

Asphaltene flocculation and collapse from petroleum fluids

Valter Antonio M. Branco^a, G. Ali Mansoori^{b,*}, Luiza Cristina De Almeida Xavier^a, Sang J. Park^b, Hussain Manafi^b

^a*Petroleo Brasileiro S.A., Petrobras/CENPES/DIGER, Cidade Universitaria, Quadra 7, Ilma Fundao, Rio de Janeiro, RJ, 21910, Brazil*

^b*Thermodynamics Research Laboratory, Department of Chemical Engineering, University of Illinois at Chicago, 810 S. Clinton Street, Chicago, IL 60607-7000, USA*

Abstract

Deposition of complex and heavy organic compounds, which exist in petroleum crude and heavy oil, can cause a number of severe problems. To prevent deposition inside the reservoir, in the well head and inside the transmission lines, it is necessary to be able to predict the onset and amount of deposition due to various factors. In the present paper, the mechanism of asphaltene deposition, which is the major cause of most organic deposition cases, is modeled based on statistical mechanics of polydisperse polymer solutions joined with the kinetic theory of aggregation and its predictive capability is discussed. Utilization of statistical mechanics of polydisperse polymer solutions joined with kinetic theory of aggregation enables us to develop a realistic model which is able to predict both reversible and irreversible heavy organic depositions. The present model is capable of describing several reversible and irreversible situations, such as the phenomena of organic deposition, growing mechanism of heavy organic aggregates, the size distributions of precipitated organics and the solubility of heavy organics in a crude oil due to variations in oil pressure, temperature and composition. As an example, the present model is applied for heavy organics deposition prediction of two different Brazilian crude oils for which experimental data are available. It is shown that the prediction results of the present model are in good agreement with the experimental data. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Organic deposition during petroleum and heavy oil production and processing is a serious problem in many areas throughout the world. The economic implications of this problem are tremendous considering the fact that a problem workover cost each time could get as high as a million dollars. For example, in a heavy crude production field, formation of asphaltic

sludge after shutting in a well temporarily and/or after stimulation treatment by acid has resulted in partial or complete plugging of the well (Lichaa and Herrera, 1975; Escobedo et al., 1997). The downtime, cleaning and maintenance costs are a sizeable factor in the economics of producing a heavy crude field prone to organic deposition. Considering the trend of the oil industry towards the utilization of heavier asphaltenic crudes and the increased utilization of miscible flooding techniques for recovering and transportation of oil, the role of organic deposition in the economic development of petroleum production will be important and crucial.

* Corresponding author. Tel.: +1-312-996-5592; fax: +1-312-996-0808.

E-mail address: mansoori@uic.edu (G.A. Mansoori).

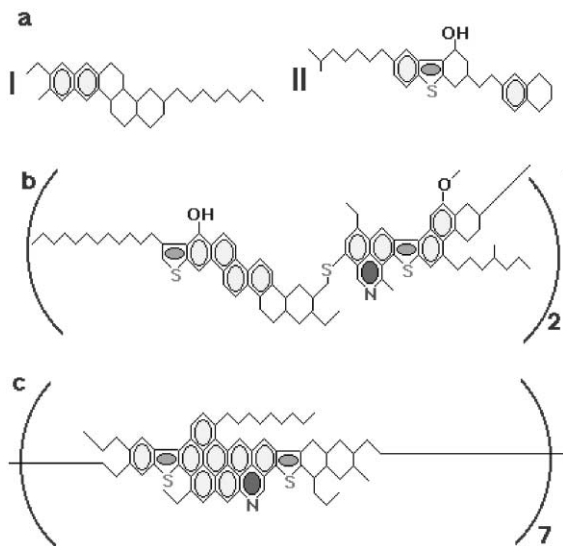


Fig. 1. Average molecular structural models of the fractions of Athabasca tar-sand bitumen and petroleum bitumen. (a) Resin fraction, (b) asphaltene fraction of tar-sand bitumen; (c) asphaltene fraction of bitumen (Suzuki et al., 1982).

The major factor that govern precipitation of heavy organic substances appear to be due to asphaltene flocculation, which is initiated due to variations in compositions of crude and injection (or blending) fluid, pressure and temperature. With alterations in these parameters, the asphaltene flocculation and, as a result, the nature of heavy organics which precipitate, will vary. In addition, it is a proven fact that the flocculation of asphaltene is generally followed by its deposition resulting with precipitates which are insoluble in petroleum fluids and containing other heavy organics and mineral deposits (Cole and Jessen, 1960; Hunt, 1962; Lhioreau et al., 1967; Shock et al., 1955; Sanchez and Mansoori, 1998).

Over the last six decades, a number of investigators have researched the nature of heavy organics and mechanisms of organics deposition. There has been good progress made in the past several years in the formulation of accurate vapor-liquid phase behavior prediction of complex petroleum fluids (Manafi et al., 1999), statistical mechanics of polydisperse polymer solutions (Scott and Magat, 1945) and kinetic theory of aggregation and precipitation (Smoluchowski, 1916). Because of the complexity of the nature of heavy organic substances, the phenomena of the organic

deposition are not well understood. In addition, in view of the complexity of the petroleum fluids, study and understanding of the in situ precipitation of organic substances seems to be a challenging and timely task. Such an understanding will help to design a more profitable route for petroleum production and transportation projects. The difficulty of dealing with organic deposits is proven to be proportional to the amount and nature of asphaltene present in such systems.

A number of investigators have constructed model structures for asphaltenes, resins and other heavy fractions based on physical and chemical methods. Physical methods include IR, NMR, ESR, mass spectrometry, X-ray, ultracentrifugation, electron microscopy, small-angle neutron scattering, small-angle X-ray scattering, quasi-elastic light scattering spectroscopy, VPO, GPC, etc. Chemical methods involve oxidation, hydrogenation, etc. Two of the representative structures for the asphaltene molecule belong to the Athabasca tar-sand bitumen and petroleum bitumens (Suzuki et al., 1982) and include carbon, hydrogen, oxygen, nitrogen, sulphur, as well as polar and nonpolar groups, as it is shown in Fig. 1.

