Modeling and simulation of asphaltene precipitation by normal pressure depletion

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ARTICLE INFO

ABSTRACT

Asphaltene precipitation is a serious and complex problem in all sections of the oil industry including oil production, transportation and processing. In this paper the analysis of several variables affecting asphaltene deposition by normal pressure depletion was carried out using the Hirschberg et al. (1984) model and experimental data from literature. The results show that the traditional Hirschberg et al. (1984) model can be applied successfully when modifications to the oil characterization, the calculation of oil and the asphaltene solubility parameter are made. We demonstrate that a quantitative representation of asphaltene deposited due to pressure depletion can be obtained with great precision using a minimum amount of experimental data.

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1. Introduction

Crude oil contains a variety of substances with different chemical structures and molecular weights. The composition of crude-oil varies widely depending on its source. In the classification for the purposes of industrial operation crude oil can be broken down into three major fractions: oils, asphaltenes and resins. Oils are mixtures of saturated hydrocarbons and aromatics of moderate molecular weight. Asphaltenes refer to the heavy fraction of the petroleum mixture, which is insoluble in some species, such as paraffins, but soluble in others, such as aromatics. Resins are defined as the fraction of the desasphalted oil which is strongly adsorbed in surface-active materials such as alumina or silica.

The precipitation of asphaltenes can be ascribed to changes in the composition of the crude oil due to blending with various gases during enhanced oil recovery (CO_2, dry and enriched gas, N_2) as well as changes in temperature and pressure thus modifying the complex equilibrium keeping the asphaltenes in solution or suspension. Phase behavior, viscosity and interface properties are strongly influenced by asphaltene components (Solaimany-Nazar and Zonnouri, 2011). Asphaltenes are known to influence many of the processes applied to oil recovery operations and crude oil refining. Furthermore, when condensate diluent is added to heavy oils to reduce viscosity, asphaltene deposition can occur in surface facilities and pipelines. Asphaltene precipitation can be investigated experimentally for each case.

However, this is usually impractical because a large number of experiments at reservoir conditions of pressures and temperature are required which are often unviable and costly. Therefore there is a need for models using only a limited amount of experimental data to predict precipitation with reasonable accuracy.

Several approaches for modeling asphaltene precipitation have been reported in the petroleum literature. According to López-Chávez et al. (2007) the mechanism of asphaltene precipitation has been described using mainly three types of models: (a) molecular thermodynamic models, (b) thermodynamic colloidal models, and (c) fractal aggregation models. However, Hamouda et al. (2009) and Pina et al. (2006) consider another classification that includes the first two groups but others including (d) micellization models and (e) solid phase models. Among other models not encompassed in these classifications it is worth mentioning Fahim (2007), Du and Zhang (2004), Nghiem and Coombe (1997) and Tavakkoli et al. (2010).

Hirschberg et al. (1984) developed a model based on the solubility model using the Flory–Huggins approach. Since then, various modifications have been made to this approach: Mansoori and Jiang (1985) and Kawanaka et al. (1991) taking into account the polydispersity of asphaltene molecules. Cimino et al. (1995) phased out the assumption that the flocculated phase is composed solely of asphaltenes.

Despite significant progress in theoretical and experimental studies, our understanding of the asphaltene precipitation process, given its complexity, is far from mature. The two main factors that determine the precipitation of asphaltenes from crude oil are not addressed in the classical models based on the classical Flory–Huggins polymer solution theory (Wu et al., 1998): (i) the

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Nomenclature

a	Soave–Redlich–Kwong interaction parameter [Eq. (6)]
b	Soave–Redlich–Kwong co-volume parameter [Eq. (6)]
CN	the component number or fraction
$F1$	parameter [Eq. (14)]
$F2$	parameter [Eq. (15)]
K	Soave–Redlich–Kwong binary interaction parameters [Eq. (7)]
MW	molecular weight
P	pressure
R	gas constant
S	weight fraction of dissolved asphaltene in oil [Eq. (5)]
T	temperature
V	volume
w	acentric factor
x	mole fraction

Abbreviations

EOS	equation of state
TBP	true boiling point

Greek letters

δ	solubility parameter
ΔH	enthalpy of vaporization
ΔS	the percent error of asphaltene weight soluble in the oil
ΔV	percentage change in volume with respect to the correct value
θ	ratio between the normal boiling temperature T_{bi} and critical temperature T_{ci}
ϕ	volume fraction

Superscripts

$*$	optimal

Subscripts

a	asphaltene
b	bubble
c	critical
i	component i
j	component j
ref	reference
L	liquid phase
m	mixture
pra	precipitated asphaltene in the oil

chemical association between asphaltene molecules; and (ii) the peptizing effect of resin molecules.

As shown above there are several constraints related to the well-known Hirschberg et al. (1984) model as well as regarding the various other models presented in literature to calculate the asphaltene deposition. The aim of this paper is to show that it is possible to use the Hirschberg et al. (1984) model to provide a precise quantitative representation of deposited asphaltene due to pressure depletion and using a minimum amount of experimental data. To do this, it is necessary to modify the characterization and the calculation of the oil and asphaltene solubility parameter, as will be shown in this paper.

2. Thermodynamic models

The phenomenon of asphaltene precipitation is a very complex multi-component process that involves a great diversity of interactions on molecular and colloidal length scales. Consequently, the theoretical modeling for this system is only possible by assuming simplified representations of crude oil. In the natural depletion of a reservoir the temperature is constant, therefore the most important and effective factor in asphaltene precipitation is the reservoir pressure change.

