[Regular Paper]

Developing of Scaling Equation with Function of Pressure to Determine Onset of Asphaltene Precipitation

Abbas Khaksar MENSHAD[†2)], Amir Mohsen MOFIDI[†1)], Farzad SHARIATPANAHI[†2)], and Mohsen EDALAT[†2)]*

[†1)] Process Engineering Dept., Iranian Central Oil Field Co., Tehran, IRAN
[†2)] Oil & Gas Center of Excellence, Chemical Engineering Dept., College of Engineering, University of Tehran, Enghelab Ave., P.O.Box 11365/4563, Tehran, IRAN

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In this study a simple and applicable scaling equation as a function of pressure, molecular weight, dilution ratio (solvent) and weight percent of precipitated asphaltene has been developed. This equation can be used to determine the weight percent of precipitated asphaltene in the presence of different precipitants (solvents) and the amount of solvent at onset point. Since increasing the pressure of crude oil decreases the amount of asphaltene precipitation, the effect of reservoir pressure has been taken into account in developing this equation. By considering the effect of reservoir pressure in developing the scaling equation and application of a genetic algorithm, the unknown parameters of the scaling equation are simultaneously and without any reservation obtained. The most important application of this unique equation is in the determination of critical point of asphaltene precipitation, known as onset point, and asphaltene precipitation in gas injection operations for enhanced oil recovery. The results predicted using the scaling equations are compared with literature precipitation data and it is shown that they are in good agreement with experimental data. The scaling equation can be used in the design of gas-injected reservoir to prevent precipitation of the asphaltene aggregates in the reservoir.

Keywords
Asphaltene, Scaling equation, Gas injection, EOR, Genetic algorithm

1. Introduction

Gas injection has become a common and efficient method and a very important practice in enhanced oil recovery (EOR) process. Enhanced oil recovery methods hold considerable promise for the recovery of additional oil from many reservoirs. In the gas injection processes the miscible or immiscible displacements are achieved by injecting different fluids into a reservoir at appropriate pressure and temperature conditions. However, injecting different fluids into an oil reservoir often causes some changes in the flow behavior and the equilibrium properties of the fluids. Under certain conditions, such changes lead to the formation of heavy organic compounds and in particular, asphaltenes. Asphaltenes are the heaviest components of a crude oil defined as the insoluble fraction in light normal alkenes but can be dissolved in toluene and benzene[1)]. The amount of asphaltenes is a function of the composition of the crude oil, the precipitating agent (*n*-alkanes), pressure and temperature of the reservoir. Asphaltene precipitation can result in plugging of the production facilities, isolation of oil from the flowing part of the reservoir and hence the eventual reduction in the efficiency of the EOR process. Therefore, asphaltene precipitation is a threat for the EOR process.

Asphaltene precipitation causes the injection process to be less economical. Therefore, knowing the amount of gas in the gas injection project that can cause problems such as precipitation of asphaltene could be helpful and could have a great impact on reducing the total project cost.

Crude oils, especially those with asphaltene, have complex structure which their stable state change with temperature and pressure. Because of this complexity, predicting the onset and other properties of asphaltene are still problems that many researchers have been working on[2)~16)].

Although asphaltene precipitation is a worldwide problem, its main cause has not been completely understood[11)]. The mechanism of asphaltene precipitation is very complex and despite a wealth of research on the topic. Controversy remains as to the nature of solving this problem[12)].

The most commonly used models[1), 2), 9)] to predict asphaltene behavior can be categorized into thermodynamic models and scaling model which is based on

* To whom correspondence should be addressed.
* E-mail: mohedalat@yahoo.com

the aggregation/gelation phenomena. The existing thermodynamic models for describing asphaltene precipitation basically fall into three groups:
(1) Statistical thermodynamic models which seek relations between macroscopic properties and intermolecular forces through partition functions and are insufficient for practical purposes. The absence of intermolecular forces and other related data are the main obstacles.
(2) Continuous thermodynamic models which are the procedure wherein the composition of a multicomponent mixture is represented through a continuous distribution function of a characterization property such as the molecular weight[17]. The difficulty encountered is the lack of suitable characterization parameters.
(3) Molecular thermodynamic models that seek to overcome some of the limitations of both classical and statistical thermodynamics[15),18),19)]. Continuous and statistical thermodynamic models need a great amount of experimental data. However, thermodynamic models based on the theory of molecular solubility have less adjustment parameters compared to other models. The molecular thermodynamic models require the knowledge of the density, molecular weight and solubility parameter of asphaltene. While it is easy to measure or estimate the density and solubility parameter of asphaltene, it is difficult to measure the molecular weight of asphaltene accurately[20]. This is due to the polydispersity nature of asphaltene in both molecular size and polarity.