Small-sized asphaltene particles may be dissolved in a petroleum fluid, whereas relatively large asphaltene particles may flocculate out of the solution due to high paraffin content of the oil, forming random aggregates, as shown in Fig. 2. Flocculation of

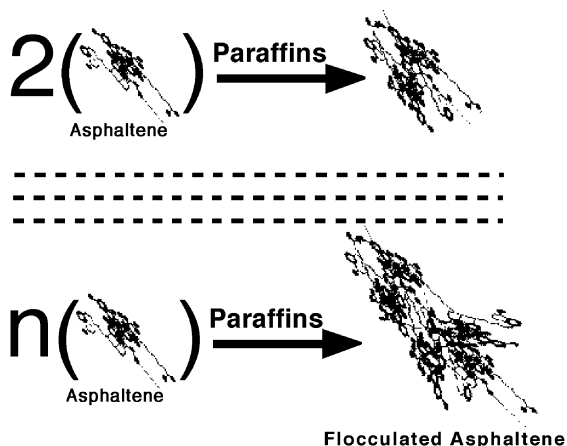


Fig. 2. Flocculation of asphaltene due to increase in paraffin (nonpolar) content of petroleum.

asphaltene in paraffinic petroleum are known to be irreversible, having hysteresis when the conditions are returned to preflocculation point (Abedi et al., 1998; Acevedo et al., 1995; Birket, 1997; Fuhr et al., 1991). Due to their large size and their adsorption affinity to solid surfaces, asphaltene flocs (random aggregates) can cause quite stable deposits which may not wash away by current remediation techniques. One of the effective and routine methods of remediation of heavy organic deposits is the use of strong aromatic solvents that could dissolve the asphaltene deposits (Sanchez and Mansoori, 1998; Acevedo et al., 1995; Dubey and Waxman, 1995; Kim et al., 1990). Asphaltene flocs (random aggregates) can form steric-colloids in the presence of excess amounts of resins and paraffin hydrocarbons (Mansoori, 1997; Park and Mansoori, 1988), as shown in Fig. 3.

The concept that asphaltene molecules are present as a colloidal system is credited to Nellensteyn (1924). He proposed that asphaltic compounds were made of flocs or aggregates of asphaltene protected by adsorbed resin and hydrocarbon materials, all dispersed in a hydrocarbon medium. He also found that the peptizing or precipitating properties of different common solvents with respect to asphaltic compounds are closely related to the surface tension. Leontaritis and Mansoori (1987) proposed a thermodynamic-colloidal model which is capable of predicting the onset of asphaltene flocculation. According to this model, asphaltenes exist in the oil as solid particles in colloidal suspension, stabilized by resins adsorbed on their surface. Kawanaka et al. (1991) proposed a continuous thermodynamics model for asphaltene solubility in petroleum fluids. Park and Mansoori (1988) developed a fractal aggregation model for

heavy organics deposition which takes into account the dual nature of asphaltene (partly colloidal and partly dissolved) and incorporates the other works presented above. Escobedo and Mansoori developed a model for solid-particle deposition during turbulent flow production operations (Escobedo and Mansoori, 1995). The present report is designed with the purpose of presenting the basic equations in order to predict asphaltene deposition from petroleum fluids. For a detailed review of the deposition mechanisms of asphaltene and other heavy organics present in crude oil, please see Mansoori (1997).

2. Kinetic theory of aggregation of asphaltene

In order to formulate the necessary mathematical model for prediction of phase behavior of heavy organics deposition, there is a need to understand the mechanism of kinetic aggregation of diffusive clusters (flocs/aggregates) of asphaltene particles present in the crude oil. Then, by joining the resulting mechanism with the theory of polydisperse polymers and the crude oil phase behavior algorithm, one will be able to predict heavy organics deposition properties. Most of the past studies on the cluster-cluster aggregation were concerned with its geometrical aspects. Recently, it has been noticed that in addition to the geometrical aspects another important characteristic of the colloidal aggregation model is the existence of a given function for the size distribution of the clusters (flocs/aggregates) of asphaltene particles (Botet and Jullien, 1984). In what follows, we present a kinetic aggregation model which incorporates both the geometrical aspects and the size distribution function. This model is then used for prediction of the phenomena of aggregation of asphaltene particles and deposition of asphaltene from petroleum fluids.

We may consider a system consisting of N_C clusters of N_0 asphaltene particles (identical particles of radius R_0 and unit mass m) which are suspended randomly in oil and are stabilized by resin molecules adsorbed on the surfaces of asphaltene particles. The clusters of asphaltene particles act as Brownian particles which are suspended due to the thermal motions of molecules of the dispersion medium. Variations in composition, temperature or pressure of introduction

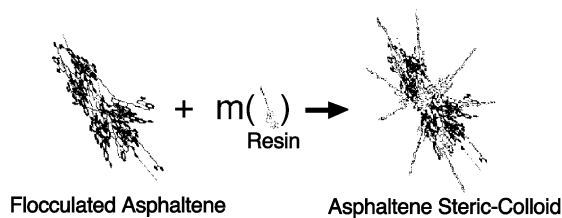
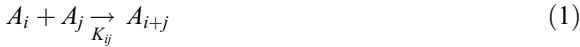


Fig. 3. Steric-colloid formation of asphaltene flocs (random aggregates) in the presence of excess amounts of resins and paraffin hydrocarbons.

of this system may result in a new condition in which the clusters of asphaltene particles would associate/stick to each other. That is, a cluster of mass m_i colliding with a cluster of mass m_j would form a single new cluster of a mass m_{i+j} . This process is then repeated. The kinetics of such an aggregation is assumed to obey the following mechanism.



where A_j is the cluster of mass m_j and K_{ij} is a concentration-independent kinetic (or collision) kernel which describes the aggregation mechanism. This mechanism was originally proposed by Smoluchowski (1916) for coagulation and by Flory (1953) for branched polymerization which, in its continuous form, is given below:

$$\frac{\partial C_k(t)}{\partial t} = (1/2) \int_0^k K(k-x, x) C(x, t) C(k-x, t) dx - C_k(k, t) \int_0^\infty K(k, x) C(x, t) dx \dots \quad (2)$$

where C_k is concentrations of k -cluster ($C_k = n_k/N_0$), n_k is the number of clusters of mass m_k (containing k asphaltene particles of unit mass m) and N_0 is the total number of particles. Eq. (2) constitutes the variation of C_k during aggregation since population of the resulting cluster k ($k=i+j$) increases by all collisions between i -clusters and j -clusters and decreases when a k -cluster combines with another cluster. A major advantage of Smoluchowski's coagulation equation is that many analytic results can be obtained from it. That is, for some forms of K_{ij} , analytic solutions to Smoluchowski's equation can be obtained. In order to apply the above-mentioned aggregation mechanism of clusters to the phenomena of aggregation and deposition of heavy organics, and specially asphaltene, from the petroleum crudes, we are more interested in both kinetic kernels which are proportional to the effective surface areas of clusters. Different investigators (Botet and Jullien, 1984; Jullien et al., 1984; Leyvraz and Tschudi, 1981; Ernst and Hendriks, 1984; Ziff, 1984; Leyvraz, 1984) have tried to improve upon the above mentioned aggregation mechanism by considering the reactivity (kinetic kernels K) of a size k cluster to be

