **2011,** *4*, 393-418.

2.   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* (2), 625-634.

3.   Speight, J. G. *The Chemistry and Technology of Petroleum*; Fourth Edition ed.2006.

4.   Kokal, S. L.; Sayegh, S. G. Asphaltenes: The Cholesterol Of Petroleum. In *SPE Middle East Oil Show*; Society of Petroleum Engineers: Bahrain, 1995.

5.   Leontaritis, K. J.; Ali Mansoori, G. Asphaltene deposition: a survey of field experiences and research approaches. *Journal of Petroleum Science and Engineering* **1988,** *1* (3), 229-239.

6.   Hirschberg, A.; deJong, L. N. J.; Schipper, B. A.; Meijer, J. G. Influence of Temperature and Pressure on Asphaltene Flocculation. *SPE Journal* **1984,** *24* (03), 283-293.

7.   de Boer, R. B.; Leerlooyer, K.; Eigner, M. R. P.; Van Bergen, A. R. D. Screening of Crude Oils for Asphalt Precipitation: Theory, Practice, and the Selection of Inhibitors. *SPE Journal* **1995,** *10* (01), 55-61.

8.   Spiecker, P. M.; Gawrys, K. L.; Kilpatrick, P. K. Aggregation and solubility behavior of asphaltenes and their subfractions. *Journal of Colloid and Interface Science* **2003,** *267* (1), 178-193.

9.   Groenzin, H.; Mullins, O. C. Asphaltene Molecular Size and Structure. *The Journal of Physical Chemistry A* **1999,** *103* (50), 11237-11245.

10.   Groenzin, H.; Mullins, O. Asphaltene Molecular Size and Weight by Time-Resolved Fluorescence Depolarization. In *Asphaltenes, Heavy Oils, and Petroleomics*, Mullins, O.; Sheu, E.; Hammami, A.; Marshall, A., Eds.; Springer New York, 2007, pp 17-62.

11.   Mullins, O. C.; Sabbah, H.; Eyssautier, J.; Pomerantz, A. E.; Barré, L.; Andrews, A. B.; Ruiz-Morales, Y.; Mostowfi, F.; McFarlane, R.; Goual, L.; Lepkowicz, R.; Cooper, T.; Orbulescu, J.; Leblanc, R. M.; Edwards, J.; Zare, R. N. Advances in Asphaltene Science and the Yen–Mullins Model. *Energy & Fuels* **2012,** *26* (7), 3986-4003.

12.   Pfeiffer, J. P.; Saal, R. N. J. Asphaltic Bitumen as Colloid System. *The Journal of Physical Chemistry* **1940,** *44* (2), 139-149.

13.   Barré, L.; Simon, S.; Palermo, T. Solution Properties of Asphaltenes. *Langmuir* **2008,** *24* (8), 3709-3717.

14.   Dickie, J. P.; Yen, T. F. Macrostructures of the asphaltic fractions by various instrumental methods. *Analytical Chemistry* **1967,** *39* (14), 1847-1852.

15.   Mullins, O. C. The Modified Yen Model†. *Energy & Fuels* **2010,** *24* (4), 2179-2207.

16.   Mullins, O. C. The Modified Yen Model. *Energy & Fuels* **2010,** *24* (4), 2179-2207.

17.   Sjöblom, J.; Simon, S.; Xu, Z. Model molecules mimicking asphaltenes. *Advances in Colloid and Interface Science* **2015,** *218* (0), 1-16.

18.   David Ting, P.; Hirasaki, G. J.; Chapman, W. G. Modeling of Asphaltene Phase Behavior with the SAFT Equation of State. *Petroleum Science and Technology* **2003,** *21* (3-4), 647-661.

19.   Leontaritis, K. J.; Mansoori, G. A. Asphaltene Flocculation During Oil Production and Processing: A Thermodynamic Collodial Model. In *SPE International Symposium on Oilfield Chemistry, 4-6 February*; Society of Petroleum Engineers: San Antonio, Texas, 1987.

