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# STATISTICAL MECHANICS AND KINETICS MODELING OF ORGANICS DEPOSITION FROM PETROLEUM FLUIDS

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## ABSTRACT

Deposition of complex and heavy organic compounds which exist in petroleum crude 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 organic deposition 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 under the influence of miscible solvents. As an example the present model is applied

for heavy organics deposition prediction of a particular crude oil for which experimental multi-phase behavior data are available. It is shown that the prediction results of the present model are in very good agreement with the experimental data.

## INTRODUCTION

Organic deposition during petroleum and heavy oil production and processing is a very 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 sludges after shutting in a well temporarily and/or after stimulation treatment by acid has resulted in partial or complete plugging of the well [1,2]. The downtime, cleaning, and maintenance costs are a sizable 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 asphaltic 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.

The parameters that govern precipitation of heavy organic substances appear to be compositions of crude and injection (or blending) fluid, pressure and temperature. With alterations in these parameters the nature of heavy organic substances which precipitate will vary. Also, it is a proven fact that the precipitation of asphaltene is generally followed with polymerization, or flocculation, of the resulting precipitate, which produces an insoluble material in the petroleum fluid which will also contain other heavy organics and mineral deposits [3-7].

Over the last six decades a number of investigators have researched the nature of heavy organics and mechanism of the organics deposition. There has been extensive progress made in the past several years in the formulation of accurate vapor-liquid phase behavior prediction of complex petroleum fluids [8], statistical mechanics of polydisperse polymer solutions [9] and kinetic theory of aggregation and precipitation [10]. Because of the complexity of the nature of heavy organic substances the phenomena of the organic deposition are not well understood. Also 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.

The concept that heavy organic compounds are present as a colloidal system is credited to Nellensteyn [11]. He proposed that asphaltic compounds were made of flocs or aggregates (he mistakenly called that micelles) 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. Swanson [12] and Witherspoon and Munir [13] proposed that resins were required for asphaltene (flocs or aggregates) to dissolve in distillate portion of a crude oil. According to Dickie and Yen [14] petroleum resins provide a transition between the polar (asphaltene) and the relatively

non-polar (oil) fractions in petroleum thus preventing the assembly of polar flocs / aggregates that would be non-dispersible in the oil. Leontaritis and Mansoori [15] proposed a thermodynamic-colloidal model which is capable of predicting the onset of asphaltene flocculation. According to their model asphaltenes exist in the oil as solid particles in colloidal suspension, stabilized by resins adsorbed on their surface. Kawanaka, Park and Mansoori proposed a continuous thermodynamics model for asphaltene solubility in petroleum fluids [16]. Also Park and Mansoori developed a fractal aggregations model for heavy organics deposition [17] For a detailed review of the mechanisms of asphaltene and other heavy organics present in crude oil please see ref. [18].

The present report is designed with the purpose of applying modern theoretical and experimental techniques of statistical mechanics, kinetics and phase behavior to develop the methods that will predict organic deposition during the production and processing of petroleum fluids.

## **KINETIC THEORY OF AGGREGATION OF HEAVY ORGANICS**

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 [19]. In what follows we have developed 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 an 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. Introduction of a miscible solvent into this system may result in a new condition in which the clusters of asphaltene particles would stick rigidly 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 [10] for coagulation and by Flory [20] and Stockmayer [21] for branched polymerization.

The rate of aggregation,  $R_{ij}$ , at which an  $i$ -cluster of a given mass  $m_i$  and a  $j$ -cluster of a given mass  $m_j$  may come into contact with each other and form an  $(i+j)$  cluster is given by

$$R_{ij} = K_{ij} C_i C_j; \quad C_i = n_i / N_0$$

where  $n_i$  is the number of clusters of mass  $m_i$  (containing  $i$  asphaltene particles of unit mass  $m$ ) and  $N_0$  is the total number of particles. Since the 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, then  $C_k(t)$  will satisfy

$$\frac{\partial C_k(t)}{\partial t} = (1/2) \sum_{j=1}^{k-1} K_{k-j,j} C_{k-j}(t) C_j(t) - C_k(t) \sum_{j=1}^{\infty} K_{k,j} C_j(t) \quad (2)$$