The aggregation/gelation phenomena are used to model scaling functions which are independent of asphaltene properties. This model is very simple and the only parameters needed for modeling are the solvent ratio of precipitant (*SR*), amount of precipitated asphaltene and molecular weight of precipitant[21~23)].

Rassamdana *et al.*[1),23)] claimed that formation of asphaltene is similar to the aggregation/gelation phenomena and thus may be described by using the scaling/fractal theory. Based on this idea, they proposed a scaling approach to describe the asphaltene precipitation behavior. Hu *et al.*[24)] studied the application of scaling equation for asphaltene precipitation. The objective of this work is to develop a new scaling equation which is also a function of pressure to predict the onset and amount of asphaltene precipitation.

2. Derivation of the Scaling Equation

The similarity of asphaltene formation mechanism to the aggregation/gelation phenomena has been exploited to develop a scaling/fractal theory for predicting the amounts of asphaltene precipitation. In deriving a scaling equation for the onset and amount of asphaltene precipitation, three variables —the weight percent of the precipitated asphaltene based on the weight of crude oil, *W*, the ratio of injected solvent to weight of crude oil called dilution ratio, *R*, and the molecular weight of the injected fluid or the precipitation agent, M_w— are involved[21)].

It has been demonstrated that the three variables are combined to form the scaling variable, *x* and *y*, as the following,

$$x = \frac{R}{M_w^z} \tag{1}$$

$$y = \frac{w}{M_w^{z'}} \tag{2}$$

where $z' = -2$ is suggested as a universal exponent, independent of the type of the crude oil and the precipitation agent and the parameter *z* is treated as an adjustable parameter and a different value is assigned to *z* for different solvents[24),25)]. The values of *z* vary from 0.25 to 0.6 depending on the type of crude oils and precipitants[21),24)].

Since at a fixed temperature and pressure, all the precipitation data can be brought onto a single universal curve, the scaling equation *Y* can be expressed in terms of *X*. The universal curve will be as the following

$$y = f(x) \tag{3}$$

Where $f(x)$ is a scaling function and can be in the form of a polynomial function.

$$f(x) = \sum_{i=0}^{i=n} a_i x^i \tag{4}$$

The coefficients a_i are determined from the precipitation data of a specific precipitant-oil system and could be extended to other precipitants.

So far in all of the studies, the effect of crude oil pressure has been either neglected or considered to be fixed. In this article the effect of pressure as a variable that can have an effect on precipitation onset and weight percent of precipitated asphaltene has been taken into account. Therefore, a new scaling equation function of three variables, the weight percent of the precipitated asphaltene based on the weight of crude oil, *W*, the ratio of injected solvent to weight of crude oil called dilution ratio, *R*, and the molecular weight of the injected fluid or the precipitation agent, M_w is presented and all the parameters including *z* calculated using a genetic algorithm without any constrains and limitations.

3. Scaling Equation as a Function of Pressure

The property of aggregation processes is that the data for various precipitated asphaltene may fall onto each other and form a universal scaling curve. This means that if the data do fall onto each other, the number of independent variables reduces by one. By taking advantage of this property, the three variables *x*, *y* and *P* can be reduced to two variables *Y* and *X* using the scal-

Table 1 Calculated Constants of Eq. (7)

Parameter	Value
C_1	0.023622
C_2	9.84164
a_0	− 622.047
a_1	− 2433.39
a_2	5905.51
a_3	2533.72
Z	0.321811

ing/fractal theory.

The two variables X and Y are defined as:

$$X = \frac{x}{P^{C_1}} = \frac{R}{M_w^{z} P^{C_1}} \tag{5}$$

$$Y = \frac{y}{x^{C_2}} = \frac{W M_w^{z'\times C_2}}{R^{C_2 - z'}} \tag{6}$$

In the above equations, $z' = -2$ is considered as a universal exponent and it is independent of the type of the crude oil and the precipitation agent. The scaling equation $Y=f(x)$ is a third-order polynomial and by substituting for X into the scaling equation the following relation for weight percent of participated asphaltene is obtained:

$$W = \frac{a_0 \times R^{C_2-2}}{{M_w}^{C_2\times Z}} + \frac{a_1 \times R^{C_2-1}}{{M_w}^{Z(C_2+1)} \times P^{C1}} + \frac{a_2 \times R^{C_2}}{{M_w}^{Z(C_2+2)} \times P^{2C_1}} + \frac{a_3 \times R^{C_2+1}}{{M_w}^{Z(C_2+3)} \times P^{3C_1}} \tag{7}$$

Equation (7) can be utilized to determine the weight percent of precipitated asphaltene at a specific pressure, temperature and precipitant. The numerical values of seven unknowns, a_0, a_1, a_2, a_3, C_1, C_2 and Z in the Eq. (7) are obtained using experimental data and a genetic algorithm.