20.   Agrawala, M.; Yarranton, H. W. An Asphaltene Association Model Analogous to Linear Polymerization. *Industrial & Engineering Chemistry Research* **2001,** *40* (21), 4664-4672.

21.   Scatchard, G. Equilibria in Non-electrolyte Solutions in Relation to the Vapor Pressures and Densities of the Components. *Chemical Reviews* **1931,** *8* (2), 321-333.

22.   Hildebrand, J. H.; Scott, R. L. *Regular Solutions*; Prentice-Hall: Englewood Cliffs, New Jearsey, 1962.

23.   Andersen, S. I.; Speight, J. G. Thermodynamic models for asphaltene solubility and precipitation. *Journal of Petroleum Science and Engineering* **1999,** *22* (1–3), 53-66.

24.   Barton, A. F. M. Solubility parameters. *Chemical Reviews* **1975,** *75* (6), 731-753.

25.   Painter, P. C.; Coleman, M. M. *Fundamentals of polymer Science: An Introductory Text*; CRC Press 1997.

26.   Flory, P. J. Thermodynamics of High Polymer Solutions. *The Journal of Chemical Physics* **1942,** *10* (1), 51-61.

27.   Huggins, M. L. Solutions of Long Chain Compounds. *The Journal of Chemical Physics* **1941,** *9* (5), 440-440.

28.   Scott, R. L.; Magat, M. The Thermodynamics of High-Polymer Solutions: I. The Free Energy of Mixing of Solvents and Polymers of Heterogeneous Distribution. *The Journal of Chemical Physics* **1945,** *13* (5), 172-177.

29.   Li, Z.; Firoozabadi, A. Modeling Asphaltene Precipitation by n-Alkanes from Heavy Oils and Bitumens Using Cubic-Plus-Association Equation of State. *Energy & Fuels* **2010,** *24* (2), 1106-1113.

30.   Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science* **1972,** *27* (6), 1197-1203.

31.   Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals* **1976,** *15* (1), 59-64.

32.   Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. SAFT: Equation-of-state solution model for associating fluids. *Fluid Phase Equilibria* **1989,** *52* (0), 31-38.

33.   Chapman, W. G.; Jackson, G.; Gubbins, K. E. Phase equilibria of associating fluids. *Molecular Physics* **1988,** *65* (5), 1057-1079.

34.   Wertheim, M. S. Fluids with highly directional attractive forces. IV. Equilibrium polymerization. *J Stat Phys* **1986,** *42* (3-4), 477-492.

35.   Wertheim, M. S. Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations. *J Stat Phys* **1984,** *35* (1-2), 35-47.

36.   Wertheim, M. S. Fluids with highly directional attractive forces. I. Statistical thermodynamics. *J Stat Phys* **1984,** *35* (1-2), 19-34.

37.   Wertheim, M. S. Fluids of dimerizing hard spheres, and fluid mixtures of hard spheres and dispheres. *The Journal of Chemical Physics* **1986,** *85* (5), 2929-2936.

38.   Wertheim, M. S. Thermodynamic perturbation theory of polymerization. *The Journal of Chemical Physics* **1987,** *87* (12), 7323-7331.

39. Wertheim, M. S. Fluids with highly directional attractive forces. III. Multiple attraction sites. *J Stat Phys* **1986,** *42* (3-4), 459-476.

40. Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Industrial & Engineering Chemistry Research* **2001,** *40* (4), 1244-1260.

41. Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An Equation of State for Associating Fluids. *Industrial & Engineering Chemistry Research* **1996,** *35* (11), 4310-4318.

42. Buckley, J.; Wang, J.; Creek, J. Solubility of the Least-Soluble Asphaltenes. In *Asphaltenes, Heavy Oils, and Petroleomics*, Mullins, O.; Sheu, E.; Hammami, A.; Marshall, A., Eds.; Springer New York, 2007, pp 401-437.