This expression is known as Smoluchowski's coagulation equation. The continuous version of Smoluchowski's coagulation equation can be written in the following form :

$$\frac{\partial C_k(t)}{\partial t} = (1/2) \int_0^k K(k-x,x) C(x,t) C(k-x,t) dx - C_k(t) \int_0^{\infty} K(k,x) C(x,t) dx \quad (3)$$

This equation is invariant under a semi-group of similarity transformation [22]. This will be discussed

later. 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. For example, when the reactivity of a cluster is independent of (or proportional to) the size of the reacting clusters (i.e.,  $K_{ij}=1$ ,  $i+j$ , or  $iX_j$ ) then the complete time-dependent analytic solutions of  $C_k(t)$  can be obtained. In recent years different investigators [19,22-27] have tried to improve upon the above mentioned aggregation mechanism by considering the reactivity of a size  $k$  cluster to be proportional to its effective surface area,  $s_k$ , ( $K_s \sim s_k$ ). Then depending on whether we use product or sum kernel we will have

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

or

$$K_{ij} \sim (s_i + s_j) \quad (5)$$

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 [17]

$$R_k \sim k^{1/D} \quad (6)$$

It should be pointed out that fractal dimension  $D$  is less than or equal to Euclidian space dimension  $d$  because  $D$  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  $k^w$ ,

$$s_k \sim k^w, \quad (7)$$

where  $w$  is an exponent (positive or negative) characterizing the cluster surface area. Exponent  $w$  is related to the fractal dimension,  $D$ , as it will be shown later. By replacing Eq. (7) in Eq.'s (4) and (5) we will get the following equations, respectively,

$$K_{ij} \sim (ij)^w \quad (\text{product kernel}) \quad (8)$$

$$K_{ij} \sim (i^w + j^w) \quad (\text{sum kernel}) \quad (9)$$

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 Eq.'s (8) and (9) which are proportional to the effective surface areas of clusters. This will be discussed later in the following sections. Consider a system composed of a number of kinetically growing clusters, in which a cluster of size  $k$ , before sticking to another cluster, diffuses randomly in space of Euclidian dimension,  $d$ , along a trajectory of the dimension of diffusion walk  $d_w$  (where  $d \geq d_w$ ). The volume,  $V_0$ , of a system can be defined as in the following expression.

$$V_0 = l_0^d \quad (10)$$

where  $l_0$  is the length of the lattice. Let us also assume that the kinetically growing cluster of size  $k$  has a surface diffusion velocity  $v_k$ .

$$v_k = l^{d_w} / t \quad (11)$$

where  $l$  is the "walk-length" which is the average distance between clusters and  $t$  is the walk time. It can be assumed that this diffusion velocity is inversely proportional to the diffusing cluster size,

$$v_k \sim k^\alpha \quad (12)$$

where  $\alpha$  is a negative exponent. A cluster of size  $k$  can be assumed to contain  $k$  identical particles of unit mass. Now using Eq. (12) we can conclude that the velocity of every cluster is inversely proportional to its mass.

$$v_k \sim m^\alpha \quad (13)$$

Following the work of Botet and Jullien [19] let us now demonstrate how the exponent,  $w$ , characterizing the surface area in the expression of kinetic kernel, Eq.'s (8) and (9), can be expressed in terms of other characteristic constants of the system ( $d, d_w, \alpha$ , and  $D$ ). By combining Eq's (11) and (12) it can be shown that the time  $t$  necessary for a cluster of size  $k$  having a walk-length  $l$  is given by the following

$$t \sim l^{d_w} k^{-\alpha} \quad (14)$$

In terms of a characteristic radius, Eq. (6), of the cluster Equation (14) becomes

$$t \sim l^{d_w} R_k^{-D\alpha} \quad (15)$$

Since Equation (3) is invariant under a semi-group of similarity transformation let us perform a change of length scale in the whole system, such that each length is rescaled by a factor of  $b$ :

