A Monodisperse Thermodynamic Model for Estimating Asphaltene Precipitation

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Asphaltene precipitation is a serious problem, which can affect oil production and transportation. To avoid this problem, knowledge of asphaltene phase behavior is of great interest. Asphaltene precipitation is traditionally modeled using the Flory–Huggins polymer theory. Two assumptions are normally made: (1) The precipitated phase consists of asphaltene only (2) The precipitated phase consists of asphaltene and nonasphaltene components and the oil phase is free of asphaltene. In this work, the Flory–Huggins theory is employed to develop a monodisperse model in which, a distribution of asphaltene and nonasphaltene components in the oil and precipitated phases is considered. It is shown the previous Flory–Huggins theory based models are specific cases of the present model. The results of the new model are finally compared with some selected experimental data from the literature. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 2940–2947, 2007
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Introduction

Crude oil is a complex mixture of hydrocarbons and other compounds. These components are often divided, somewhat arbitrarily, into saturates, aromatics, resins, and asphaltenes (SARA). The amorphous compounds that are toluene/benzene soluble but *n*-heptane/*n*-pentane insoluble, are called asphaltenes (The portion which is soluble in normal alkane is termed as "maltene" and the insoluble portion is called "asphaltene"), which are the most aromatic and highest molecular weight fraction of petroleum. This fraction alone contains at least 100,000 different molecules and has not been positively identified yet.[1] The yield and quality of this fraction depends on how it was separated: the ratio of *n*-heptane/*n*-pentane to oil, the time before filtration, the pore size and material of the filter, and etc. This is also the case for the resins, separated from *n*-heptane/*n*-pentane solution by adsorption on Attapulagus clay and desorbed by a mixture of toluene and acetone. Saturates are the compounds that crystallize out of the remaining oil after evaporating the *n*-heptane/*n*-pentane and cooling a methyl ethyl ketone (MEK) solution of the oil to 195 K with dry ice. The remaining oil is called aromatics.[1–6]

As early as 1938, it was recognized that asphaltenes and resins form micelle particles.[4] Asphaltene micelle particle has a core, which is formed by several aggregated asphaltene molecules; bipolar resin molecules are adhered on the surface of the core (The amount of monomeric asphaltenes is very small compared with asphaltene amount in micelles).[5] If not for the resins, most of the asphaltene material would immediately precipitate from the oil because of a low solubility of asphaltene monomeric molecules in the bulk of the petroleum fluid.[4,5,7–32]

Asphaltene precipitation can cause fouling in the reservoir, in the well, in the pipeline and in the oil production and processing facilities.[1–15,18,19,22–32] During production as the oil pressure drops, above the bubble point of some crudes oils, especially those containing high fractions of saturates, asphaltenes may precipitate.[1–15,18,19,22–32] During enhanced oil recovery when compressed gases, such as methane or carbon dioxide, are injected into the reservoir, asphaltene may also precipitate.[1–15,18,19,22–32] Once crude oils are brought to the surface, they are commonly mixed in the field, in tankers

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and/or pipelines. Blending crude oils can also upset the delicate balance and precipitate asphaltene.[1–15,18,19,22–32]

Asphaltene precipitation has therefore been the subject of numerous theoretical investigations.[2,5,7–9,11,14,15,17,18,22–28,30–32] One of the fundamental difficulties encountered in describing the phase behavior of asphaltene-containing systems is the lack of suitable characterization parameters.[7] In fact, asphaltenes are not well-identified components/mixtures. They consist of several polar components of aromatic nature with high molecular weight. In the majority of cases, the complexity of the asphaltene fraction leads to the assumption that the asphaltenes can be regarded as one single pseudo-component (monodisperse).[7] The main drawback of the monodisperse models is that they do not take into account the aggregation phenomena of asphaltenes.[7] In fact, the aggregation process produces a molecular weight distribution of aggregates, which also causes a polydispersity in asphaltene properties.[7] A few models use a polydisperse concept in terms of asphaltene properties, especially molecular weight and size.[23,24]

Most of the traditional models in the literature are based on polymer solutions theories (e.g., Scatchard-Hildebrand,[20] Flory–Huggins,[20] and Scott–Magat[21] theories] to model the phase behavior of asphaltene-containing fluids (e.g., Hirschberg et al.,[8] Burke et al.,[22] Kawanaka et al.,[23] Park[24]). In addition to these models, there are also a few models, which are based on cubic equations of state (EOS) (e.g. Nghiem et al.[25]). The main assumption in these models is that the precipitation process is reversible. While these models are simple and can explain some experimental results and have some use in describing selected asphaltene precipitation phenomenon in petroleum fluids, they are inadequate for explaining other experimental results. The two factors that determine the precipitation of asphaltene from crude oil are not addressed in these classical models: one is the chemical association between asphaltene molecules and the second one is the peptizing effect of resin molecules.[7] In other word, the micellar nature of asphaltene is neglected in these models.[7]

Although new thermodynamic models have recently been developed, which can take into account the micellar and aggregation natures of asphaltene,[5,15,27,28,30–32] none of them is still capable of predicting precipitation of asphaltene satisfactorily,[7] and therefore there is still a need for simple, yet robust, model for estimating the asphaltene precipitation.