43. Burke, N. E.; Hobbs, R. E.; Kashou, S. F. Measurement and modeling of asphaltene precipitation. *JPT, Journal of Petroleum Technology* **1990,** *42* (11), 1440-1446.

44. Zudkevitch, D.; Joffe, J. Correlation and prediction of vapor-liquid equilibria with the redlich-kwong equation of state. *AIChE Journal* **1970,** *16* (1), 112-119.

45. Novosad, Z.; Costain, T. G. Experimental and Modeling Studies of Asphaltene Equilibria for a Reservoir Under CO2 Injection. In *SPE Annual Technical Conference and Exhibition, 23-26 September,* ; Society of Petroleum Engineers: New Orleans, Louisiana, 1990.

46. Rassamdana, H.; Dabir, B.; Nematy, M.; Farhani, M.; Sahimi, M. Asphalt flocculation and deposition: I. The onset of precipitation. *AIChE Journal* **1996,** *42* (1), 10-22.

47. Thomas, F. B.; Bennion, D. B.; Bennion, D. W.; Hunter, B. E. Experimental And Theoretical Studies Of Solids Precipitation From Reservoir Fluid. *Journal of Canadian Petroleum Technology* **1992,** *31* (01).

48.   Won, K. W. Continuous Thermodynamics for Solid-Liquid Equilibria: Wax Formation From Heavy Hydrocarbon Mixtures. In *A.I.Ch.E. Spring National Meeting, Session 1A, Houston, Texas, March 24-28*, 1986.

49.   Won, K. W. Thermodynamics for solid solution-liquid-vapor equilibria: wax phase formation from heavy hydrocarbon mixtures. *Fluid Phase Equilibria* **1986,** *30* (0), 265-279.

50.   MacMillan, D. J.; Tackett, J. E., Jr.; Jessee, M. A.; Monger-McClure, T. G. A Unified Approach to Asphaltene Precipitation: Laboratory Measurement and Modeling. *Journal of Petroleum Technology* **1995,** *47* (09), 788-793.

51.   Chung, T.-H. Thermodynamic Modeling for Organic Solid Precipitation. In *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers: Washington DC, 1992.

52.   Nor-Azlan, N.; Adewumi, M. A. Development of Asphaltene Phase Equilibria Predictive Model. In *SPE Eastern Regional Meeting, 2-4 November,*; Society of Petroleum Engineers: Pittsburgh, Pennsylvania, 1993.

53.   Cimino, R.; Correra, S.; Sacomani, P. A.; Carnniani, C. In *Thermodynamic Modelling for Prediction of Asphaltene Deposition in Live Oils*, SPE 28993, Presented at SPE International Symposium on Oilfield Chemistry, 14-17 February, San Antonio, TX, USA, 1995.

54.   Wang, J.; Creek, J. L.; Buckley, J. S. Screening for Potential Asphaltene Problems. In *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers: San Antonio, Texas, USA, 2006.

55.   Yarranton, H. W.; Masliyah, J. H. Molar mass distribution and solubility modeling of asphaltenes. *AIChE Journal* **1996,** *42* (12), 3533-3543.

56.   Alboudwarej, H.; Akbarzadeh, K.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W. Regular solution model for asphaltene precipitation from bitumens and solvents. *AIChE Journal* **2003,** *49* (11), 2948-2956.

57.   Akbarzadeh, K.; Dhillon, A.; Svrcek, W. Y.; Yarranton, H. W. Methodology for the Characterization and Modeling of Asphaltene Precipitation from Heavy Oils Diluted with n-Alkanes. *Energy & Fuels* **2004,** *18* (5), 1434-1441.

58.   Akbarzadeh, K.; Alboudwarej, H.; Svrcek, W. Y.; Yarranton, H. W. A generalized regular solution model for asphaltene precipitation from n-alkane diluted heavy oils and bitumens. *Fluid Phase Equilibria* **2005,** *232* (1–2), 159-170.