2.1. Hirschberg et al. (1984) model

Here, given the wide acceptance of the reversibility of asphaltene precipitation (Danesh et al., 1987; Kokal et al., 1992; Ramos et al., 1997; Beck et al., 2005), the thermodynamic model presented by Hirschberg et al. (1984) was used. They developed a molecular thermodynamic model by applying a modified Flory–Huggins (F–H) polymer theory (Flory, 1953) with a lumped compositional representation (two or three components), as described in detail elsewhere (Hirschberg et al. (1984)). The asphaltene solution is considered as a two-constituent system: the asphaltenes, which

may form a pure phase, and the other constituents (including the resins), which form the oil phase (the surrounding medium). Hirschberg et al. (1984) obtained the following equation for the volume fraction of dissolved asphaltene in oil:

$$(\phi_a)_{max} = \exp\left\{\frac{V_a}{V_L}\left[1-\frac{V_L}{V_a}-\frac{V_L}{RT}(\delta_a-\delta_L)^2\right]\right\} \tag{1}$$

where ϕ_a is the volume fraction of asphaltene in oil, the volume V_L and solubility parameter δ_L are the properties of the liquid phase obtained from the calculated vapor/liquid split of the crude (or crude/solvent mixture) in the pressure and temperature conditions considered and δ_a and V_a are the asphaltene properties.

The volume fraction of component i is expressed as

$$\phi_i = \frac{x_i V_i}{V_m} \tag{2}$$

where x_i is the mole fraction of component i. The molar volume V_m of the mixture is calculated by:

$$V_m = \sum_i x_i V_i \tag{3}$$

and the solubility parameter δ_m of the mixture is given by

$$\delta_m = \sum_i \phi_i \delta_i \tag{4}$$

After performing the ϕ_a and ϕ_L calculations, the weight fraction of the dissolved asphaltene in oil, S_a, can be obtained as follows:

$$S_a = \frac{\phi_a \times MW_a/V_a}{(1-\phi_a)MW_L/V_L + \phi_a \times MW_a/V_a} \tag{5}$$

where MW_L and MW_a are the molecular weight of the oil and asphaltene, respectively.

2.2. Soave–Redlich–Kwong equation of state

To perform the flash and liquid phase molar volume calculations, the Soave–Redlich–Kwong (SRK) (Soave, 1972) was selected and it is

detailed in Eqs. (6)–(8):

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{6}$$

where T is the temperature, P is the pressure, V is the molar volume, R is the universal gas constant and a and b are mixture specific parameters.

The pure components parameters a_i and b_i are described in terms of critical temperature T_{ci}, critical pressure P_{ci} and acentric factor w_i:

For mixtures the model parameters become composition dependent through the following mixing rules:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - K_{ij}) \tag{7}$$

$$b = \sum_i x_i b_i \tag{8}$$

where x_i is the component molar fraction and K_{ij} are the binary interaction parameters between components i and j.

2.3. Characterization procedure

In order to use an EOS it is necessary to know the critical temperature, T_c, critical pressure, P_c, and acentric factor w for each component in the mixture. For the True Boiling Point (TBP) fractions, which are pseudo components covering from C_7 and up, these three properties are not available. Therefore a characterization procedure for the heavy hydrocarbon fraction (C_7^+) is required. Furthermore, a lumping procedure is required to reduce the number of components. In this study the boiling point calculations were performed with SPECS program (Technical University of Denmark). The critical properties and the acentric factor of each TBP fraction are calculated by using the Pedersen method (Pedersen et al., 1989). To estimate the composition of the TBP residue, a logarithmic distribution of the mole fraction x_i versus carbon number of component (CN) or fraction i has been suggested by Pedersen et al. (1984). The models used to divide and lump the components or TBP fractions into groups are presented in Pedersen et al. (1985).

2.4. Solubility parameter calculation

The most prevalent thermodynamic approach to describe asphaltene solubility has been the application of the solubility parameter.

Several models are presented in the literature to calculate the solubility parameter: Anderson and Speight (1999) and Pazuki and Nikookar (2006).

The solubility parameter can be estimated from

$$\delta = \sqrt{\frac{\Delta H - RT}{V}} \tag{9}$$

where ΔH is the enthalpy of vaporization at temperature T.

The calculation of the enthalpy of vaporization of the component at the temperature T requires several steps and the first one is its computation at normal boiling temperature and it is obtained by Edmister (1958):

$$w = \frac{3}{7} \left(\frac{\theta}{1.0 - \theta} \right) \log(P)_c - 1.0 \tag{10}$$

where $\theta = T_{bi}/T_{ci}$ is the ratio between the normal boiling temperature T_{bi} and the critical temperature T_{ci}.

In this work the procedure for calculating the oil and asphaltene solubility parameter developed by Chung et al. (1991) was partially adopted. The following step is therefore used to calculate the enthalpy of vaporization of the component i at its normal boiling point (in BTU/lb-mole):

$$(\Delta H_i)_{Tbi} = 1.014[T_{bi}(8.75 + 4.571 \log(T_{bi}))] \tag{11}$$

In order to correct the enthalpy of vaporization at a temperature T different from the normal boiling point Watson's (1943) equation is used:

$$(\Delta H_i)_T = (\Delta H_i)_{Tbi} \left(\frac{T_{ci} - T}{T_{ci} - T_{bi}} \right)^{0.38} \tag{12}$$

where T_{ci} and T_{bi} correspond to the critical temperature and the normal boiling temperature of component i, respectively.

3. Results and discussion

Six oils were selected from literature and the relevant information regarding their characteristics is displayed in Table 1. It is important to note that there are two pressures shown in Table 1: the saturation pressure and the reference pressure. The latter refers the pressure nearer to the saturation pressure at which there is an experimental value of the amount of asphaltene precipitated.

In the following sections the main operations of the fluid calculations summarized in Fig. 1 are described.