proportional to its effective surface area. Then, depending on whether one uses product or sum kernel, we will have:

$$K_{ij} \sim (s_i \times s_j) \quad (3)$$

or

$$K_{ij} \sim (s_i + s_j) \quad (4)$$

Let us now specify a characteristic radius, R_k , for a cluster of size k . This characteristic radius will be proportional to the size of the cluster. The fractal dimension, D , of cluster is defined through the following expression (Park and Mansoori, 1988):

$$R_k \sim k^{1/D} \quad (5)$$

It should be pointed out that fractal dimension D is less than or equal to Euclidian space dimension, d , because is equal to d when the clusters cover the whole space as the clusters grow. Since the size, k , of a cluster can be expressed in terms of its characteristic radius, R_k , then one can assume s_k to be proportional to k^w :

$$s_k \sim k^w, \quad (6)$$

where w is an exponent (positive or negative) characterizing the cluster surface area. By substituting Eq. (6) into Eqs. (3) and (4), we will get the following equations, respectively:

$$K_{ij} \sim (i \times j)^w \quad (\text{product kernel}) \quad (7)$$

$$K_{ij} \sim (i^w + j^w) \quad (\text{sum kernel}) \quad (8)$$

Exponent w is related to the fractal dimension, D , Euclidian dimension, d , and diffusion walk dimension d_w by the following expression (Botet and Jullien, 1984; Meakin, 1983; Kolb et al., 1983):

$$w = \alpha + (d - d_w)/D \quad \text{for the sum kernel} \quad (9)$$

$$w = \{\alpha + (d - d_w)/D\}/2 \quad \text{for the product kernel}$$

Mansoori (1997) derived the expression of the irreversible growing average mass of clusters of par-

icles, $\langle m_{(t)} \rangle$, which can be shown in the following form:

$$\langle m_{(t)} \rangle \sim t^\gamma; \quad \gamma = 1/\{1 - [\alpha + (d - d_w)/D]\} \quad (10)$$

This concludes the formulation of considering the geometrical aspects of clusters in the expression of kinetic kernels. Using the above equations, Botet and Jullien (1984) have derived the size distribution of clusters which gives us the analytical expression of a “reduced” size distribution of clusters at a given step of the growing aggregation mechanism. The analytic equation for the “reduced” size distribution of clusters of asphaltene molecules can be shown as the following (Park and Mansoori, 1988):

$$F(y; w) = (1 - 2w)^{1-2w} y^{-2w} \exp[-(1 - 2w)y] / \Gamma(1 - 2w) \quad (11)$$

where $y = m_{(t)}/\langle m_{(t)} \rangle$ and Γ is the gamma function. Eq. (11) has the following characteristics. (i) For $w < 0$, the size distribution exhibits a maximum. (ii) For $0 < w < 1/2$, the size distribution is always decreasing. (iii) For $w > 1/2$, the shape of the size distribution function inverts at a finite time, which is known as the signature of the gelation phenomenon (Botet and Jullien, 1984). There are, in general, no such trivial global scaling laws as those considered here and physics before and after gelation must be treated differently.

In petroleum fluids, if the concentration of resin is in excess of the critical resin concentration large asphaltene particles will be fully peptized by resin molecules, thus preventing further clustering (flocculation/aggregation) of clusters (flocs/aggregates) of such particles. This is the case so long as such large asphaltene particles remain completely covered by resin molecules regardless of the changes in the nature of the oil mixture. Addition of a miscible solvent into an oil will cause the amount of resins adsorbed on macromolecular asphaltene surfaces to reduce and cause empty active sites on the surface of macromolecules. This will permit the clusters of large asphaltene particles to cluster further, grow in size, and eventually precipitate. The above discussions indicate that the further clustering driving force of the clusters of large particles should be a function of

concentration of resin in the mixture of oil and a miscible solvent. Thus, the exponent w in Eq. (6), which characterizes the effective surface area of clusters that is available for interaction with other clusters in the process of aggregation and growth of asphaltene aggregates, should depend on the concentration of resin, C_R , in a mixture of stock tank oil and a miscible solvent as in the following functional form:

$$w = w(C_R) \quad (12)$$

Eq. (12) will be utilized in the expressions of the growing average mass of clusters of asphaltene particles and the analytical expression of a “reduced” size distribution of clusters of asphaltene particles. By utilizing Eq. (11) and (12), Eq. (11) also can be written in the following functional form:

$$F(y; C_R) = (1 - 2w)^{1-2w} y^{-2w} \exp[-(1 - 2w)y] / \Gamma(1 - 2w) \quad (13)$$

for the mechanism of irreversible kinetic aggregation of diffusive clusters.

It appears from the above discussions that the concentration of resin is an important factor to describe the mechanism of asphaltene deposition. Utilization of the kinetic aggregation of diffusive clusters has enabled us to relate the concentration of resin in a mixture of an oil and a miscible solvent with the growing size distribution of clusters of asphaltene particles. By using the above equations and the principle of phase equilibrium, one can derive the expressions for predicting the phase behavior of asphaltene particles under the influence of miscible solvents, at various temperatures and pressures as it will be shown in the following sections.

3. Statistical mechanics of asphaltene deposition

The “reduced” growing size distribution of clusters of asphaltene particles, Eq. (13), can be utilized with the statistical mechanical theory of polydisperse polymer solutions and the principle of phase behavior in order to determine the solubility of asphaltene in the solution, the size distributions of asphaltene in the precipitated asphaltene phase and of asphaltene

remaining soluble in a mixture of a petroleum fluid due to changes in pressure, temperature and composition or under the influence of a miscible solvent/blend.