59.   Whitson, C. H. Characterizing Hydrocarbon Plus Fractions. *SPE Journal* **1983,** *23* (04), 683-694.

60.   Buckley, J. S.; Hirasaki, G. J.; Liu, Y.; Von Drasek, S.; Wang, J. X.; Gill, B. S. Asphaltene Precipitation and Solvent Properties of Crude Oils. *Petroleum Science and Technology* **1998,** *16* (3-4), 251-285.

61.   Buckley, J. S. Predicting the Onset of Asphaltene Precipitation from Refractive Index Measurements. *Energy & Fuels* **1999,** *13* (2), 328-332.

62.   Wang, J. X.; Buckley, J. S. An Experimental Approach to Prediction of Asphaltene Flocculation. In *SPE International Symposium on Oilfield Chemistry*; Society of Petroleum Engineers: Houston, Texas, 2001.

63.   Buckley, J. S.; Wang, J. Crude oil and asphaltene characterization for prediction of wetting alteration. *Journal of Petroleum Science and Engineering* **2002,** *33* (1–3), 195-202.

64.   Wiehe, I. A. Two-Dimensional Solubility Parameter Mapping of Heavy Oils. *Fuel Science and Technology International* **1996,** *14* (1-2), 289-312.

65.   Wattana, P.; Wojciechowski, D. J.; Bolaños, G.; Fogler, H. S. Study of Asphaltene Precipitation Using Refractive Index Measurement. *Petroleum Science and Technology* **2003,** *21* (3-4), 591-613.

66.   Vargas, F. M.; Gonzalez, D. L.; Creek, J. L.; Wang, J.; Buckley, J.; Hirasaki, G. J.; Chapman, W. G. Development of a General Method for Modeling Asphaltene Stability†. *Energy & Fuels* **2009,** *23* (3), 1147-1154.

67.   Vargas, F. M.; Chapman, W. G. Application of the One-Third rule in hydrocarbon and crude oil systems. *Fluid Phase Equilibria* **2010,** *290* (1–2), 103-108.

68.   Wang, J. X.; Buckley, J. S. A Two-Component Solubility Model of the Onset of Asphaltene Flocculation in Crude Oils. *Energy & Fuels* **2001,** *15* (5), 1004-1012.

69.   Shokrlu, Y. H.; Kharrat, R.; Ghazanfari, M. H.; Saraji, S. Modified Screening Criteria of Potential Asphaltene Precipitation in Oil Reservoirs. *Petroleum Science and Technology* **2011,** *29* (13), 1407-1418.

70.   Mohammadi, A. H.; Rixon, D. The Scott-Magat Polymer Theory for Determining Onset of Precipitation of Dissolved Asphaltene in the Solvent + Precipitant Solution. *The Open Thermodynamics Journal* **2008,** *2*, 13-16.

71.   Mansoori, G. A.; Jiang, T. S. In *Asphaltene Deposition and its Role in Enhanced Oil Recovery Miscible Gas Flooding*, Third European Conference on Enhanced Oil Recovery, Rome, 1985.

72.   Kawanaka, S.; Park, S. J.; Mansoori, G. A. Organic Deposition From Reservoir Fluids: A Thermodynamic Predictive Technique. *SPE Journal* **1991,** *6* (02), 185 - 192.

73.   Gupta, A. K. A Model for Asphaltene Flocculation Using an Equation of State. MSc. Thesis, University of Calgary1986.

74.   Nghiem, L. X.; Hassam, M. S.; Nutakki, R.; George, A. E. D. Efficient Modelling of Asphaltene Precipitation. In *SPE Annual Technical Conference and Exhibition,*; Society of Petroleum Engineers: Houston, Texas, 1993.

75.   Nghiem, L. X.; Coombe, D. A. Modelling Asphaltene Precipitation During Primary Depletion. *SPE Journal* **1997,** *2* (02), 170-176.