Table 1
Composition and properties of crude oil samples.[a]

Components	Oil					
	O1	O2	O3	O4	O5	O6
N_2	0.00	0.57	0.48	0.27	0.13	1.082
CO_2	0.97	2.46	0.92	1.65	2.07	4.643
H_2S	0.00	0.00	0.00	0.03	0.02	7.284
C_1	38.25	36.37	43.43	30.24	17.06	43.146
C_2	6.16	3.47	11.02	7.86	8.05	7.159
C_3	5.07	4.05	6.55	5.49	6.88	4.227
i-C_4	1.00	0.59	0.79	0.87	1.33	1.078
n-C_4	2.84	1.34	3.70	2.50	4.43	2.715
i-C_5	1.32	0.74	1.28	1.03	2.38	1.458
n-C_5	1.62	0.83	2.25	1.49	2.79	2.096
C_6	2.31	1.62	2.70	7.38	3.35	2.917
C_7^+	40.46	47.96	26.88	41.19	51.51	22.195
MW C_7^+	245.00	329.00	228.07	350.00	340.35	231.21
Reservoir temperature (K)	327.55	373.15	389.15	369.26	369.15	386.15
Bubble pressure at reservoir temperature (bar)	156.20	203.40	226.80	144.79	75.13	238.77
Reference pressure (bar)	156.20	209.24	226.80	137.90	63.27	250.82

[a] Oil O1 (Hirschberg et al., 1984); Oil O2 (Burke et al., 1990); Oil O3 (Mohammadi and Richon, 2007); Oil O4 (Vafaie-Sefti and Mousavi-Dehghani, 2006); Oils O5 and O6 (Nakhli et al., 2011).
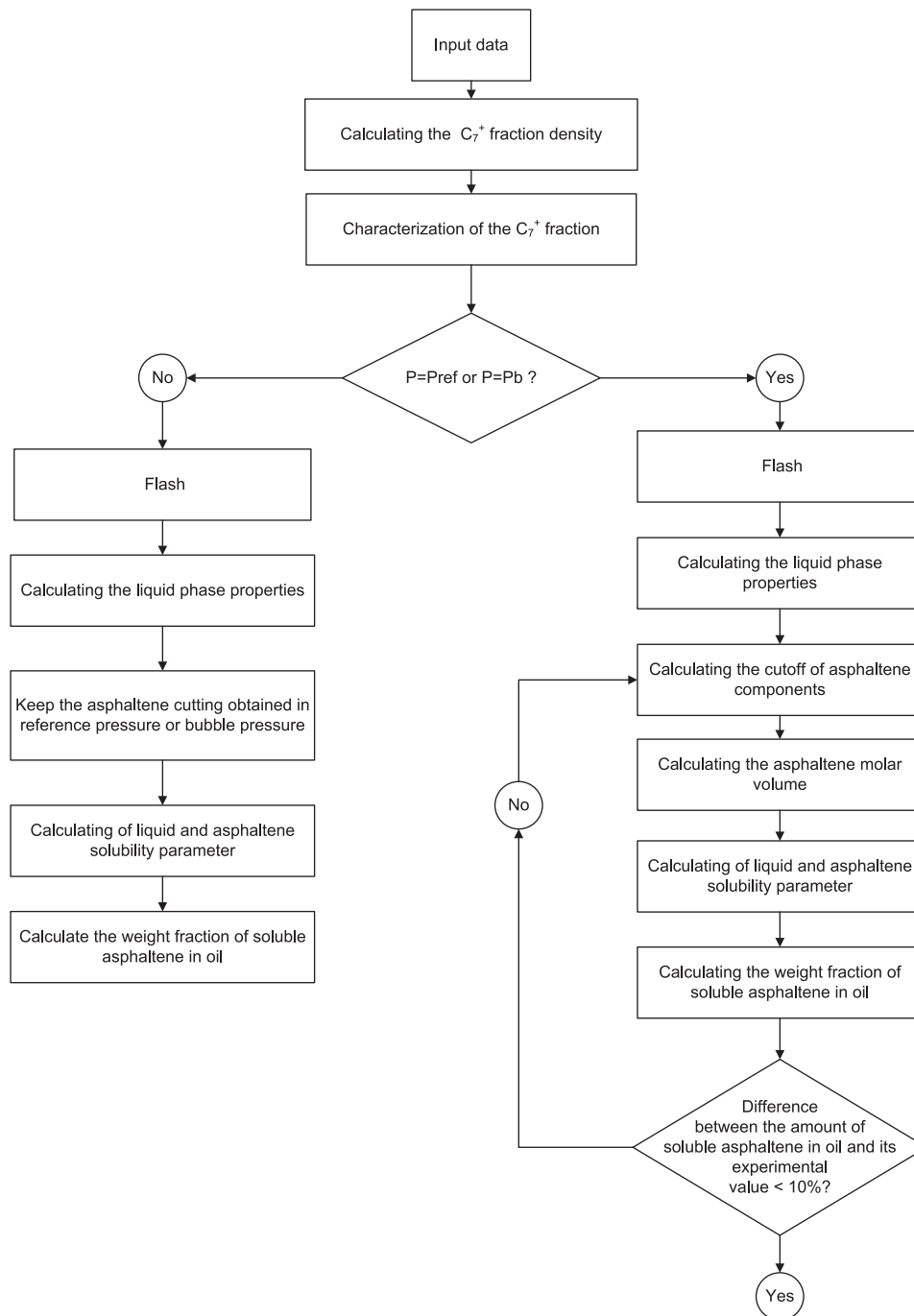
Fig. 1. Flow diagram of the algorithm for calculation of dissolved asphaltenes using the Hirschberg et al. (1984) model.

The initial step of asphaltene precipitated by depletion consists of detailing (characterization) the C_7^+ fraction. This is an extremely important step because the asphaltene representative components are selected from this characterization. In the model of Pedersen et al. (1988), there is flexibility regarding the number of components that constitute the C_7^+ fraction. To perform the characterization the original composition of the oil and the molecular weight of the C_7^+ fraction is needed. The property to be tuned is its density. The density of C_7^+ fraction is estimated by trial and error and the correct value will be achieved by comparing the calculated saturation pressure and its experimental value at the reservoir temperature.