The aim of this work is to provide a simple thermodynamic tool for predicting asphaltene precipitation. For this purpose, a discussion is first made on traditional Flory–Huggins[20] theory based asphaltene models,[8,14] which have frequently been used in the literature. It is shown that the existing Flory–Huggins[20] theory based models require some modifications to take into account distributions of asphaltene and nonasphaltene components in the oil and precipitated phases. A more comprehensive thermodynamic model is then introduced to solve this shortcoming. The main assumption in this model is that the asphaltene precipitation is considered as a reversible process, allowing the use of molecular thermodynamics. The results of this model are finally compared with some experimental data reported in the literature.

Flory–Huggins Theory Based Models

The Flory–Huggins[20] polymer theory has traditionally been used to estimate asphaltene precipitation conditions. Two assumptions are normally made for modeling asphaltene precipitation: (1) The precipitated phase consists of asphaltene only or (2) The precipitated phase consists of asphaltene and nonasphaltene components while the oil phase is free of asphaltene (because of lower concentration of asphaltene than maltene concentration). The model developed by Hirschberg et al.[8] is one of the first developed models, which uses the first assumption, i.e., it is assumed that asphaltene volume fraction Φ_a^{Asph} in the precipitated phase can generally be assumed equal to unity. The second assumption has been used in the model developed by Cimino et al.[14] In this model, it is assumed that the oil phase can safely be assumed to be pure as typical asphaltene volume fraction Φ_a^{Oil} in oils is in the range of 10^{-2}–10^{-3} for oils with asphaltene weight percent from 1 to 10. Despite the model of Hirschberg et al.[8], the model of Cimino et al.[14] can be used only for estimating onset of asphaltene precipitation. This model cannot be used for determining the amount of asphaltene precipitation. A more detailed description of these two models is given in the Appendix.

Figure 1 shows limiting volume fraction of asphaltene in the precipitated phase (Φ_a^{Asph}) versus interaction parameter (χ) in Flory–Huggins[20] theory. As can be seen, limited solubility is often observed in macromolecule (polymeric component) containing systems. The Flory–Huggins[20] theory indicates that, for a solvent–macromolecule system, the value of χ may not exceed 0.5 for miscibility in all proportions.[33] According to this figure, at $\chi \gg 0.5$, $\Phi_a^{\mathrm{Asph}} \cong 1$. That is, the Hirschberg et al.'s model[8] can be resulted. However, at χ near 0.5, $\Phi_a^{\mathrm{Asph}} \ll 1$ and therefore using the assumptions may be conservative. In other word, by taking into account the presence of maltene in the precipitated phase and the presence of asphaltene in the oil phase, a more comprehensive model can be obtained than the models developed by Hirschberg et al.[8] and Cimino et al.[14]

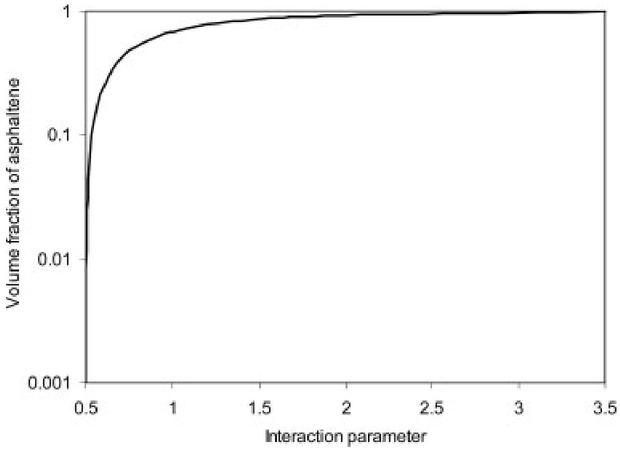

Figure 1. Typical limiting volume fraction of asphaltene in the precipitated phase versus interaction parameter.