$$\frac{l}{l'} = \frac{l_0}{l_0'} = \frac{R_k}{R_k'} = b \quad (16)$$

The corresponding rescaling of time (from  $t$  to  $t'$ ) will be

$$t \sim b^{d_w - D\alpha} t' \quad (17)$$

Considering that Smoluchowski equation, Eq. (3), is scale-invariant, the  $K_{ij}$ , which has the dimension of a volume divided by time, must be rescaled as,

$$\frac{K_{ij}}{(K_{ij})'} = \frac{\frac{V_0}{t}}{\frac{V_0'}{t'}} = \frac{\frac{l_0^d}{t}}{\frac{l_0'^d}{t'}} = b^{d - d_w + D\alpha} \quad (18)$$

For convenience we may redefine parameter  $b = \lambda^{1/D}$ . As a result the general scaling relation of coagulation kernels, Eq. (18), can be written as

$$K_{\lambda, \lambda} = \lambda^n K_{ij} \quad (19)$$

where  $K_{\lambda, \lambda}$  is the new notation for the transformed coagulation kernel  $K'_{ij}$  and

$$n = (d - d_w) / D + \alpha \quad (20)$$

The reason for writing the transformed coagulation kernel in the form of Eq. (3) is to demonstrate that it is a homogeneous function of degree  $n$ . By referring to Eq.'s (4) and (5) it can be concluded that when  $n=2w$  the product kernel is used and when  $n=w$  the sum kernel is used (Ernst and Hendrick [25]):

$$\begin{aligned} w = \alpha + (d - d_w) / D & \quad \text{for the sum kernel} \\ w = \{\alpha + (d - d_w) / D\} / 2 & \quad \text{for the product kernel} \end{aligned} \quad (21)$$

This concludes the formulation of considering the geometrical aspects of clusters in the expression of kinetic kernels. The fractal dimension,  $D$ , as defined by Eq. (6) for a kinetic clustering phenomena can be determined with the use of two related measures characterizing the clusters:

1. The characteristic radius,  $R$ , of a cluster can be determined as a function of the number,  $N$ , of particles in that cluster using the definition of fractal dimension as given by Eq. (6):

$$R \sim N^{1/D} \text{ or } N \sim R^D, \quad (22)$$

where  $D \leq d$ . A growing cluster is called "compact" when  $D=d$  and it is called "ramified" when  $D < d$ .

2. Inside a growing cluster, the density correlation function,  $C(\vec{r})$ , of a cluster can be defined as the configurational average of local density,  $\rho(\vec{r})$ , over all values (directions and distances from center) of  $\vec{r}$ :

$$C(\vec{r}) = \langle \rho(\vec{r}) \rangle \quad (23)$$

where  $\rho(\vec{r}) = 0$  or  $1$  at any location,  $\vec{r}$ , inside of the cluster, i.e.,  $r \leq R$ . Since  $N \sim R^D$  which is shown in Eq. (22), the mean density of a cluster,  $\langle \rho \rangle_c$ , can be written as the following.

$$\langle \rho(\vec{r}) \rangle_c \sim N / R^d \sim R^{D-d} \quad (24)$$

Similarly the density correlation function,  $C(\vec{r})$ , inside the cluster can be written as

$$C(\vec{r}) = \langle \rho(\vec{r}) \rangle \sim r^{D-d} \quad (25)$$

By utilizing Eq's. (22-25) the fractal dimension of growing clusters can be obtained through numerical simulations [28,29] or experimental measurements (Allain and Jouhier [30]). Then using Eq. (22) from the slope of the radius versus mass (on a log-log plot) the fractal dimension of clusters can be derived.