76.   Kohse, B. F.; Nghiem, L. X.; Maeda, H.; Ohno, K. Modelling Phase Behaviour Including the Effect of Pressure and Temperature on Asphaltene Precipitation. In *SPE Asia Pacific Oil and Gas Conference and Exhibition, 16-18 October*; Society of Petroleum Engineers: Brisbance, Australia, 2000.

77.   Lindeloff, N.; Heidemann, R. A.; Andersen, S. I.; Stenby, E. H. A thermodynamic mixed-solid asphaltene precipitation model. *Petroleum Science and Technology* **1998,** *16* (3-4), 307-321.

78.   Du, J. L.; Zhang, D. A Thermodynamic Model for the Prediction of Asphaltene Precipitation. *Petroleum Science and Technology* **2004,** *22* (7-8), 1023-1033.

79.   Huang, S. H.; Radosz, M. Equation of state for small, large, polydisperse, and associating molecules. *Industrial & Engineering Chemistry Research* **1990,** *29* (11), 2284-2294.

80.   Kraska, T.; Gubbins, K. E. Phase Equilibria Calculations with a Modified SAFT Equation of State. 1. Pure Alkanes, Alkanols, and Water. *Industrial & Engineering Chemistry Research* **1996,** *35* (12), 4727-4737.

81.   Kraska, T.; Gubbins, K. E. Phase Equilibria Calculations with a Modified SAFT Equation of State. 2. Binary Mixtures of n-Alkanes, 1-Alkanols, and Water. *Industrial & Engineering Chemistry Research* **1996,** *35* (12), 4738-4746.

82. Gil-Villegas, A.; Galindo, A.; Whitehead, P. J.; Mills, S. J.; Jackson, G.; Burgess, A. N. Statistical associating fluid theory for chain molecules with attractive potentials of variable range. *The Journal of Chemical Physics* **1997,** *106* (10), 4168-4186.

83. 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* (4), 1230-1234.

84. 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 Associating Fluid Theory Equation of State†. *Energy & Fuels* **2007,** *21* (3), 1231-1242.

85. 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* **2012,** *93* (0), 658-669.

86. Punnapala, S.; Vargas, F. M. Revisiting the PC-SAFT characterization procedure for an improved asphaltene precipitation prediction. *Fuel* **2013,** *108* (0), 417-429.

87. Zúñiga-Hinojosa, M. A.; Justo-García, D. N.; Aquino-Olivos, M. A.; Román-Ramírez, L. A.; García-Sánchez, F. Modeling of asphaltene precipitation from n-alkane diluted heavy oils and bitumens using the PC-SAFT equation of state. *Fluid Phase Equilibria* **2014,** *376* (0), 210-224.

88. Wu, J.; Prausnitz, J. M.; Firoozabadi, A. Molecular-thermodynamic framework for asphaltene-oil equilibria. *AIChE Journal* **1998,** *44* (5), 1188-1199.

89. Wu, J.; Prausnitz, J. M.; Firoozabadi, A. Molecular thermodynamics of asphaltene precipitation in reservoir fluids. *AIChE Journal* **2000,** *46* (1), 197-209.

90. Buenrostro-Gonzalez, E.; Lira-Galeana, C.; Gil-Villegas, A.; Wu, J. Asphaltene precipitation in crude oils: Theory and experiments. *AIChE Journal* **2004,** *50* (10), 2552-2570.

91. Monteagudo, J. E. P.; Lage, P. L. C.; Rajagopal, K. Towards a polydisperse molecular thermodynamic model for asphaltene precipitation in live-oil. *Fluid Phase Equilibria* **2001,** *187–188* (0), 443-471.

92. Li, Z.; Firoozabadi, A. Cubic-plus-association equation of state for asphaltene precipitation in live oils. *Energy & Fuels* **2010,** *24* (5), 2956-2963.

93. Shirani, B.; Nikazar, M.; Mousavi-Dehghani, S. A. Prediction of asphaltene phase behavior in live oil with CPA equation of state. *Fuel* **2012,** *97* (0), 89-96.