Limited solubility is often observed in macromolecule (polymer) / solvent systems. The Flory–Huggins[20] theory indicates that, for a solvent / macromolecule system, the value of interaction parameter may not exceed 0.5 for miscibility in all proportions.[33]

Development of a Monodisperse Model Based on Flory–Huggins theory

The equations for the activity coefficients of asphaltene and maltene based on the Flory–Huggins[20] polymer theory can be expressed as below:[34]

$$\ln\gamma_{\mathrm{m}} = \ln\frac{\Phi_{\mathrm{m}}}{x_{\mathrm{m}}} + \left(1 - \frac{v_{\mathrm{m}}}{v_{\mathrm{a}}}\right)\Phi_{\mathrm{a}} + \chi\,\Phi_{\mathrm{a}}^2 \tag{1}$$

$$\ln\gamma_{\mathrm{a}} = \ln\frac{\Phi_{\mathrm{a}}}{x_{\mathrm{a}}} - \left(\frac{v_{\mathrm{a}}}{v_{\mathrm{m}}} - 1\right)\Phi_{\mathrm{m}} + \chi\,\Phi_{\mathrm{m}}^2 \tag{2}$$

where γ_{m}, γ_{a}, Φ_{m}, Φ_{a}, v_{m}, v_{a}, x_{m}, and x_{a}, are the activity coefficient of maltene, activity coefficient of asphaltene, volume fraction of maltene, volume fraction of asphaltene, molar volume of maltene, molar volume of asphaltene, mole fraction of maltene, and mole fraction of asphaltene, respectively. χ stands for interaction parameter between asphaltene and maltene, as mentioned earlier. In Eqs. 1 and 2[33,34]

$$\Phi_{\mathrm{a}} = \frac{x_{\mathrm{a}}v_{\mathrm{a}}}{x_{\mathrm{a}}v_{\mathrm{a}} + x_{\mathrm{m}}v_{\mathrm{m}}} \tag{3}$$

and

$$\Phi_{\mathrm{m}} = \frac{x_{\mathrm{m}}v_{\mathrm{m}}}{x_{\mathrm{a}}v_{\mathrm{a}} + x_{\mathrm{m}}v_{\mathrm{m}}}. \tag{4}$$

It should be noted that in macromolecule containing systems, volume fractions are very different from mole fractions because the molar volume of a macromolecule is much larger than that of the solvent.[33] Furthermore, since the molecular weight of the macromolecule components is not known accurately, it is difficult to determine the mole fraction. Therefore, an equivalent definition, volume fraction Φ is used.[33] Equations 3 and 4 can be also written as below:[33]

$$\Phi_{\mathrm{a}} = \frac{w_{\mathrm{a}}/\rho_{\mathrm{a}}}{w_{\mathrm{a}}/\rho_{\mathrm{a}} + w_{\mathrm{m}}/\rho_{\mathrm{m}}} \tag{5}$$

$$\Phi_{\mathrm{m}} = \frac{w_{\mathrm{m}}/\rho_{\mathrm{m}}}{w_{\mathrm{a}}/\rho_{\mathrm{a}} + w_{\mathrm{m}}/\rho_{\mathrm{m}}} \tag{6}$$

where w_{a} and w_{m} are the weight fractions of asphaltene and maltene, respectively and ρ_{a} and ρ_{m} represent the mass densities of asphaltene (1.2 g/cm^3) and maltene, respectively.

The liquid–liquid equilibrium equations to be solved are:[34]

$$x_{\mathrm{a}}^{\mathrm{Oil}}\gamma_{\mathrm{a}}^{\mathrm{Oil}} = x_{\mathrm{a}}^{\mathrm{Asph}}\gamma_{\mathrm{a}}^{\mathrm{Asph}} \tag{7}$$

$$x_{\mathrm{m}}^{\mathrm{Oil}}\gamma_{\mathrm{m}}^{\mathrm{Oil}} = x_{\mathrm{m}}^{\mathrm{Asph}}\gamma_{\mathrm{m}}^{\mathrm{Asph}} \tag{8}$$

Using the activity coefficient expressions reported in Eqs. 1 and 2, Eqs. 7 and 8 can be written as:[34]

$$\ln\left(\frac{\Phi_{\mathrm{m}}^{\mathrm{Oil}}}{\Phi_{\mathrm{m}}^{\mathrm{Asph}}}\right) + \left(1 - \frac{v_{\mathrm{m}}}{v_{\mathrm{a}}}\right)\left(\Phi_{\mathrm{a}}^{\mathrm{Oil}} - \Phi_{\mathrm{a}}^{\mathrm{Asph}}\right) + \chi\left[\left(\Phi_{\mathrm{a}}^{\mathrm{Oil}}\right)^2 - \left(\Phi_{\mathrm{a}}^{\mathrm{Asph}}\right)^2\right] = 0 \tag{9}$$

$$\ln\left(\frac{\Phi_{\mathrm{a}}^{\mathrm{Oil}}}{\Phi_{\mathrm{a}}^{\mathrm{Asph}}}\right) + \left(1 - \frac{v_{\mathrm{a}}}{v_{\mathrm{m}}}\right)\left(\Phi_{\mathrm{m}}^{\mathrm{Oil}} - \Phi_{\mathrm{m}}^{\mathrm{Asph}}\right) + \chi\left[\left(\Phi_{\mathrm{m}}^{\mathrm{Oil}}\right)^2 - \left(\Phi_{\mathrm{m}}^{\mathrm{Asph}}\right)^2\right] = 0 \tag{10}$$

where superscripts oil and Asph stand for oil and asphaltene, respectively.