In order to determine the best-fit value for the constants in Eq. (7), experimental data of precipitation is used[21]. These parameters are calculated spontaneously using a genetic algorithm without considering any constraints and reservations. The calculated parameters are depicted in **Table 1**.

By substituting the appropriate values of parameters into Eqs. (5) and (6), the following relations are obtained for X and Y:

$$X = \frac{R}{{M_w}^{0.321811} \times P^{0.023622}} \tag{8}$$

$$Y = \frac{W \times {M_w}^{3.16714}}{R^{7.84164}} \tag{9}$$

The scaling function Y, Eq. (4), and weight percent of participated asphaltene W, Eq. (7), will be as the following:

$$Y = 2533.72X^3 + 5905.51X^2 - 2433.39X - 622.047 \tag{10}$$

$$W = \frac{-622.047 \times R^{7.84164}}{M_w^{3.16714}} + \frac{-2433.39 \times R^{8.84164}}{M_w^{3.4889} \times P^{0.023622}} + \frac{5905.51 \times R^{9.84164}}{M_w^{3.8107} \times P^{0.04724}} + \frac{2533.72 \times R^{10.84164}}{M_w^{4.1325} \times P^{0.07086}} \tag{11}$$

Equation (11) can now be used for predicting the onset and the amount of asphaltene precipitation at any pressure, dilution ratio R and weight of the injected fluid or M_w molecular weight of precipitation agent.

4. Asphaltene Onset of Percipitation

The questions under investigation are: under what conditions the asphaltene will precipitate, what will be the amount of precipitation and the physical properties of asphaltenes and oil rich phases? Since the prediction of the onset of asphaltene precipitation is of practical significance, particularly in the gas injection project, the main objective of all of the models which have been developed so far was to determine the onset of precipitation.

Many studies have been made to define a model to predict the onset conditions and the magnitude of asphaltene precipitation upon changes in pressure, temperature, or composition of crude oil and a number of methods have been proposed in the literature to determine the onset of asphaltene precipitation[26]. From the operational and practical point of view, most of these methods for determining the incipient of asphaltene precipitation are quite tedious.

A method based on the scaling equation is developed to predict the incipient of asphaltene precipitation and calculate the amount of asphaltene precipitation. From the practical point of view, the asphaltene precipitation is occurring when the asphaltene starts precipitating. It means for $W < 0$, no precipitation occurs, whereas for $W \geq 0$ asphaltene precipitation does occur, where the equal sign stands for incipient of asphaltene precipitation and is called the critical point. Therefore, by equating Eq. (11) to zero, the conditions of critical point can be determined. By equating Eq. (11) or the scaling Eq. (10) to zero the following equation is obtained and can be solved for X_c which is the value of X at the onset of asphaltene precipitation.

$$-622.047 - 2433.39X_c + 5905.51{X_c}^2 + 2533.72{X_c}^3 = 0 \tag{12}$$

Substituting X_c into Eq. (8):

$$X_c = \frac{R_c}{{M_w}^{0.321811} \times {P_c}^{0.023622}} \tag{13}$$

Where R_c is the critical value of the dilution ratio R and

Table 2 Solvent Ratio at Onset of Asphaltene Precipitation (n-C_6 as precipitant, $M_w = 86.16$)

P [psia][a)]	R_c [solvent, cm^3/oil, g]
100	0.092018
1100	0.097381
2100	0.09888
3100	0.099793
4100	0.100455
5100	0.100974

a) 1 psia = 6.895×10^3 Pa.

Table 3 Solvent Ratio at Onset of Asphaltene Precipitation (n-C_7 as Precipitant, $M_w = 100.21$)

P [psia][a)]	R_c [solvent, cm^3/oil, g]
100	0.096601891
1100	0.102231658
2100	0.103805196
3100	0.104764604
4100	0.105458796
5100	0.106003902

a) 1 psia = 6.895×10^3 Pa.

it is defined as the dilution ratio at the onset of asphaltene precipitation. Equation (13) can be rearranged to obtain a correlation for critical dilution ratio as a function of pressure as follows:

$$R_c = X_c \times M_w^{0.321811} \times P_c^{0.023622} \qquad (14)$$

P_c is critical pressure at which asphaltene precipitate. For an n-alkane-oil system at a given temperature, R_c depends on the composition of crude oil, type of precipitant and pressure.

The calculation has been done for the same oil with two solvents (n-C_6, n-C_7) as precipitant results are shown in **Tables 2** and **3**. These tables indicate that as the pressure decreases, the amount of precipitant at critical point (R_c) decreases. This is a common behavior of asphaltene which has been predicted by the scaling equation.