94. Victorov, A. I.; Firoozabadi, A. Thermodynamic micellizatin model of asphaltene precipitation from petroleum fluids. *AIChE Journal* **1996,** *42* (6), 1753-1764.

95. Pan, H.; Firoozabadi, A. Thermodynamic micellization model for asphaltene precipitation inhibition. *AIChE Journal* **2000,** *46* (2), 416-426.

96. Nellensteyn, F. J. The Constitution of Asphalt. *Journal of the Institute of Petroleum Technology* **1924,** *10*, 311-325.

97. Friberg, S. Micellization. In *Asphaltenes, Heavy Oils, and Petroleomics*, Mullins, O.; Sheu, E.; Hammami, A.; Marshall, A., Eds.; Springer New York, 2007, pp 189-203.

98. Tavakkoli, M.; Masihi, M.; Kharrat, R.; Ghazanfari, M. H. Thermodynamic Modelling of Asphaltene Precipitation for Heavy Crude: A Comparative Study of Thermodynamic Micellization Model and Solid Model. In *Canadian International Petroleum Conference, 16-18 June*; Petroleum Society of Canada: Calgary, Alberta, 2009.

99. Tavakkoli, M.; Masihi, M.; Ghazanfari, M. H.; Kharrat, R. An improvement of thermodynamic micellization model for prediction of asphaltene precipitation during gas injection in heavy crude. *Fluid Phase Equilibria* **2011,** *308* (1–2), 153-163.

100. Pan, H.; Firoozabadi, A. Thermodynamic Micellization Model for Asphaltene Aggregation and Precipitation in Petroleum Fluids. *SPE Production & Facilities* **1998,** *13*, 118-127.

101.   Pan, H.; Firoozabadi, A. Thermodynamic Micellization Model for Asphaltene Precipitation from Reservoir Crudes at High Pressures and Temperatures. In *SPE Annual Technical Conference and Exhibition, 5-8 October*: San Antonio, Texas, 1997.

102.   Ting, P. D. Thermodynamic Stability and Phase Behavior of Asphaltenes in Oil and of Other Highly Asymmetric Mixtures. Doctor of Philosophy, Rice University 2003.

103.   Jafari Behbahani, T.; Ghotbi, C.; Taghikhani, V.; Shahrabadi, A. Experimental investigation and thermodynamic modeling of asphaltene precipitation. *Scientia Iranica* **2011,** *18* (6), 1384-1390.

104.   Ting, P. D.; Gonzalez, D.; Hirasaki, G.; Chapman, W. Application of the PC-SAFT Equation of State to Asphaltene Phase Behavior. In *Asphaltenes, Heavy Oils, and Petroleomics*, Mullins, O.; Sheu, E.; Hammami, A.; Marshall, A., Eds.; Springer New York, 2007, pp 301-327.

Caption for Tables:

Table 1: Fractionation of recombined oil with GOR=152 m^3/m^3 into a 6 component mixture.[104] [Reprinted from Ting et al.[104], Copyright©2007 with kind permission from Springer Science and Business Media].

Table 2: PC-SAFT parameters for asphaltene subfractions of the oil sample at 580 scf/bbl[84] [Adapted with permission from Gonzalez et al.[84], Copyright©2007, American Chemical Society].

Table 3: PC-SAFT parameter correlations for saturates, aromatics and resins.[85] Note: If $\gamma=1$, the correlation reduces to correlation for Poly-nuclear-aromatic (PNA) while for $\gamma=0$, the correlation reduces to correlation for benzene derivatives. [Adapted from Panuganti et al. [85], Copyright©2012 with permission from Elsevier].

Caption for Figures:

Figure 1: Schematic Representation of lattice model. Black and white balls represent the solvent and solute molecules respectively of equal size [Redrawn from Painter and Coleman[25]].