The detailed calculations of asphaltene deposited as a consequence of pressure variation can be tracked through Fig. 1. Initially,

the calculation of the amount of asphaltene soluble at the oil reference pressure (or saturation pressure) is considered. This is following the right side of the flow diagram presented in Fig. 1. The computation of the liquid phase properties consists of determining the physical properties of each fraction as well as the molecular weight and liquid phase molar volume calculations. Assuming the number of components that constitute the asphaltene as known, we can calculate the oil and asphaltene solubility parameters as well as the asphaltene molar volume. After making these calculations the asphaltene mass fraction that has remained soluble is known. If this fraction is not framed in our convergence criterion (that is, the difference between the calculated and experimental fraction values are lower than 10%), a new assignment of the number of components that constitute the asphaltene is performed.

From the experimental value of the asphaltene mass fraction that remains soluble in the oil (or deposited), we can evaluate the mass fraction of asphaltene deposited at any other pressure. Therefore we can monitor the calculation sequence through the left side of the flow diagram shown in Fig. 1.

3.1. The effect of an inaccurate C_7^+ fraction density assignment on the asphaltene deposition

To calculate the amount of asphaltene deposited the correct simulation of the bubble pressure compared to its experimental value is extremely important. The property directly related to the bubble pressure simulation accuracy is the C_7^+ fraction density. Errors in the calculation cause great differences in the asphaltene deposition figures mainly at pressures below the bubble pressure (two-phase region). The oil and asphaltene solubility parameters and molar volumes are required to calculate the volume fraction of dissolved asphaltene in oil as can be seen in Eq. (1). All these calculations require the liquid phase composition. Therefore, if the bubble pressure is incorrect the composition will also be incorrect and in turn the solubility parameter and the volume parameter. For pressures above the bubble pressure the problems are smaller because only one phase is involved. The error would then account for the oil molar volume which is pressure dependent. As the calculations of the oil solubility parameter and the fraction of asphaltene in the oil depend on the composition and molar volume of the oil, error propagation also takes place.

Table 2 shows the effects of adjusting C_7^+ density ($SG_{C_{7+}}$) on the saturation pressure (P_b) and on the liquid phase properties: molar volume (V_L) and percent volume variation (ΔV_L). Furthermore, it also displays the reference pressure (P_{ref}) in which there is an experimental value for the amount of asphaltene precipitated that is used to determine the asphaltene cutoff point. Since this density influences the oil characterization, changing its value will influence the calculation of the amount of deposited asphaltene. This table also shows the influence of this density on the final result of the asphaltene weight percent soluble error in the oil (ΔS_a).

When the C_7^+ fraction density value is greater than the correct value, there is a decrease in the liquid phase molar volume value. The reason for this is the fact that the molar volume calculation is always carried out using a pressure lower than the corresponding saturation pressure. Another point to note is that for oils O2, O4 and O5 the largest percent volume variation occurs in the lowest C_7^+ fraction density values: 83.49%, 75.79% and 72.21%, respectively. This is due to the fact that the liquid phase molar volume in the correct density is already a high value. It is also important to note that the oils O3 and O6, which have a lower amount of dissolved asphaltenes, are those for which there is a less pronounced lower influence of the incorrect assignment of the fraction C_7^+ density. Also shown are the values of the properties involved in these final calculations, such as molar volume (V_L) and solubility parameters (δ_a and δ_L). Indeed, we observe a ripple effect of the wrong assignment of the C_7^+ density fraction value.

For this study we assess the influence using higher or lower density values compared with the correct density value (reference value), but keeping the pressure at its reference value (as at this pressure the experimental value of the precipitated or dissolved asphaltene is known). For each density value we assigned the corresponding saturation pressure value which can be higher or lower than the value of the reference pressure. If the reference pressure is greater than the saturation pressure the system is located in the single phase region. If the reference pressure is lower, we are therefore in a two-phase region.

As expected, an increase in density causes an increase in saturation pressure. Table 2 highlights the importance of setting the appropriate density for the calculation of the amount of asphaltene soluble in the oil. Note that regardless of its reference pressure (either above, below or equal to the bubble point), the errors are significant when calculated with the incorrect density. The results show that oils containing lower quantities of asphaltenes are more

Table 2
The influence of C_7^+ fraction density on the bubble pressure calculation up to the weight percent error of asphaltene soluble in the oil.

Oil	SG_{C7}^+ (g/cm^3)	P_b (bar)	V_L (cm^3/mol)	ΔV_L (%)	δ_a (cal$^{1/2}$/cm$^{3/2}$)	δ_L (cal$^{1/2}$/cm$^{3/2}$)	ΔS_a (%)
O1, $P_{ref}=156.20$ bar	0.60000	64.43	229.859	51.91	1.19	7.73	16.70
	0.70000	125.49	166.804	10.24	1.57	9.32	9.53
	0.82364[a]	156.20	151.312	0.00	1.91	9.81	1.79
	0.90000	180.39	148.379	-1.94	2.19	11.31	58.23
O2, $P_{ref}=209.24$ bar	0.60000	54.42	344.704	83.49	0.16	6.95	9.39
	0.70000	147.64	218.114	16.11	0.21	9.26	2.24
	0.87026[a]	203.40	187.855	0.00	0.22	10.06	1.11
	0.90000	215.85	184.841	-1.60	0.24	10.45	3.75
O3, $P_{ref}=226.80$ bar	0.60000	91.06	189.254	39.75	0.32	6.85	213.90
	0.70000	190.77	144.289	6.54	0.44	7.99	38.01
	0.79321[a]	226.80	135.428	0.00	0.46	8.27	6.17
	0.90000	280.73	135.000	-0.32	0.81	9.92	69.46
O4, $P_{ref}=137.90$ bar	0.60000	47.51	346.236	75.79	0.65	8.07	160.47
	0.70000	119.85	213.880	8.59	0.73	10.81	24.42
	0.81617[a]	144.79	196.956	0.00	0.77	11.86	1.40
	0.90000	167.11	190.797	-3.13	0.87	13.70	30.19
O5, $P_{ref}=63.27$ bar	0.60000	30.08	413.789	72.21	0.10	12.02	45.45
	0.70000	68.29	250.157	4.11	0.14	17.60	17.02
	0.76541[a]	75.13	240.279	0.00	0.16	19.10	1.11
	0.90000	92.02	220.218	-8.35	0.18	22.11	26.16
O6, $P_{ref}=250.82$ bar	0.60000	102.50	169.377	34.58	0.96	6.96	418.95
	0.70000	211.07	131.338	4.36	1.20	8.01	30.43
	0.76733[a]	238.77	125.853	0.00	1.24	8.20	0.44
	0.90000	312.78	124.824	-0.82	2.23	9.83	60.68