In the earlier equations, χ describes the maltene solvency power with respect to the asphaltene. This parameter depends on temperature, but for systems containing macromolecules in which the molecular weight of the macromolecule is very large, it is nearly independent of molecular weight of macromolecule.[33] In theory, this parameter is also independent of macro molecule concentration, but in fact, it often varies with concentration, especially in mixtures containing polar molecules, for which the Flory–Huggins[20] theory provides only a rough approximation.[33] This parameter can be calculated using the following equation:[7]

$$\chi = \frac{v_{\mathrm{m}}\left[(\delta_{\mathrm{m}} - \delta_{\mathrm{a}})^2 + 2l\delta_{\mathrm{m}}\delta_{\mathrm{a}}\right]}{RT} \tag{11}$$

where δ stands for the solubility parameter and subscripts m and a indicate maltene and asphaltene, respectively. R, T, and l represent the universal gas constant, temperature, and a binary interaction parameter, respectively. An appropriate value for l equal to 0.02 has been recommended for Flory–Huggins[20] based models.[7]

These equations can be solved using an equation-solving program. It is obvious that Eqs. 9 and 10 can be simplified to obtain the models developed by Hirschberg et al.[8] and Cimino et al.[14]

Fluid Characterization

For calculating asphaltene solubility/precipitation, solubility parameter of asphaltene, solubility parameter of maltene, molar volume of asphaltene and molar volume of maltene are required. The solubility parameter of asphaltene δ_{a} can be calculated using the following relation:[8]

$$\delta_{\mathrm{a}} = 20.04\left[1 - 1.07 \times 10^{-3}(T - 273.15)\right] \tag{12}$$

where T is in K and δ_{a} is in MPa$^{0.5}$. The solubility parameter of the maltene can be calculated from:[8]

$$\delta_{\mathrm{m}} = \sqrt{\frac{\Delta u_{\mathrm{m}}^{\mathrm{V}}}{v_{\mathrm{m}}}} \tag{13}$$

where $\Delta u_{\mathrm{m}}^{\mathrm{V}}$ is the energy change upon isothermal vaporization of 1 mole of the maltene to the ideal gas state and v_{m} is the molar volume of the maltene. It is known that the Peng–Robinson (PR-EoS)[35] gives better results for predicting v, whereas the results of the Soave–Redlich–Kwong (SRK-EoS)[36] for Δu^{V} are in better agreement with the reported experimental data.[8] Therefore, v_{m} is calculated using the PR-EoS.[35] From the SRK-EoS,[36] the expression of Δu^{V} is as follows:[8]

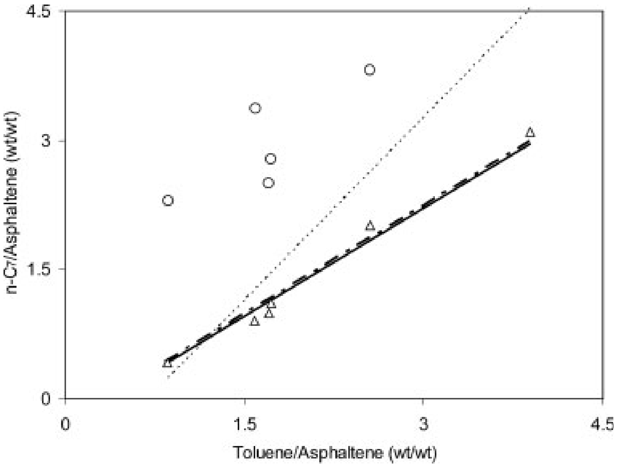

Figure 2. Comparison of predicting onset of precipitation asphaltene by several models against experimental data.

Δ, Experimental data[14]; ○, Predictions of colloidal model[26]; dashed line, Predictions of Hirschberg et al.'s model[8] (quoted in ref. 2 and 14); bold dashed line Predictions of Cimino et al.'s model[14]; solid line: Predictions of this model.

$$\Delta u^{V} = \left(\frac{a}{b} - \frac{T}{b}\frac{da}{dT}\right)\ln\left(1 + \frac{b}{v}\right) \tag{14}$$

where a and b are parameters of the SRK equation of state[36] and v is molar volume. In this work, Twu's correlation[37] for critical properties and the Lee–Kesler correlation[38] for acentric factor have been used for the petroleum fractions, as recommended by Danesh.[39] The binary interaction parameters (BIP) for the PR[35] and SRK-EoS,[36] which have been used in this work, were derived from Knapp and Doring.[40] For the BIPs between hydrocarbon–hydrocarbon (excluding those reported by Knapp and Doring[40]), the Chueh–Prausnitz's correlation[41] can also be used. The molar volume of asphaltene can be regarded as an adjustable parameter.