Figure 2: De Boer's plot distinguishing crude oils with severe problems, slight problems and no problems. [Redrawn from Wang et al.[54]]

Figure 3: Comparison of asphaltene fractional yield obtained experimentally and predictions based on Alboudwarej et al. model for Canadian Llyodminster bitumen diluted with n-alkanes.[56] Solids refer to non-asphaltenic solids including clay, sand and adsorbed organics.

Fractional yield refers to the mass fraction of asphaltene precipitated. [Reprinted from Alboudwarej et al.[56], Copyright©2004 with permission from John Wiley and Sons].

Figure 4: Prediction of asphaltene precipitation yield from Llyodminster bitumen diluted with n-alkanes at ambient conditions.[58] [Reprinted from Akbarzedah et al.[58], Copyright©2005, with permission from Elsevier].

Figure 5: Comparison of experimental asphaltene fractional yield and prediction based on Akbarzedeh et al. model for Cold Lake bitumen diluted with n-pentane (C5) and n-heptane (C7) at different temperatures.[58] [Reprinted from Akbarzedah et al.[58], Copyright©2005 with permission from Elsevier].

Figure 6: Plot of F_{RI} and crude oil volume fraction for asphaltic oil from California.[61] The onset of asphaltene precipitation (P_{RI}) is indicated as a horizontal band. [Reprinted with permission from Jill Buckley[61], Copyright©1999, American Chemical Society].

Figure 7: Comparison of experimental (symbol) and predicted (line) asphaltene onset conditions for crude oils by ASM.[68] The precipitants used were n-alkanes from pentane to pentadecane. P_{RI} represents the onset of asphaltene precipitation. [Reprinted with permission from Wang and Buckley[68], Copyright©2001, American Chemical Society].

Figure 8: The linear ASphaltene Instability Trend (ASIST).[42] [Reprinted from Buckley et al.[42], Copyright©2007 with kind permission from Springer Science and Business Media].

Figure 9: Onset pressure predictions for oil C-AG3-02.[42] [Reprinted from Buckley et al.[42], Copyright©2007 with kind permission from Springer Science and Business Media].

Figure 10: SAFT EoS expressed in the form of Residual Helmholtz energy.[104] [Reprinted from Ting et al.[104], Copyright©2007 with kind permission from Springer Science and Business Media].

Figure 11: PC-SAFT predicted and measured asphaltene instability onset and mixture bubble points for recombined oil.[104] [Reprinted from Ting et al.[104], Copyright©2007 with kind permission from Springer Science and Business Media].

Figure 12: Comparison of SAFT prediction (lines) with experimental bubble point (open circles) and asphaltene stability onset (filled circles) for CO_2 or methane injection.[83] [Reprinted with permission from Gonzalez et al.[83], Copyright©2005, American Chemical Society].

Figure 13: Prediction of amount of asphaltene subfraction precipitation (based on parameters in table 2) using PC-SAFT EoS.[84] [Reprinted with permission from Gonzalez et al.[84], Copyright©2007, American Chemical Society].

Figure 14: Prediction of asphaltene precipitation using PC-SAFT EoS. The asphaltenes were considered to be monodisperse.[84] [Reprinted with permission from Gonzalez et al.[84], Copyright©2007, American Chemical Society].

Figure 15: Addition of n-decane (precipitant) to tank oil-1 (Hirschberg et al.[6]) at 295K.[94] [Reprinted from Victorov and Firoozabadi[94], Copyright©1996 with permission from John Wiley and Sons].

Figure 16: Prediction of asphaltene precipitation for tank oil-1(Hirschberg et al.[6]) on addition of different n-alkane precipitants at 295K.[94] [Reprinted from Victorov and Firoozabadi[94], Copyright©1996 with permission from John Wiley and Sons].

Figure 17: Influence of resin content on the predicted asphaltene precipitation curves for tank oil-1 (Hirschberg et al.[6]) at 295K.[94] [Reprinted from Victorov and Firoozabadi[94], Copyright©1996 with permission from John Wiley and Sons].