[a] Correct value.

Table 3
Influence of binary interaction parameter on the bubble pressure calculation up to the weight percent error of asphaltene soluble in the oil.

Oil	K_{ij}	P_b (bar)	V_L (cm^3/mol)	ΔV_L (%)	δ_a (cal$^{1/2}$/cm$^{3/2}$)	δ_L (cal$^{1/2}$/cm$^{3/2}$)	ΔS_a (%)
O1, $P_{ref}=156.20$ bar	0.00[a]	156.20	151.312	−0.10	1.91	9.81	1.79
	0.01	156.39	151.400	-0.04	1.67	9.84	7.31
	0.02	156.57	151.457	0.00	1.68	9.85	6.55
	0.03	156.76	151.514	0.04	1.68	9.86	5.79
O2, $P_{ref}=209.24$ bar	0.00[a]	203.40	187.855	0.00	0.22	10.06	1.11
	0.01	203.55	187.856	0.00	0.22	10.06	1.11
	0.02	203.72	187.856	0.00	0.22	10.06	1.11
	0.03	203.88	187.857	0.00	0.22	10.06	1.11
O3, $P_{ref}=226.80$ bar	0.00[a]	226.800	135.428	-0.07	0.46	8.27	6.17
	0.01	226.977	135.485	-0.03	0.46	8.27	6.77
	0.02	227.169	135.529	0.00	0.47	8.28	7.27
	0.03	227.361	135.574	0.03	0.47	8.28	7.78
O4, $P_{ref}=137.90$ bar	0.00[a]	144.79	196.956	-0.04	0.77	11.86	1.40
	0.01	144.88	196.991	-0.02	0.77	11.86	1.46
	0.02	144.97	197.028	0.00	0.77	11.87	1.52
	0.03	145.07	197.066	0.02	0.77	11.88	1.59
O5, $P_{ref}=63.27$ bar	0.00[a]	75.13	240.279	-0.02	0.16	19.10	1.11
	0.01	75.17	240.300	-0.01	0.16	19.10	1.04
	0.02	75.21	240.322	0.00	0.16	19.11	0.96
	0.03	75.25	240.345	0.01	0.16	19.11	0.89
O6, $P_{ref}=250.82$ bar	0.00[a]	238.77	125.853	0.00	1.24	8.20	0.44
	0.01	238.93	125.855	0.00	1.24	8.20	0.45
	0.02	239.19	125.858	0.00	1.24	8.20	0.46
	0.03	239.31	125.860	0.00	1.24	8.20	0.47

[a] Correct value.

sensitive to errors in density. The same problem occurs for oils with a reference pressure lower than the saturation pressure. Another important fact is that the further the density is from its real value, the larger the errors.

3.2. The effect of an inaccurate binary interaction parameter assignment on asphaltene deposition

A different approach is related to the adjustment of the binary interaction parameter between methane and the heaviest fraction in the SRK equation of state. This influence on the saturation pressure and liquid molar volume calculations is shown in Table 3.

Comparison of the results in Tables 2 and 3 shows that the influence of the binary interaction parameters on the oil molar volume is smaller than the influence of the density of fraction C_7^+. Such a result is due to the fact that a small variation in the saturation pressure corresponds to a small change in the binary interaction parameter and therefore a small change in the properties of the components that make up the C_7^+ fraction.

Table 3 also presents the regression results extended up to the final calculation of the asphaltene fraction which remains soluble in oil. A very small change in the binary interaction parameter usually does not cause substantial changes in the value of saturation pressure and other properties, and consequently does not lead to an increase in the mass fraction percentage error of asphaltenes which remain soluble in oil. Table 3 shows that the only marked effect of this variation is observed in oil O1. For this oil there is a relatively sharp variation in the asphaltene solubility parameter.

The results in Table 3 show that in the case of oil O1, although the oil molar volume changes very little, this small change causes a wide variation in the amount of asphaltene precipitated. This is due to the fact that in this oil the asphaltene solubility parameter undergoes considerable change. For this reason the errors are more pronounced when we compare O1 with O4 and O2 oils. This can also be justified by the change in the properties of the components that make up the C_7^+ fraction. In oils O2 and O6 the

binary interaction parameter does not have great influence either on the saturation pressure or on the amount of asphaltene soluble in the oil. In the case of these oils the errors do not change very much because the properties of the components that make up the C_7^+ fraction, as well as composition and molar volume, are not strongly influenced by the binary interaction parameter. These properties are necessary in the calculation of deposited asphaltene. Therefore, if these properties do not change very much with the variations of the binary interaction, the calculated amount of soluble asphaltene will follow the same behavior.

With respect to oils O4 and O5 we can observe that the binary interaction parameter affects the saturation pressure slightly and hence the molar volume and solubility parameters of oil and asphaltene. However, as the reference pressures of these oils are below the saturation pressure, this causes a small change in the composition. Therefore, in addition to the molar volume of oil and the properties of the components that make up the C_7^+ fraction, there is also a change in composition. With this buildup of changes the error suffers a modest increase. As the variation of the error is small, it shows the weak influence of the binary interaction parameter on the amount of soluble asphaltene in the oil.