Results and Discussion

The reliability of the model is investigated for four systems, a synthetic system, a tank oil, a live oil, and a gas condensate. Cimino et al.[14] performed some tests to find the onset of asphaltene precipitation points of dissolved asphaltenes in different ratios of solvent and precipitant and then indicated that the precipitated asphaltenes do dissolve in appropriate solvents and at the onset of asphaltene precipitation, the ratio of "solvent mass per asphaltene mass" and "precipitant mass per asphaltene mass" is linear and is independent of the asphaltene concentration. It is of interest to be able to predict this behavior using the new model. Figure 2 shows a comparison between the behavior of traditional activity coefficient based model,[8] colloidal model,[26] Cimino et al.'s model,[14] model developed in this work and experimental data (Table 1) reported by Cimino et al.[14] As can be seen, the capability of colloidal model[26] and traditional activity coefficient based model[8] to reproduce the observed behavior is poor.[2,14] However, the newly developed model produces encouraging results. This also shows that the use of the solubility concept of asphaltenes may be in better agreement with the mechanism of asphaltene flocculation/precipitation in light systems. In other word, the colloidal/micellar models can be helpful especially for understanding the effect of resin on asphaltene precipitation and the mechanism of asphaltene precipitation from crude oil.[2,14] That is, according to the mathematical description underlying the colloidal/micellar models, resins must be present in the system to stabilize the asphaltenes. However, such models may forecasts complete insolubility in light systems.[2,14] More comparisons as shown in Figures 3 and 4.

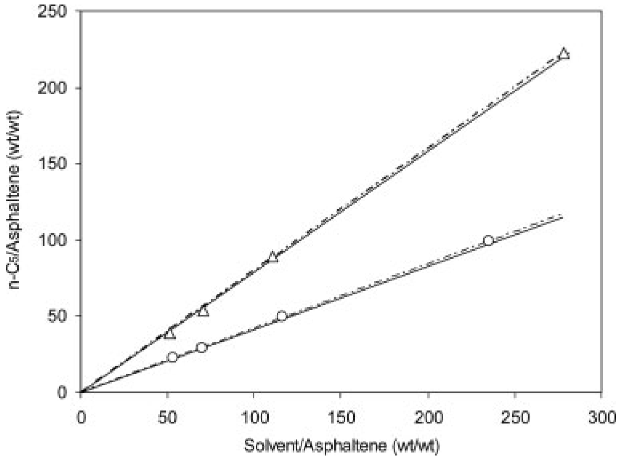

Figure 3. Comparison of predicting onset of C-asphaltene precipitation against experimental data.

Points: experimental data[14] (solvent: Δ, Tetraline; ○, toluene); dashed lines, Predictions of Cimino et al.'s model[14]; solid lines, Predictions of this model.

To show the capability of the model for estimating asphaltene precipitation in oil systems, the data of a tank oil[42] reported in Tables 2 and 3 are used. The model is tuned using the experimental titration data with n-pentane and n-decane. Figure 5 shows the results. The experimental titration data for n-heptane were not used for tuning as it is believed it does not confirm with the other titration data.[42] As can be

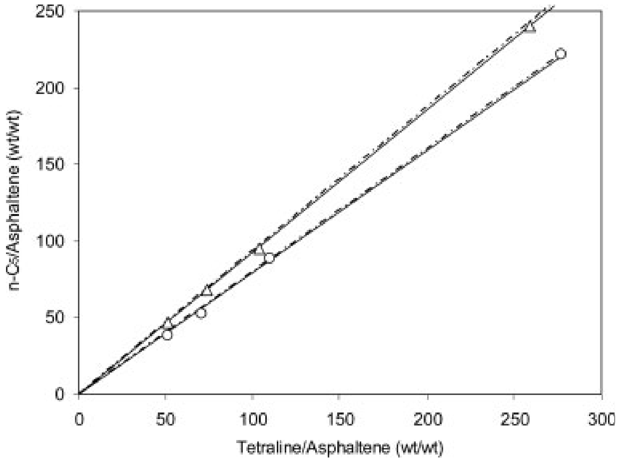

Figure 4. Comparison of predicting onset of asphaltene precipitation against experimental data.

Points: experimental data[14] (Δ, C_5-asphaltenes; ○, C_7-asphaltene) dashed lines, Predictions of Cimino et al.'s model[14]; solid lines, Predictions of this model.