In a heterogeneous polymer mixture, one can specify different fractions of the polymer based on their molecular weights. Assuming that asphaltene behaves as a heterogeneous polymer, one can equate chemical potentials of every asphaltene fraction in the oil phase, μ_y^L , and the asphaltene phase, μ_y^S . This corresponds to the asphaltene remaining soluble in an oil phase in equilibrium with the asphaltene content of a precipitated asphaltene phase.

$$\mu_y^S = \mu_y^L; y = m/\langle m \rangle = M_y/\langle M_A \rangle, 0 < y < \infty \quad (14)$$

The Scott and Magat (1945) statistical mechanical theory of heterogeneous polymer solutions permits calculation of chemical potentials of asphaltene fractions through the following equation:

$$\Delta\mu_y/RT = m\phi_y + 1 - (m_y/\langle m_y \rangle)(1 - \phi_B) - m_y\phi_B + fm_y\phi_B^2 \quad (15)$$

Subscripts y and B refer to the y th fraction of asphaltene and the solvent, respectively. The volume fraction, ϕ , is defined by the volume, V , of a component divided by the total volume, V_{mix} , of a mixture. Therefore:

$$\phi_y = V_y/V_{\text{mix}}, \phi_B = V_B/V_{\text{mix}} \text{ and } (\sum\phi_y) + \phi_B = 1 \quad (16)$$

The segment number of the y fraction of asphaltene, m_y , is defined by the ratio of molar volume, v_y , of the y th fraction of asphaltene over the molar volume, v_B , of a solvent:

$$m_y = v_y/v_B = M_y/(\langle\rho_A^{\text{mass}}\rangle v_B) \quad (17)$$

where $\langle\rho_A^{\text{mass}}\rangle$ is the average mass density of the y th fraction. The segment number of the solvent is unity. The average segment number, $\langle m_y \rangle$, of asphaltene may be defined by:

$$\langle m_y \rangle = \sum x_y m_y \quad (18)$$

where x_y is the mole fraction of the y th fraction of asphaltene with respect to the total asphaltene; i.e., $\sum x_{yi} = 1$. The parameter f in Eq. (15) is defined by:

$$f = 1/r + v_B\{(\delta_A - \delta_B)^2 + 2K_{AB}\delta_A\delta_B\}/RT \quad (19)$$

where r is the coordination number between two successive segments in asphaltene molecules (r has a value between 3 and 4), K_{AB} is the interaction parameter between asphaltene and asphaltene-free oil, δ_A is the average solubility parameter of asphaltene and δ_B is the solubility parameter of asphaltene-free oil. Obviously, it may be assumed that the molecular interaction parameter, between asphaltene and asphaltene-free oil is linearly proportional to the average molecular weight of asphaltene-free oil, $\langle M_B \rangle$.

$$K_{AB} = a + b\langle M_B \rangle \quad (20)$$

Solubility parameter δ is defined by the square root of the molar internal energy change of vaporization, Δu^{vap} , over the molar volume:

$$\delta = (\Delta u^{\text{vap}}/v)^{1/2} \quad (21)$$

By utilizing Eqs. (14) and (15), after simple mathematical manipulations, the following equation can be obtained (Dubey and Waxman, 1995):

$$\phi_y^L/\phi_y^S = \exp(m_y\theta) \quad (22)$$

where

$$\theta = (1/\langle m_y^L \rangle - 1/\langle m_y^S \rangle) + (1 - 1/\langle m_y^L \rangle)\phi_B^L - f^L(\phi_B^L)^2 \quad (23)$$

Eq. (22) is obtained by assuming that the molar volumes in both phases are identical (i.e., $v_y^S = v_y^L = v_y$ and $v_B^S = v_B^L = v_B$, so $m_y^S = m_y^L = m_y$) and the precipitated asphaltene phase is free of the solvent ($\phi_B^S = 0$). The “reduced” growing size distribution of clusters of asphaltene molecules will be joined with Eq. (22) for calculation of the total volume fraction of asphaltene remaining soluble in a mixture in equilibrium with a precipitated asphaltene phase. The “reduced”

growing size distribution of clusters of asphaltene particles due to the change of concentration of resin in a mixture of an oil and a miscible solvent is utilized in order to calculate the total volume fraction of asphaltene remaining soluble in a mixture in equilibrium with a precipitated asphaltene phase. The growing size distribution of clusters of asphaltene particles can be defined as follows:

$$F(y; C_R) = (1/N_A)(dn_y/dy) \\ = (1-w)^{1-w}y^{-w}\exp[-(1-w)y] \\ / \Gamma(1-w) \quad (24)$$

and the normalization condition is:

$$\int_0^\infty F(y; C_R)dy = 1 \quad (25)$$

In Eq. (24), y is the y th fraction of asphaltene, dn_y is the differential of number of moles of the y th fraction of asphaltene whose reduced molecular weight is in the range of y to $y+dy$, N_A is the total number of moles of asphaltene and Γ is the gamma function. The exponent, w , characterizing effective surface area of clusters to interact with each other, may be assumed to have the following functional form:

$$w = w(C_R) = C_1 + C_2(C_R)^{1/2} \quad (26)$$

From Eq. (29), the average molecular weight of asphaltene under the influence of a miscible solvent can be derived in the following form:

$$\langle M(C_R) \rangle = \langle M_{A0} \rangle^{[1-w(C_{R0})]/[1-w(C_R)]} \quad (27)$$

where $\langle M_{A0} \rangle$ is the initial average molecular weight of asphaltene before introducing miscible solvents (i.e., $C_R = C_{R0}$). Then, the molecular weight of the y th fraction of asphaltene can be written as:

$$M_y = y\langle M_A(C_R) \rangle \quad (28)$$

It should be noted here that the segment number, Eq. (17), of the y th fraction of asphaltene, m_y , is a function of the resin concentration in a mixture

because the average molecular weight of asphaltene clusters is growing due to a decrease of resin concentration in the oil phase by, for example, introduction of a light miscible solvent to the oil. Thus:

$$m_y = v_y/v_B = (y\langle M_A(C_R) \rangle)/(\langle \rho_A^{\text{mass}} \rangle v_B) \quad (29)$$

The expression for the average segment numbers of asphaltene in a given phase, Eq. (18), can be defined by using the continuous reduced growing size distribution of clusters of asphaltene particles as the following:

$$\langle m_y \rangle = [1/(\langle \rho_A^{\text{mass}} \rangle v_B)] \int_0^\infty y\langle M_A(C_R) \rangle F(y; C_R)dy \quad (30)$$