3.3. Influence of the number of components in the C_7^+ fraction on the weight fraction of dissolved asphaltene in oil

The detailed asphaltene composition is unknown, so selecting the representative residue components is one of the most critical steps in this work. This explains the importance of splitting the C_7^+ fraction. We observe that the greater the numbers of components chosen to represent the C_7^+, the closer the calculated fractions of asphaltene in oil are to the experimental data. That is, the greater the number of components used to represent the C_7^+ fraction, the smaller the mole fractions of each one of these components. The solubility parameter and the molar volume of the oil depend on the mole fraction of its components. With a smaller mole fraction of its components the adjustment is more

flexible and therefore is easier to perform. Here we are referring to oils O1, O2, O4 and O5, as they contain the greatest amounts of soluble asphaltenes. The results of this analysis are shown in Table 4 where NC_7^+ represents the number of components making up the C_7^+ fraction and S_a the weight fraction of dissolved asphaltene in oil.

With regard to oil O3 we noted that different splitting (of the number of components making up the C_7^+ fraction) does not

cause great differences in the amount of asphaltene soluble in the oil, like other oils. Such behavior is due to two factors. The first is related to the fact that this oil has a small amount of asphaltene; therefore its molar volume should be high whereas its volume fraction should be small. The second lies in that oils with low asphaltene have a higher sensitivity in the solubility parameter calculation. That is, the solubility parameter of asphaltene also undergoes drastic change in the molar volume of asphaltene due to the variation in the number of fractions. Thus, there is a compensation. That is, as the choice of more components to represent the asphaltene increases asphaltene molar volume and decreases its volume fraction, the increase in these components decreases the difference between the oil and asphaltene solubility parameters, and consequently the volume fraction increases.

Table 4
Influence of the number of C_7^+ fraction representative components on the weight fraction of asphaltene dissolved in oil.

Oil	NC_7^+	P_{ref} (bar)	S_a calculated (%)	S_a experimental (%)
O1	5	156.20	2.33	1.82
	10		1.93	1.82
	17		1.85	1.82
O2	5	209.24	12.07	15.06
	10		12.89	15.06
	17		15.22	15.06
O3	5	226.80	0.60	0.63
	10		0.66	0.63
	17		0.59	0.63
O4	5	137.90	9.32	10.88
	10		9.97	10.88
	17		10.59	10.88
O5	5	63.27	1.52	10.13
	10		5.57	10.13
	17		10.24	10.13
O6	5	250.82	0.106	0.057
	10		0.075	0.057
	17		0.057	0.057

3.4. Relationship between the oil and asphaltene properties and the asphaltene volume fraction in oil

In this section the direct influence of each term that comprises the final volume fraction of soluble asphaltene expressed by Eq. (1) is evaluated: the difference between solubility parameters and molar volume of asphaltene. In Fig. 2 the results of this sensitivity evaluation regarding the difference between oil and asphaltene solubility parameter and asphaltene molar volume are shown. The purpose of this study is to show the influence of the difference between the oil and asphaltene solubility parameters on the calculus procedure by keeping the oil and asphaltene molar volumes constant and equal to their correct values and the influence of the asphaltene molar volume on the calculus procedure by keeping the oil molar volume and the solubility parameters constant and equal to their correct values.
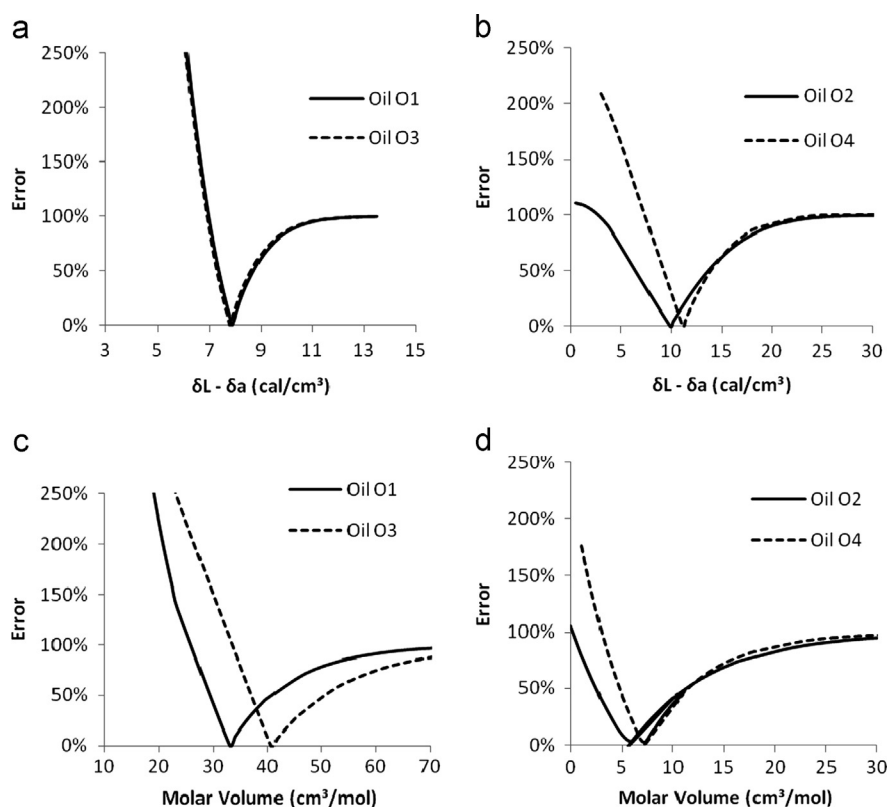

Fig. 2. Influence of the difference between the oil and asphaltene solubility parameters (a) and (b), and the asphaltene molar volume (c) and (d) on the amount of deposited asphaltene.