Table 1. Weight Fractions of Components of Synthetic Mixtures at Onset of asphaltene Precipitation Points Measured at 298.15 K and 0.1 MPa[14]

	C_5-Asphaltene			C_7-Asphaltenes		
Precipitant/Solvent	Precipitant	Solvent	Asphaltene	Precipitant	Solvent	Asphaltene
C_5/Toluene	0.367	0.621	0.012	0.293	0.694	0.013
	0.369	0.623	0.008	0.294	0.696	0.010
	0.370	0.624	0.006	0.297	0.696	0.007
	0.403	0.594	0.003	0.294	0.703	0.003
C_5/Tetraline	0.477	0.513	0.010	0.427	0.562	0.011
	0.480	0.513	0.007	0.430	0.562	0.008
	0.480	0.515	0.005	0.445	0.550	0.005
	0.480	0.518	0.002	0.444	0.554	0.002
C_7/Toluene	0.420	0.569	0.011	0.352	0.636	0.012
	0.422	0.570	0.008	0.354	0.637	0.009
	0.423	0.571	0.006	0.355	0.639	0.006
	0.422	0.576	0.002	0.389	0.608	0.003
C_7/Tetraline	0.521	0.470	0.009	0.481	0.509	0.010
	0.527	0.466	0.007	0.494	0.499	0.007
	0.524	0.471	0.005	0.501	0.494	0.005
	0.524	0.474	0.002	0.525	0.473	0.002
C_{10}/Toluene	0.437	0.553	0.010	0.366	0.622	0.012
	0.440	0.552	0.008	0.407	0.585	0.008
	0.440	0.555	0.005	0.407	0.588	0.005
	0.440	0.558	0.002	0.407	0.591	0.002
C_{10}/Tetraline	0.538	0.453	0.009	0.492	0.498	0.010
				0.496	0.497	0.007
				0.520	0.475	0.005
				0.542	0.456	0.002

seen, there is acceptable agreement between the experimental data and the model results. The deviations between experimental titration data on n-C_7 and predictions can be attributed to unreliability of the experimental data.[42] At high concentrations of n-C_{10}, the predicted weight percent of the precipitated asphaltene from the tank oil decreases. This behavior is in correct agreement with the results of the previous models.[5,8,42] Furthermore, the model shows that the asphaltene volume fraction Φ_a^{Asph} in the precipitated phase approaches unity for all titrations done on the tank oil.

To further study the capability of the model, asphaltene precipitation in a live oil system from the Middle East region is studied.[43] The reservoir fluid properties and its compositions are presented in Tables 4 and 5, respectively. Figure 6 shows the results. In Figure 6, only the experimental data on the onset of asphaltene precipitation were used for tuning. This figure shows that the model can estimate asphaltene precipitation/content. That is, when reducing pressure at reservoir temperature, asphaltene starts precipitating at the onset of asphaltene precipitation point and therefore oil asphaltene content decreases. The asphaltene content of oil is reduced as the pressure decreases more. The asphaltene content reaches a minimum near the bubble point conditions. The oil asphaltene content then increases as the pressure decreases farther below the bubble point conditions. From this figure, it is clear that the model cannot predict the asphaltene content of oil reliably, which can be attributed to monodisperse nature of the model. More reliable results would be expected by taking into account the polydispersity in asphaltene properties.

One of the major problems affecting production in some gas condensate reservoirs is asphaltene precipitation. It is believed that there is an oil rim in reservoir, which is thought to be one of the possible regions of the asphaltenes. In this case, the gas condensate could have migrated through these layers in the reservoir and CO_2 could have extracted the asphaltenes.[44,45] Some gas condensates contain as low as 0.001 wt % asphaltenes but form deposits in the flow-lines and production facilities.[44] Andersen and Potsch[44] performed the precipitation tests on the various samples containing asphaltenes to understand the stability of the samples. The examination of samples was hampered by the very low content of asphaltenes, which made detection of the onset of precipitation impossible. Various detection principles were tested without success. Hence, stabil-

Table 2. Compositions of Tank Oil[42]

Components	Mole %
C_1	0.10
C_2	0.48
C_3	2.05
i-C_4	0.88
n-C_4	3.16
i-C_5	1.93
n-C_5	2.58
C_6	4.32
C_{7+}	84.50

Table 3. Properties of Tank Oil, Asphaltene, C_6 and C_{7+}[42]

Property	Value
Average molecular weight	221.5
Specific gravity	0.873
Density of asphaltene, g/cm^3	1.2
Molecular weight of C_6	84
Molecular weight of C_{7+}	249.9
Density of C_6, g/cm^3	0.685
Density of C_{7+}, g/cm^3	0.868
Bubble point temperature of C_6,K	337
Bubble point temperature of C_{7+} K	585