Upon partial deposition of asphaltene from a petroleum crude due to the introduction of a miscible solvent, there will be two phases (one liquid and one solid) formed. As a result of the mass balance for the y th fraction of asphaltene between the precipitated asphaltene phase (S) and oil phase (L), one can write:

$$dn_y^T = dn_y^S + dn_y^L \quad (31)$$

$$F(y; C_R)N_A^T = F^S(y; C_R)N_A^S + F^L(y; C_R)N_A^L \quad (32)$$

where

$$dn_y^T = V^T d\phi_y^T/v_y, \quad dn_y^S = V^S d\phi_y^S/v_y,$$

$$dn_y^L = V^L d\phi_y^L/v_y,$$

$$V^T = V^S + V^L; \quad V_A^T = w_{A,T}/\langle \rho_A^{\text{mass}} \rangle$$

where V^T , V^S and V^L are the total volumes of the mixture, precipitated asphaltene phase and the liquid phase, respectively; $w_{A,T}$ is the total weight of asphaltene in the oil and $\langle \rho_A^{\text{mass}} \rangle$ is the mass average density of asphaltene. Eq. (22), which is valid for a given fraction of asphaltene, can be written in the following differential form when considering a differ-

ential fraction of asphaltene in the context of its continuous model:

$$d\phi_y^L/d\phi_y^S = \exp(m_y\theta) \quad (33)$$

By joining Eqs. (24), (24), (31), (32) and (33), the following size distributions of asphaltene, $F^L(y; C_R)$, $F^S(y; C_R)$, in a phase due to the introduction of a miscible solvent can be derived:

$$F^L(y; C_R) = [V^L/\{V^L + V^S \exp(-m_y\theta)\}] \times (N_A^T/N_A^L)F(y; C_R) \quad (34)$$

and

$$F^S(y; C_R) = [V^S/\{V^L \exp(m_y\theta) + V^S\}] \times (N_A^T/N_A^S)F(y; C_R) \quad (35)$$

Since

$$\int F^L(y; C_R)dy = 1 \quad \text{and} \quad \int F^S(y; C_R)dy = 1,$$

then by rearranging Eqs. (34) and (35), one can get:

$$N_A^T/N_A^L = 1 / \int [V^L/\{V^L + V^S \exp(-m_y\theta)\}] \times F(y; C_R)dy \quad (36)$$

and

$$N_A^T/N_A^S = 1 / \int [V^S/\{V^L \exp(m_y\theta) + V^S\}] \times F(y; C_R)dy \quad (37)$$

Using the growing size distribution of clusters of asphaltene particles Eqs. (36) and (37) can be used for calculation of total numbers of moles of asphaltene in the precipitated asphaltene, N_A^S , and liquid, N_A^L , phases. In addition, by substituting Eqs. (34) or (35) into Eq. (30), the expression of the average segment numbers, $\langle m_y^L \rangle$ or $\langle m_y^S \rangle$, in a phase can be obtained. By utilizing Eqs. (24), (31), (32) and (33), the total volume fraction of asphaltene in the liquid phase, ϕ_A^L ,

in equilibrium with the solid phase can be derived in the following form:

$$\phi_A^L = \int d\phi_y^L = \int [yV_A^F/\{V^L + V^S \exp(-m_y\theta)\}] \times F(y; C_R)dy \quad (38)$$

All the terms in the above equation are already defined except for V_A^T which is the total volume of asphaltene in a mixture of oil and miscible solvent ($V_A^T = V^T - \phi_B^L V^L$). Using the above Eq. (38), the onset of asphaltene deposition from a petroleum crude and of asphaltene remaining soluble in a mixture in equilibrium with a precipitated asphaltene phase can be calculated.

Asphaltene clusters associated with resin molecules could well be dominant species which allow the asphaltenes to exist in the colloidal state in a petroleum fluid. The change of the concentration of resin due to the introduction of miscible solvents may result in a system that the clusters of asphaltene particles contact each other, grow in size, and start to flocculate at which the concentration of resin in a particular oil mixture is just enough to keep the clusters of asphaltene particles stabilized in a colloidal state. At the onset of asphaltene deposition, the concentration of resin can be called the critical resin concentration (CRC). It should be noted here that addition of more miscible solvent into stock tank oil will tend to make the concentration of resin in a mixture lower which will result in an aggregation of asphaltene clusters and precipitation from the mixture. This implies that if $C_R < \text{CRC}$ asphaltene flocculation is possible and if $C_R > \text{CRC}$ the amount of miscible solvent scan be calculated without getting into the asphaltene flocculation condition. Since the amount of asphaltene precipitated at the onset of deposition is zero, then the total amount of asphaltene, $w_{A,T}$, can be calculated by knowing the critical resin concentration in the mixture:

$$w_{A,T} = \phi_A [\phi_A^L V^L]_{\text{at CRC}} \quad (39)$$

Knowing the concentration of resins in a particular mixture of stock tank oil and miscible solvent, the total volume fraction of asphaltene in the liquid phase, ϕ_A^L , as given by Eq. (39), can be calculated. Then, the

amount of asphaltene remaining soluble in the liquid phase in equilibrium with the precipitated asphaltene phase will be equal to $\rho_A \phi_A^L V^L$. Therefore, the amount of asphaltene deposition will be given by:

$$w_{A,D} = w_{A,T} - \rho_A \phi_A^L V^L \quad (40)$$

Eq. (40) can be used in conjunction with the growing size distribution function of asphaltene clusters, Eq. (24), for the calculation of the onset and the amount of asphaltene deposition.

4. Results and discussion

The proposed model for prediction of asphaltene deposition from petroleum fluids is based on the fact that asphaltene clusters (flocs/aggregates) are dispersed colloiddally in an oil and peptized due to the resins adsorbed on the surface of asphaltene clusters. Utilization of the kinetic aggregation theory of diffu-

Table 1
Oil A composition

Component	Stock tank oil (CAL) (mol%)	Live oil (EXP) (mol%)
N ₂	0.0001	0.05
CO ₂	0.0015	0.08
CH ₄	0.4581	53.89
C ₂	0.1206	2.76
C ₃	0.2395	1.75
<i>i</i> -C ₄	0.1463	0.45
<i>n</i> -C ₄	0.5033	1.17
<i>i</i> -C ₅	0.3793	0.45
<i>n</i> -C ₅	0.6353	0.63
C ₆	1.4158	0.88
C ₇	5.3281	2.51
C ₈	6.3504	2.66
C ₉	4.6747	1.86
C ₁₀	2.9178	1.14
C ₁₁	3.5286	1.37
C ₁₂₊	73.300	28.35
Total	100.00	100.00
MW	438.18	
Density (lb/ft ³)	43.731	
T _c (°F)	329.12	
P _c (psia)	172.14	
Acentric factor	0.88656	

EXP: experimental values; CAL: calculated values.