Fig. 2(a) and (b) shows the significance of the difference between the oil and asphaltene solubility parameters ($\delta_L - \delta_a$). Fig. 2(a) and (b) shows that small changes regarding the correct value of the solubility parameter differences give rise to great errors in the calculation of the asphaltene deposited. Another important conclusion is that oils with little asphaltene are even more sensitive to changes in the difference ($\delta_L - \delta_a$). This can be seen by tilting the left side of the graph. In oils that have little asphaltene (O1 and O3) it is more pronounced. This is one of the factors that hinders the optimal adjustment of the fraction that should represent the asphaltene.

Another factor to be analyzed is the asphaltene molar volume. The results of this evaluation are shown in Fig. 2(c) and (d). Fig. 2(c) and (d) shows that small changes regarding the correct value of the asphaltene molar volume give rise to great errors in the calculation of asphaltene deposited. This sensitivity to the asphaltene molar volume for oils with a small amount of asphaltene renders the simulation difficult. For this reason the greater the number of components involved in the splitting of the C_7^+ fraction, the better the results because the oil molar volume will not suffer great variations due to the variation in the number of fractions involved in the residue details.

The asphaltene molar volume and the difference between the oil and asphaltene solubility parameters are the most important factors to be observed in this simulation.

It is important to emphasize that neither the values of the asphaltene solubility parameter nor the asphaltene molar volume provided by Hirschberg et al. (1984) were used. The molar volume provided by Hirschberg et al. (1984) is equal to 4 m³/kmol and the asphaltene solubility parameter is given by the following equation:

$$\delta_a = 9.99(1 - 5.94 \times 10^{-4}T) \tag{13}$$

where T is the temperature expressed in Fahrenheit and δ_a is the asphaltene solubility parameter expressed in (cal/cm³)$^{0.5}$.

3.5. Pressure effect on the amount of soluble asphaltene

This section contains the asphaltene simulation results by depletion. Some additional information is needed. As noted above the residue is considered to consist of 17 fractions. The key point is to determine the cutoff point. The fractions that comprise the residue start with the fraction with the highest molecular weight. Subsequent fractions are considered toward the decreasing molecular weight of each fraction. After several tests it was detected that the best option is to track the amount of asphaltene deposited in the bubble point or reference pressure. This is accomplished by trial and error in the fraction which gives rise to the nearest value to the experimental value of the amount of soluble asphaltene. This is the cutoff fraction not only in the saturation pressure but also for any reference pressure (the pressure at which there is an available experimental amount of soluble or deposited asphaltene).

From the experimental value of the asphaltene mass fraction that remains soluble in the oil (or deposited), we can evaluate the mass fraction of asphaltene deposited at any other pressure. Therefore we can monitor the calculation sequence through the left side of the flow diagram shown in Fig. 1. For this purpose two monitoring parameters $F1$ and $F2$ both calculated at the reference pressure (or saturation pressure) expressed by Eqs. (14) and (15) must be used:

$$F1 = \delta_a^* - \delta_a \tag{14}$$

$$F2 = \delta_L - \delta_a \tag{15}$$

where δ_a is the previously calculated asphaltene solubility parameter and δ_a^* is the optimal parameter, in other words the value of

the solubility parameter which corresponds to a calculated asphaltene deposited weight fraction equal to the experimental value, and δ_L is the liquid phase solubility parameter.

As outlined in the flow diagram in Fig. 1, to calculate the asphaltene soluble fraction at different pressures from the reference pressure, the same optimal number of components (cut) comprising the asphaltene at the reference pressure and the asphaltene molar volume are kept. However, the difference between the liquid and asphaltene solubility parameter ($\delta_L - \delta_a$) is different depending on the pressure at which the estimated amount of soluble asphaltene is higher or lower than the saturation pressure. The reason for this is that at pressures below the saturation pressure the oil composition will be different due to the vapor evolution.

If the pressure at which we estimate the soluble amount of asphaltene is higher than the saturation pressure and the ratio between these pressures is greater than 0.6, the ($\delta_L - \delta_a$) computation is usually carried out following all the steps previously evaluated. If this ratio is less than 0.6 the ($\delta_L - \delta_a$) is just calculated as

$$\delta_L - \delta_a = \frac{P_b}{P}F2 \tag{16}$$

where P_b is the saturation pressure and P is the pressure at which we estimate the soluble amount of asphaltene.

The reason why this approach is effective is related to the fact that normally the pressure at which factor $F2$ is calculated is the reference pressure and in most of the oils this is the saturation pressure—where the amount of soluble asphaltene is minimal (i.e. maximum precipitated amount). Another relevant factor is that at pressures above the saturation pressure composition changes with pressure are not observed.

To calculate the amount of asphaltene soluble at a pressure lower than the saturation pressure, the difference between asphaltene and liquid solubility parameters ($\delta_L - \delta_a$) is calculated

Table 5
Prediction of dissolved asphaltene during pressure depletion.

| Oil	Pressure (bar)	S_a calculated (%)	S_a experimental (%)
O1	50.00	2.25	2.12
	100.00	2.30	2.24
	156.2	1.85	1.82
	170.6	2.57	2.88
O2	69.96	15.59	15.73
	138.91	14.96	14.98
	209.24	15.22	15.06
	276.80	14.98	14.86
O3	100.00	1.00	0.98
	150.00	0.93	0.96
	226.80	0.59	0.63
	300.00	0.76	0.83
	430.00	1.06	1.00
O4	67.82	10.62	10.66
	137.90	10.59	10.88
	204.58	10.15	10.96
	340.22	12.08	12.78
O5	21.43	10.08	10.21
	63.27	10.56	10.13
	142.86	10.06	10.24
O6	107.28	0.120	0.143
	181.58	0.078	0.081
	250.82	0.057	0.057
	277.78	0.056	0.060
	316.53	0.044	0.077