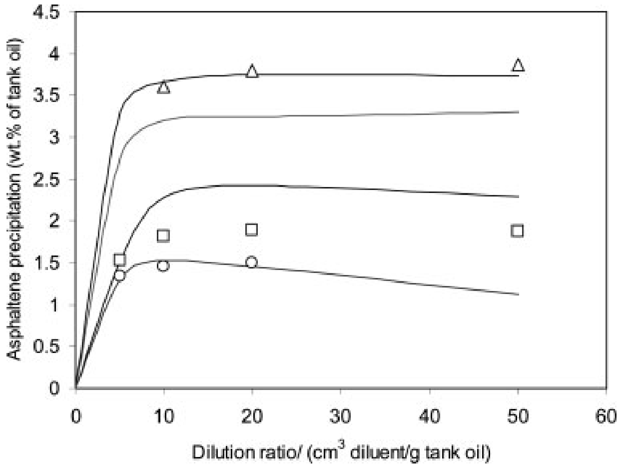

Figure 5. Experimental data[42] and model results for the weight percent of asphaltene precipitation from the tank oil mentioned in Tables 2 and 3.

Solid curves, model results (from top to bottom: n-C_5; n-C_6; n-C_7; n-C_{10}); points, experimental data[42]; Δ, n-C_5; $\square$, n-C_7; $\bigcirc$, n-C_{10}.

Table 4. Characteristics of Live Oil[43]

Property	Value
Reservoir temperature, K	389.15
Reservoir pressure, MPa	62.05
Bubble point pressure at reservoir temperature, MPa	22.68
Gas/oil ratio (GOR), m^3/m^3	195.9
API	39
Saturates, wt% of STO*	68.3
Aromatics, wt% of STO	11.6
Resins, wt% of STO	18.8
Asphaltenes (*n*-pentane insoluble), wt% of STO	1.3

*STO, stock tank oil.

ity parameters could not be derived from the samples. However, they indicated that the deposit from drying the liquid sludge from a separator (black viscous oil, solubility parameter equal to 15.70 $MPa^{0.5}$) was more instable compared with the liquid sludge (solubility parameter equal to 15.84 $MPa^{0.5}$) and the asphaltene (solubility parameter equal to 15.93 $MPa^{0.5}$) derived from this. The solubility parameter of the condensate was reported to be 15.84 $MPa^{0.5}$ at room temperature which is close to the solubility parameter of the sludge χ therefore approaches 0.5 showing that the use of the assumptions of Hirschberg et al.'s model[8] and Cimino et al.'s model[14] is conservative, as discussed earlier.

Table 5. Compositions of Oil System[43]

Components	Mole%
N_2	0.48
CO_2	0.92
C_1	43.43
C_2	11.02
C_3	6.55
i-C_4	0.79
n-C_4	3.7
i-C_5	1.28
n-C_5	2.25
C_6	2.7
C_{7+}	26.88
Molecular weight	82.49
C_{7+} Molecular weight	228.07
C_{7+} density	0.865

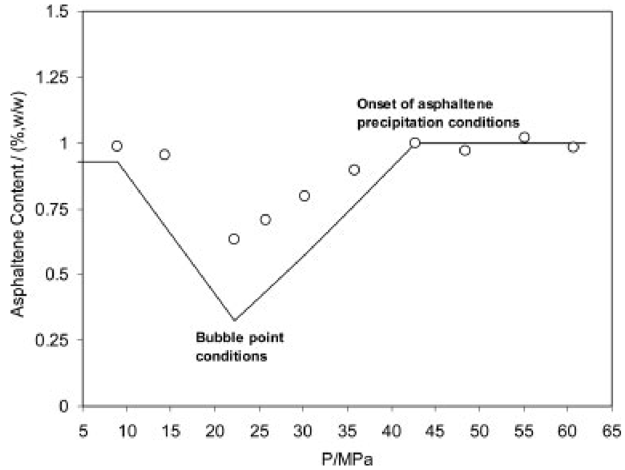

Figure 6. Experimental data[43] and model predictions for asphaltene content of reservoir fluid mentioned in Tables 4 and 5 as a function of pressure at reservoir temperature, 389.15 K.

Curve, model predictions; points ($\bigcirc$), experimental data.[43]

Conclusions

In this work, it was shown that the traditional asphaltene models based on the Flory–Huggins[20] polymer theory, which assume either the precipitated phase consists of asphaltene only or the precipitated phase consists of asphaltene and non-asphaltene components and the oil phase is free of asphaltene, may not be helpful for the conditions where the interaction parameter (χ) is near 0.5 and may require some modifications. A thermodynamic model based on the Flory–Huggins[20] theory, in which it is assumed that asphaltene forms a pseudo-component and the precipitated and oil phases contain asphaltene and nonasphaltene components was then introduced. The study showed that the existing *traditional* Flory–Huggins[20] based models could be specific cases of the developed model. The capability of this model for estimating asphaltene precipitation was finally tested against some experimental data reported in the literature. More reliable results would be expected by taking into account the polydispersity in asphaltene properties.