Table 2

Comparison of experimental vs. calculated bubble point pressures of live Oil A

Temperature (°F)	Saturation pressure (psig)	
	Experiment	Calculated
70	3200.0	3201.7
131	3734.0	3733.7
149	3848.7	3842.2
158	3855.0	3866.1
176	3902.0	3897.0
194	3917.0	3918.1

sive clusters of asphaltene particles has enabled us to relate the change of resin concentration in a petroleum fluid due to changes of its composition, temperature and pressure with the growing size distribution function of asphaltene clusters. This implies that the change of resin concentration in an oil due to changes of composition, temperature and pressure plays an important role on the effect of the growing size distribution of asphaltene clusters.

In order to illustrate the application of the present model for prediction of heavy organics deposition, it is first necessary to tune the model to the petroleum fluid vapor–liquid phase behavior data and low pressure heavy organics deposition titrations due to addition of various paraffin hydrocarbon miscible solvents. In all the calculations reported here, it is assumed there is no asphaltene present in the gas phase, and that there is no effect by asphaltene content of the liquid phase on the vapor–liquid equilibrium of mixtures of miscible gas and stock tank oil. However other heavy organics, including wax, resin, diamondoids, etc., could be present in gas, liquid and solid phases. The newly developed phase behavior prediction algorithm developed by Manafi et al. (1999) is used to perform vapor–liquid phase behavior calculation, including the flash calculations from which compositions of liquid mixture leaving the flash tank are calculated.

The experimental composition and phase behavior data received from a pvt lab for a particular Brazilian petroleum fluid (Oil A) are reported in Tables 1–3. To produce this data the usual pvt laboratory techniques were employed. In Table 1, the experimental live crude composition under study as well as calculated stock tank oil composition at 60 °F and 1 atm for a petroleum fluid (Oil A) are reported. Using the

Table 3
Differential liberation test data and prediction of live Oil A at 149 °F

P [lb/ft ²]	3527		2647	
	Experimental	Predicted	Experimental	Predicted
CH ₄ composition	95.11	93.90	95.15	94.00
MW	17.328	18.100	17.260	17.9
Specific gravity (with respect to air)	0.598	0.624	0.596	0.617

algorithm proposed by Manafi et al. (1999) and the experimental live crude data of Tables 1 and 2, the calculated results reported in Tables 1–3 are produced. Table 2 shows the comparison between the experimental and calculated bubble point data for the live oil. The results of differential liberation study of live oil at 149 °F and two different pressures of 3527 and 2647 lb/ft² are reported in Table 3. According to Tables 2 and 3 the predictions by Manafi et al. (1999) model are in very good agreement with the experimental data.

The parameters of the proposed model (a , b , $\langle M_B \rangle$, r) need to be tuned to some deposition titration data. The easiest way of producing the necessary deposition titration data is to use the stock tank oil and titrate it

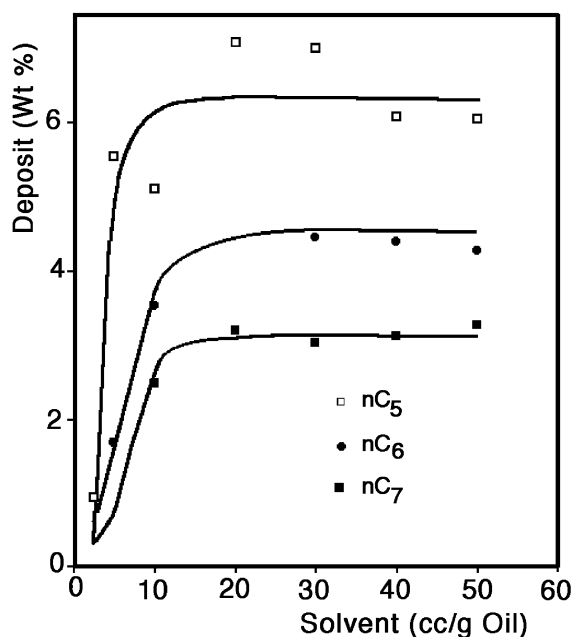


Fig. 4. Comparison of low pressure (stock tank Oil A) deposition data with the model calculations due to the addition of *n*-pentane, *n*-hexane and *n*-heptane as miscible solvents.

with the addition of a number of paraffin hydrocarbons at various concentrations and measure the amount of heavy organics deposits generated according to modified IP 143 standard procedure (Vazquez et al., 1998; Vasquez and Mansoori, 2000) using various aliphatic solvents (*n*-pentane, *n*-hexane, *n*-heptane, etc.). There exist also accurate techniques of detection of the onset of asphaltene precipitation (Kim et al., 1990) and flocculation (Escobedo and Mansoori, 1997) which may be used for additional characterization of asphaltene phase transitions.

In Fig. 4, we report such data for the stock tank oil of Oil A under study using *n*-pentane, *n*-hexane and *n*-heptane as the precipitating miscible solvents. The lines reported in this figure are the results of correlation/tuning of the model to the experimental data. The parameters calculated by tuning the model to this data were found to be $a = -12.91356 \times 10^{-3}$, $b = 3.40384 \times 10^{-5}$, $r = 3.5$. Other properties of the system which are then calculated are the total asphaltene in the live oil $w_{A,T} = 7.31$, the asphaltene average molecular weight $\langle M_A \rangle = 5800$ and the asphaltene distribution variance $\eta = 7.416$. The experimental titration data for *n*-pentane, *n*-hexane and *n*-heptane reported in Fig. 4 are in good agreement with the tuned model.