#### EFFECT OF RESIN CONCENTRATION ON THE KINETICS OF GROWING ASPHALTENE CLUSTERS

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 (floculation / 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 a mixture of stock tank oil and a miscible solvent. Thus the exponent  $w$  in Eq. (7) 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 :

$$w = w(C_R) \quad (26)$$

Eq. (26) 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. This will be discussed in the following. Since the asphaltene cluster of size  $k$  can be assumed to contain  $k$  identical particles of unit mass, Eq. (14) can be written in the following form.

$$t \sim t^{d_w} m^{-\alpha} \quad (27)$$

From Eq. (27), the dynamical behavior with respect to time for the asphaltene cluster of mass  $m$  can be written in the following power law form.

$$m(t) \sim t^\gamma \quad (28)$$

where  $\gamma$  is an exponent. The dynamical behavior of average mass of clusters of asphaltene particles with respect to time can be expressed in terms of the fractal dimension  $D$  in Eq. (6) and the exponent  $\alpha$  in Eq. (12) of the diffusion velocity of the growing clusters. Through the mean field scaling argument,

## PHASE BEHAVIOR CALCULATION

Botet and Jullien [19] derived the expression of the growing average mass of clusters of asphaltene particles,  $\langle m(t) \rangle$ , which can be shown in the following form.

$$\langle m(t) \rangle \sim t^\gamma; \quad \gamma = 1 / \{1 - [\alpha + (d - d_w) / D]\} \quad (29)$$

By utilizing Eq.'s (21) and (26), Eq. (29) also can be written in the following functional form.

$$\langle m(t) \rangle \sim t^\gamma; \quad \gamma = \gamma(w; C_R) \quad (30)$$

For the mechanism of irreversible kinetic aggregation of diffusive clusters, Botet and Jullien 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 [17]

$$F(y; C_R) = (1-2w)^{1-2w} y^{-2w} \exp[-(1-2w)y] / \Gamma(1-2w) \quad (31)$$

where  $y = m / \langle m \rangle$  and  $w = w(C_R)$  as shown in Eq. (26). Eq. (31) have 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 [19]). There are, in general, no such trivial global scaling laws as those considered here and physics before and after gelation must be treated differently.

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 stock tank 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 equilibria, 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.

The "reduced" growing size distribution of clusters of asphaltene particles, Eq. (31), 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,  $\mu_y^L$ , and the asphaltene phase,  $\mu_y^S$ . This corresponds to the asphaltene remaining soluble in an oil phase in equilibrium with the asphaltene content of a precipitated asphaltene phase.

$$\mu_y^S = \mu_y^L; \quad y = m / \langle m \rangle = M_y / \langle M_A \rangle, \quad 0 < y < \infty \quad (33)$$

The Scott and Magat statistical mechanical theory of heterogeneous polymer solutions [9] permits calculation of chemical potentials of asphaltene fractions through the following equation:

$$\Delta \mu_y / RT = \ln \phi_y + 1 - (m_y / \langle m_y \rangle) (1 - \phi_B) - m_y \phi_B + f m_y \phi_B^2 \quad (34)$$

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

$$\phi_y = V_y / V_{\text{mix}}, \quad \phi_B = V_B / V_{\text{mix}}, \quad \text{and} \quad (\sum \phi_y) + \phi_B = 1 \quad (35)$$

The segment number of the  $y$  fraction of asphaltene,  $m_y$ , is defined by the ratio of molar volume,  $v_y$ , of the  $y^{\text{th}}$  fraction of asphaltene over the molar volume,  $v_B$ , of a solvent,

$$m_y = v_y / v_B = M_y / (\langle \rho_A^{\text{mass}} \rangle v_B) \quad (36)$$

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

$$\langle m_y \rangle = \sum x_y m_y \quad (37)$$

where  $x_y$  is the mole fraction of the  $y^{\text{th}}$  fraction of asphaltene with respect to the total asphaltene; i.e.,  $\sum x_y = 1$ . The parameter  $f$  in Eq. (34) is defined by (see Appendix A)

$$f = 1/r + v_B \{ (\delta_A - \delta_B)^2 + 2 K_{AB} \delta_A \delta_B \} / RT \quad (38)$$