Notation

BIP = binary interaction parameter in classical mixing rules of equation of state
EOS = equation of state
GOR = gas-oil ratio
MEK = methyl ethyl ketone
PR = Peng–Robinson
SARA = saturates, aromatics, resins and asphaltenes
SRK = Soave–Redlich–Kwong
STO = stock tank oil
R = universal gas constant
T = temperature
a = parameter of the SRK equation of state
b = parameter of the SRK equation of state

l = binary interaction parameter in Flory-Huggins[20] theory
u = energy change upon isothermal vaporization of 1 mole of the maltene to the ideal gas state
v = molar volume
w = weight fraction
x = mole fraction

Greek letters

Δ = difference
Φ = volume fraction
χ = interaction parameter in Flory–Huggins[20] theory
δ = solubility parameter
γ = activity coefficient
μ = chemical potential
ρ = mass density

Superscripts

Asph = asphaltene
Oil = oil
A = asphaltene-rich phase
B = oil-rich phase
V = vaporization

Subscripts

ref = reference state
a = asphaltene
m = maltene

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Appendix

Cimino et al.'s model

According to this model,[14] thermodynamic equilibrium is described by means of the equality of chemical potentials relative to the two species (asphaltene and maltene) in the two phases, on phase splitting. Some simplification is done by considering the physics of phase splitting. Considering typical asphaltene volume fraction Φ_a^{Oil} in oils, which is estimated in the range of 10^{-2}–10^{-3} for oils with asphaltene weight percent from 1 to 10, the oil phase can safely be assumed to be pure solvent, that is $\Phi_a^{\mathrm{Oil}} = 0$. Such an assumption leads to the following final equation, using Flory–Huggins[20] theory:[14]

$$\ln\left[1 - \Phi_a^{\mathrm{Asph}}\right] + \left(1 - \frac{v_m}{v_a}\right)\Phi_a^{\mathrm{Asph}} + \chi\Phi_a^{\mathrm{Asph2}} = 0 \qquad \text{(A1)}$$

where the *prime* represents the asphaltene phase, Φ_a^{Asph} is the volume fraction of asphaltene in asphaltene phase, χ stands for interaction parameter between asphaltene and maltene, v_m and v_a are molar volume of maltene and asphaltene, respectively.

In the above equations, $\frac{v_m}{v_a}$ is negligibly small compared with unity, and therefore it may be neglected.[14]

Hirschberg et al.'s model

In this model,[8] once the liquid/vapor split has been calculated, asphaltene precipitation is estimated with a modified Flory–Huggins[20] theory. The conditions for oil equilibrium between an asphaltene-rich phase A (μ_i^A) and an oil-rich phase B (μ_i^B) are as follows[8]:

$$\mu_i^A = \mu_i^B \qquad \text{(A2)}$$

Following the Flory–Huggins[20] theory, the chemical potential μ_i of component i is given by:[8]

$$\frac{\mu_i - (\mu_i)_{\mathrm{ref}}}{RT} = \ln(\Phi_i) + 1 - \frac{v_i}{v} + \chi_i \qquad \text{(A3)}$$

where $(\mu_i)_{\mathrm{ref}}$ is the chemical potential at the reference state of pure liquid i. Φ_i is the volume fraction of component i. Hence,[8]

$$\Phi_i = \frac{x_i v_i}{v} \qquad \text{(A4)}$$

where v_i represents the molar volume of component i.

The molar volume v, of the mixture and the interaction parameter, χ_i are calculated by using Hildebrand's approximation:[8]

$$v = \sum x_i v_i \qquad \text{(A5)}$$

and

$$\chi_i = \frac{v_i}{RT}(\delta - \delta_i)^2 \qquad \text{(A6)}$$

where x_i is the mole fraction of component i and δ is given by:[8]

$$\delta = \sum \Phi_i \delta_i \qquad \text{(A7)}$$

where δ_i stands for the solubility parameter of component i. T is the absolute temperature and R is the universal gas constant. Assuming that the precipitated phase is pure asphaltene, $\mu_a^{\mathrm{Asph}} = (\mu_a)_{\mathrm{ref}}$ which in combination of above equations, finally yields:[8]

$$\Phi_a^{\mathrm{Oil}} = \exp\left[\frac{v_a}{v_m} - 1 - \frac{v_a}{RT}(\delta_a - \delta_m)^2\right] \qquad \text{(A8)}$$

where δ_a and δ_m represent the solubility parameter of asphaltene and maltene, respectively. Φ_a^{Oil} is the volume fraction of asphaltene in oil phase.

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