In order to test the accuracy of the proposed model for predictions of the onset pressure of deposition of heavy organics in a petroleum fluid at various temperatures Table 4 is reported in which the pressures at which the onset of heavy organics depositions are visually observed in a high pressure cell are compared

Table 4
Onset of heavy organics depositions in the live Oil A at various temperatures and pressures

T (°F)	Experimental P (psig)	Predicted P (psig)
158	no deposit observed	no deposit predicted
176	4200	3900
194	4500	3950

with the results of the predictions by the present model. Considering that visual observation of the onset of deposition in dark live crude at high pressure is rather difficult, one may safely assume that the observations reported are at a stage later than the onset of deposition. As a result the predictions, which indicate onsets at lower pressures than visual, experimental, data, are considered quite satisfactory and in good agreement with the experimental data. The proposed model can be applied for predictions of the deposition region of heavy organics in a petroleum fluid at various pressures and temperatures. In Fig. 5, we report the predictions by the present models for the phase behavior and heavy organics deposition envelopes of the live oil at various temperatures and pressures. According to this figure, asphaltene deposition occurs in the liquid phase. The fact that asphaltene deposition could occur in the liquid phase at various temperatures and pressures is well known. Of course, the composition of the petroleum fluid at pressures above the bubble point is constant, but one can argue that the level of polarity of the petroleum fluid is a function of temperature while the solubility of resin in petroleum fluid is a function of its density. As a result at various temperatures and pressures, these two variables (which are effective on the asphaltene deposition) will vary and, as a result,

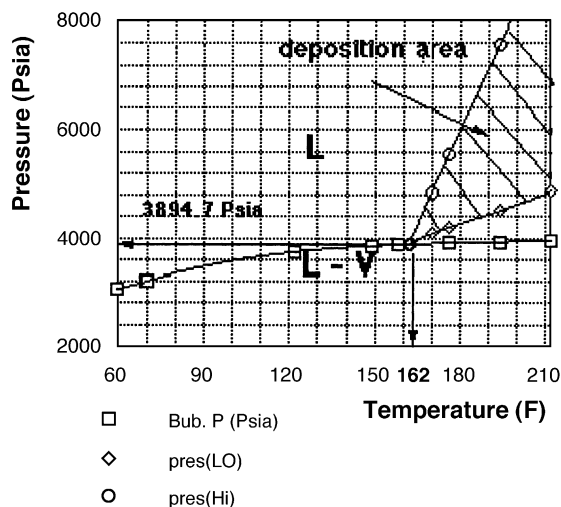


Fig. 5. Heavy organics deposition envelope for Oil A which contains lower and upper pressure bounds of deposition region at different temperatures and pressures.

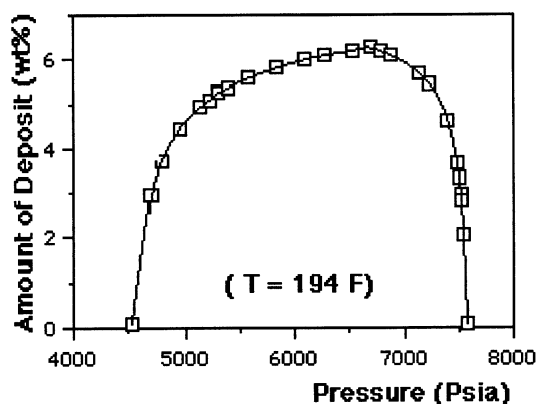


Fig. 6. The pressure dependence of the amount of heavy organics deposition for live Oil A at $T = 194\text{ }^{\circ}\text{F}$.

asphaltene deposition will be a function of temperature and pressure in the liquid state.

In Fig. 5, the hatched area of the asphaltene deposition envelop is a result of calculation by the model. The hatched shape must not be interpreted implying that at higher pressures asphaltene will redissolve considering that the modeling presented here is not a reversible model, but an irreversible one.

Fig. 6 shows the pressure dependence of the amount of heavy organics deposition for live Oil A at $T = 194\text{ }^{\circ}\text{F}$ as calculated by this model. Fig. 7 shows predicted trends of amount of asphaltene deposited

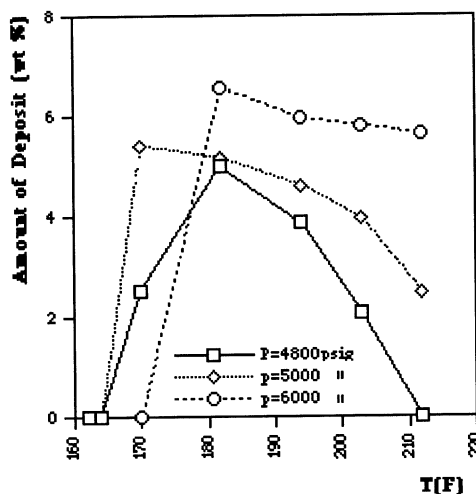


Fig. 7. Predicted trends of amount of asphaltene deposited from live Oil A as the temperature and pressure change.

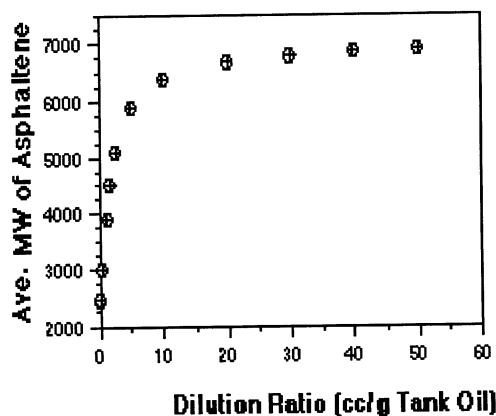


Fig. 8. Predicted growing average molecular weight of asphaltene flocs/aggregates as a function of dilution ratio (the volume of *n*-C₅ precipitating solvent added per gram of Oil A).

from live Oil A as the temperature and pressure change. Fig. 8 shows the growing average molecular weight of asphaltene clusters (flocs/aggregates) as the volume of *n*-C₅ precipitating solvent added increases. This tendency can be explained by the effect of resin concentration on the growing size of asphaltene clusters (flocs/aggregates). This is because the effective surface area of asphaltene clusters for further clustering and growing in size depends on resin concentrations. Fig. 9 shows the results of calculation for the molecular weight distribution of asphaltene in the original live oil. In Fig. 10, the results of calculations for the molecular weight distribution of the heavy organics precipitated from the crude oil due to addition of *n*-C₅ is reported.

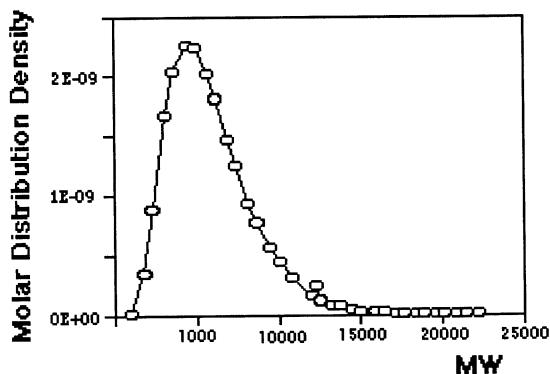


Fig. 9. Molecular weight distribution of asphaltene in the live crude Oil A.