a

b
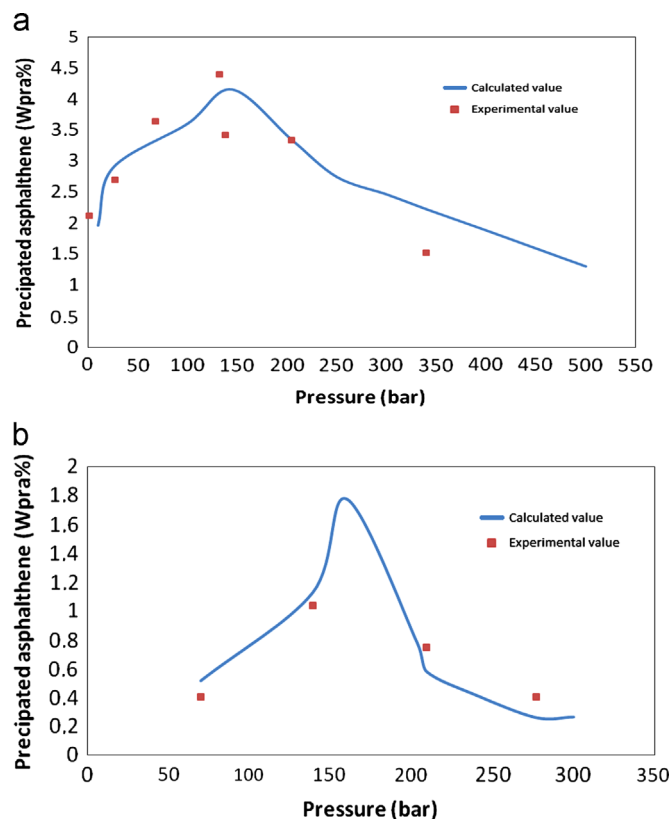
Fig. 3. Percentage of precipitated asphaltene in a reservoir during depletion [oil O4 (a) experimental data from Vafaie-Sefti et al. (2006); and oil O2 (b) experimental data from Burke et al. (1990)].

by Eq. (17). We can see from Eq. (17) that the two factors $F1$ and $F2$, previously calculated in the reference pressure, are used and two additional corrections are needed: the ratio of the saturation pressure (P_b) and the pressure of interest P and the molar volume liquid phase (V_L) calculated at pressure P and the molar volume of liquid phase (V_b) calculated at the saturation pressure ratio:

$$\delta_L - \delta_a = F2 + \left(\frac{P_b}{P} + \frac{V_L}{V_b}\right) F1 \qquad (17)$$

Despite the fact that the pressure of interest is lower than the saturation pressure, this simplified way to calculate the difference between the solubility parameters provides very good results as will be shown below.

The simulation results of weight fraction of dissolved asphaltene in oil (S_a) and comparisons with experimental values from the literature for the oils for which the composition and properties are displayed in Table 1. It is interesting to note that in all the oils only one experimental value of the amount of soluble or deposited asphaltene is used (saturation pressure or reference pressure) in order to reach the set of fractions that make up the asphaltene. The obtained information is then used at other pressures and the simulation results are compared with experimental values.

The results in Table 5 show that for oils with higher amounts of asphaltene the results are better. For oils with lower amounts of asphaltene the sensitivity to the asphaltene molar volume and the solubility parameter is even higher making tuning more difficult.

As shown in Fig. 3, there is a greater amount of deposited asphaltene near the saturation pressure. At pressures higher than the saturation pressure, the asphaltene solubilizes due to the pressure change while at lower pressures besides the pressure change there is also the effect of the change in composition.

It is possible to see in Fig. 3(a) that there are two experimental points at pressures near the saturation pressure at which precipitated asphaltene values are very distinct from each other. One of these points is further from the curve because it is not a good representation of the general oil behavior. Fig. 3(a) shows that the experimental points obtained at pressures furthest from the bubble pressure are more distant from the calculated curve because the reference pressure is a value near the bubble pressure, and the more distant from the reference pressure, the larger the extrapolation and the greater the errors therefore.

4. Conclusions

Precipitated asphaltene inside reservoirs, wellbores and in refineries can cause severe problems, adversely affecting efficiencies and the cost of petroleum production. Despite the fact that there are numerous models in the literature to predict the onset of asphaltene precipitation and the setting conditions of precipitation, the work presented here shows that the traditional Hirschberg et al. (1984) can be successfully applied to perform modifications with respect to the oil characterization and the calculation of the oil and asphaltene solubility parameter. We have attempted to show that it is possible to obtain a precise quantitative representation of asphaltene deposited due to pressure depletion by using a minimum amount of experimental data.

Experimental data from literature regarding the deposition of asphaltene with six oils from different geographical regions were used to evaluate this model with good results. It is worth emphasizing that we analyzed the influence that numerous properties play on the final calculation of the asphaltene weight fraction deposited.

The first property analyzed was the saturation pressure. Due to the importance of the saturation pressure calculation on asphaltene deposition, it was relevant to evaluate the influence of some variables in its final computation. Therefore in this study the influence of the density value assigned to the C_7^+ fraction was evaluated as well as the value of the binary interaction parameter between methane and the heavier components on the saturation pressure calculations. It is extremely important to note that a small difference in the C_7^+ fraction density can cause great errors in the calculation of the asphaltene weight fraction deposited. This is due to the influence of this variable on all the other properties that determine the amount of asphaltene deposited, such as the values of the solubility parameter and the molar volume of the oil and asphaltene.

Another relevant property is the number of fractions that comprise the residue and the fractions that are considered asphaltene constituents within this residue. It was noted that the smallest errors are achieved when this is accomplished at saturation pressure. However, if there is no experimental value at this pressure, the adjustment to be performed at another pressure should be selected as close as possible to the saturation pressure. However, in this case the adjustment is more sensitive to small variations in the properties involved. If experimental data are available for both higher or lower pressures than the saturation pressure, the higher pressure should be selected.

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