5. Conclusion

In order to examine the accuracy of the derived equation, the scaling equation has been used to predict the asphaltene precipitation for n-C_6 (n-hexane, $M_w = 8616$). and n-C_7 (n-heptane, $M_w = 100.21$) as precipitant with $R =$ 3 (solvent, cm^3/oil, g). A comparison between predicted results and experimental data is shown in **Figs. 1** and **2**. These figures show a good agreement between predicted and gas injection experimental data. The derived scaling equation can be used to predict weight percent of precipitated asphaltene at different pressures and with different solvents (precipitant) and solvent ratios, in a gas injection process. Equations (11) and

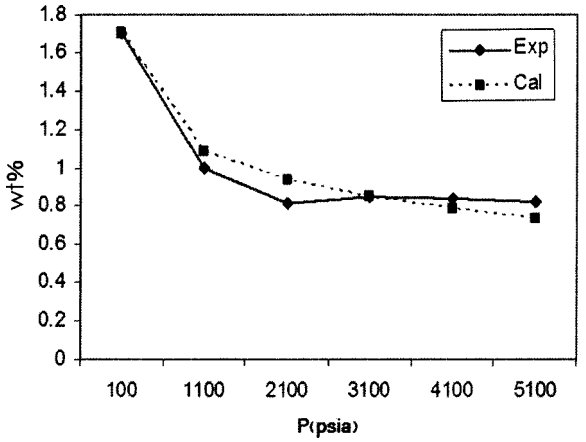

Fig. 1 Comparison between Experimental and Predicted Data by the Scaling Equation (n-C_7 as precipitant, $R = 3$ solvent, cm^3/oil, g)

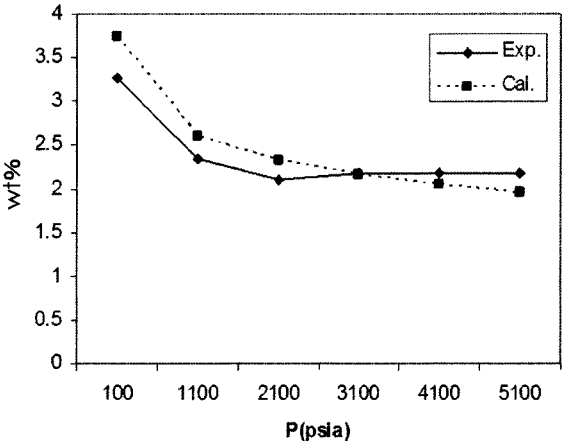

Fig. 2 Comparison between Experimental and Predicted Data by the Scaling Equation (n-C_6 as precipitant, $R = 3$ solvent, cm^3/oil, g)

(14) are independent of physical properties of asphaltene and can be used simply to predict weight percent of precipitated asphaltene and onset of asphaltene precipitation. It has been shown that only one set of proper experimental data is required to obtain the scaling equation. The obtained scaling equations can be used to predict asphaltene precipitation. Finally, having enough knowledge of the critical condition is crucial to the design of a gas injection operation for an EOR process. The scaling Eq. (11) can be used in the design of gas-injected reservoir to predict the onset of precipitation of the asphaltene aggregates, critical condition, in the reservoir. It is simple and the properties of complex asphaltenes are not involved.

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Nomenclatures

a_0, a_1, a_2 and a_3 : coefficient of Eq. (4)		[—]
C_1 and C_2 : parameters of equations		[—]
M	: solvent molecular weight	[g/mol]
P	: pressure	[Pa]
R	: solvent ratio	[solvent, cm^3/oil, g]
T	: temperature	[K]
W	: weight percent of precipitated asphaltene	[—]
X	: variable defined by Eq. (5)	[—]
Y	: scaling function defined by Eq. (6)	[—]
Z	: adjustable parameter of Eq. (1)	[—]

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アスファルテン析出開始点決定のための圧力を関数としたスケーリング式の開発

Abbas Khaksar MENSHAD[†2)], Amir Mohsen MOFIDI[†1)], Farzad SHARIATPANAHI[†2)], Mohsen EDALAT[†2)]

[†1)] Process Engineering Dept., Iranian Central Oil Field Co., Tehran, IRAN

[†2)] Oil & Gas Center of Excellence, Chemical Engineering Dept., College of Engineering, University of Tehran, Enghelab Ave., P.O. Box 11365/4563, Tehran, IRAN

種々の溶剤添加による原油中のアスファルテン析出量ならびに析出開始時の溶剤添加量を予測することを目的として，圧力，分子量，溶剤希釈比ならびに析出重量％を関数とすることにより，簡易かつ適用範囲の広いスケーリング式を開発した。アスファルテンの析出には圧力が大きな影響要因となるため，スケーリング式の構築には圧力を考慮する必要がある。本論文では過去の文献のアスファルテン析出実験データ結果とスケーリング式から求めた結果とを比較することにより開発したスケーリング式の有効性を確認した。本手法は特に油田におけるアスファルテン析出開始圧力，さらには増進回収（EOR）としてガス攻法を実施する際のガス圧入による析出挙動の把握に有効となる。

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