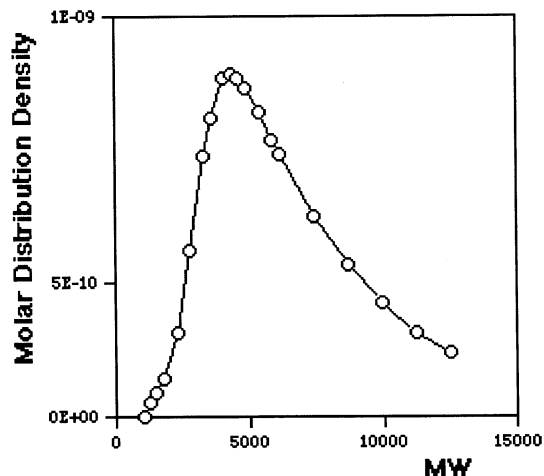


Fig. 10. Predicted size distribution of asphaltene precipitated from the crude Oil A due to addition of *n*-C₅.

The experimental composition data for stock tank oil and live oil received from a pvt lab for another particular petroleum fluid (Oil B) are reported in Table 5. In Table 6, we report deposition titration data for the stock tank Oil B under study using *n*-pentane, *n*-

Table 5
Oil B composition

Component	Stock tank oil (EXP) (mol%)	Live oil (EXP) (mol%)
N ₂	0.000	0.00
CO ₂	0.000	0.59
Methane	0.000	40.61
Ethane	0.000	7.22
Propane	0.000	5.09
Butane	0.033	2.30
<i>i</i> -Butane	0.003	
<i>n</i> -Butane	0.030	
Pentane	0.261	0.83
<i>i</i> -Pentane	0.086	
<i>n</i> -Pentane	0.175	
C ₆ -C ₇	5.685	2.93
C ₈ -C ₁₀	23.432	10.14
C ₁₁ -C ₁₄	21.823	9.36
C ₁₅ -C ₁₉	19.383	8.32
C ₂₀ -C ₂₉	18.017	7.73
C ₃₀ +	11.366	4.88
Total	100.00	100.00
MW	254.03	122.6
Bubble point	Pressure at 160 °F	2754 psia

EXP: experimental values.

Table 6

The experiment vs. prediction of amounts of heavy organics deposition from stock tank Oil B

Dilution ratio (cc diluent/g tank oil)	<i>n</i> -C5		<i>n</i> -C7		<i>n</i> -C10	
	EXP	CAL	EXP	CAL	EXP	CAL
5.0	13.80	13.80	4.06	4.00	1.60	1.59
10.0	14.60	14.75	8.10	8.20	2.40	2.49
15.0	14.95	14.89	8.90	8.69	2.45	2.39

Absolute average deviation (AAD)=3.8%. EXP: experimental values; CAL: calculated values.

heptane and *n*-decane as the precipitating miscible solvents. The calculations results reported in this table are a result of tuning of the model to the experimental data. The parameters calculated by tuning the model to this data were found to be $a = -3.7942 \times 10^{-3}$, $b = 1.5105 \times 10^{-5}$, $r = 3.5$. Other properties of the system which are then calculated are the total asphaltene in the live oil $w_{A,T} = 15.98$, the asphaltene average molecular weight (M_A) = 5589, and the asphaltene distribution variance $\eta = 8.73$. The experimental titration data *n*-pentane, *n*-heptane and *n*-decane reported in Table 5 are in good agreement with the tuned model.

In order to test the accuracy of the proposed model for predictions of the onset of deposition of heavy organics in petroleum fluid at various temperatures, Table 7 is reported in which the pressure, temperature and solvent composition at which the onset of heavy organics depositions are accurately measured in a high pressure cell are compared with the results of the

Table 7

The experiment vs. prediction of onset of heavy organics deposition from stock tank Oil B

Solvent	<i>P</i> (psig)	<i>T</i> (°F)	EXP	CAL
<i>n</i> -C ₃	1000.0	160.0	1.86	1.87
	2000.0	160.0	1.84	1.79
<i>n</i> -C ₄	200.0	160.0	1.89	2.02
	1000.0	160.0	2.02	2.51
	2000.0	160.0	2.04	2.32
	1000.0	75.0	2.7	1.75
<i>n</i> -C ₅	700.0	160.0	2.55	2.39
	1000.0	160.0	2.80	2.91
	2000.0	160.0	2.57	2.45
	0.0	75.0	1.64	0.95
<i>n</i> -C ₈	40.0	160.0	1.74	1.75
	1000.0	160.0	1.97	1.78
	2000.0	160.0	1.91	1.50
	1000.0	160.0	1.91	1.95
<i>n</i> -C ₁₂	1000.0	160.0	1.97	1.14

Table 8

The experiment vs. prediction of amounts of heavy organics deposition from stock tank Oil B

Dilution ratio (cc solvent/g tank oil)	Solvent	<i>P</i> (psig)	<i>T</i> (°F)	EXP	CAL
35.0	<i>n</i> -C ₃	150.0	160.0	1.86	1.87
35.0		3000.0	160.0	19.01	21.05
35.0	<i>n</i> -C ₄	40.0	75.0	18.11	18.61
35.0		3000.0	160.0	15.72	16.71
35.0	<i>n</i> -C ₅	0.0	75.0	14.52	14.53
35.0		3000.0	160.0	13.44	13.06
35.0	<i>n</i> -C ₈	0.0	75.0	10.55	10.89
35.0		<i>n</i> -C ₁₂	0.0	75.0	8.96

EXP: experimental values; CAL: calculated values.

predictions by the present model. The predictions reported in this table are in good agreement with the experimental data. Another set of experimental data available to us for Oil B are the experimental amounts of heavy organic deposits at various temperatures and pressures as a result of addition of various precipitating solvents (*n*-C₃, *n*-C₄, *n*-C₅, *n*-C₈, *n*-C₁₂) to stock tank Oil B as reported in Table 8. According to this table also, the predictions by the present model are in good agreement with the experimental data.

As it is shown above, the proposed model is capable of predicting the flocculation and collapse of asphaltene from petroleum systems. It must be pointed out that the availability of appropriate deposition characterization data is very important in the accuracy of prediction of the model. This is because with the deposition data we can tune the parameters of the model. Since the model is theoretically accurate and parameters of the model have, all, physical meaning, the theory is applicable for extrapolations to the ranges of pressure, temperature and compositions where experimental data are not available. That is what is demonstrated in this research paper.

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