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,  $\delta_A$  is the average solubility parameter of asphaltene, and  $\delta_B$  is the solubility parameter of asphaltene-free oil. 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,  $\langle M_B \rangle$ ;

$$K_{AB} = a + b \langle M_B \rangle \quad (39)$$

Solubility parameter  $\delta$  is defined by the square root of the molar internal energy change of vaporization,  $\Delta u^{\text{vap}}$ , over the molar volume;

$$\delta = (\Delta u^{\text{vap}}/V)^{1/2} \quad (40)$$

By utilizing Eq.'s (33) and (34), after simple mathematical manipulations, the following equation can be obtained [17]

$$\phi_y^L / \phi_y^S = \exp(m_y \theta) \quad (41)$$

where

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

This 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. (41) 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 stock tank 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

$$F(y; C_R) = (1/N_A) (dn_y / dy) \\ = (1-w)^{1-w} y^{-w} \exp[-(1-w)y] / \Gamma(1-w) \quad (42)$$

and the normalization condition is

$$\int_0^{\infty} F(y; C_R) dy = 1 \quad (43)$$

In the above Eq. (42),  $y$  is the  $y^{\text{th}}$  fraction of asphaltene,  $dn_y$  is the differential of number of moles of the  $y^{\text{th}}$  fraction of asphaltene whose reduced molecular weight is in the range of  $y$  to  $y+dy$ , and  $N_A$  is the total number of moles of asphaltene. This reduced growing size distribution of clusters of asphaltene particles is valid for all  $x$  except when  $x$  is close to zero. This distribution function shows, for  $w < 0$ , a unique maximum at

$$y_{\text{max}} = -w/(1-w) \quad (44)$$

The exponent,  $w$ , characterizing effective surface area of clusters to interact with each other, may be assumed to have the following functional form :

$$w = w(C_R) = C_1 + C_2 \sqrt{C_R} \quad (45)$$

From Eq. (30), the average molecular weight of asphaltene under the influence of a miscible solvent can be derived in the following form:

$$\langle M_A(C_R) \rangle = \langle M_{A0} \rangle \frac{1-w(C_{R0})}{1-w(C_R)} \quad (46)$$

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  $y^{\text{th}}$  fraction of asphaltene can be written as

$$M_y = y \langle M_A(C_R) \rangle \quad (47)$$

It should be noted here that the segment number [Eq. (21)] of the  $y^{\text{th}}$  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 the introduction of miscible solvents. Thus,

$$m_y = v_y/v_B = (y \langle M_A(C_R) \rangle) / (\langle \rho_A^{\text{mass}} \rangle v_B) \quad (48)$$

The expression for the average segment numbers of asphaltene in a given phase, Eq. (37), can be defined by using the continuous reduced growing size distribution of clusters of asphaltene particles as the following:

$$\langle m_y \rangle = [1/(\langle \rho_A^{\text{mass}} \rangle v_B)] \int_0^1 y \langle M_A(C_R) \rangle F(y;C_R) dy \quad (49)$$

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  $y^{\text{th}}$  fraction of asphaltene between the precipitated asphaltene phase (S) and oil phase (L) one can write

$$dn_y^T = dn_y^S + dn_y^L \quad (50)$$

$$F(y;C_R)N_A^T = F^S(y;C_R)N_A^S + F^L(y;C_R)N_A^L \quad (51)$$

where

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

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

$V^T$ ,  $V^S$  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. (41), which is valid for a given fraction

of asphaltene, can be written in the following differential form when considering a differential fraction of asphaltene in the context of its continuous model

$$d\phi_y^L / d\phi_y^S = \exp(m_y \theta) \quad (52)$$

By joining Eq.'s (42), (50), (51), and (52) 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;

$$F^L(y;C_R) = [V^L / (V^L + V^S \exp(-m_y \theta))] (N_A^T / N_A^L) F(y;C_R) \quad (53)$$

and

$$F^S(y;C_R) = [V^S / (V^L \exp(m_y \theta) + V^S)] (N_A^T / N_A^S) F(y;C_R) \quad (54)$$

$$\text{Since } \int_0^1 F^L(y;C_R) dy = 1 \text{ and } \int_0^1 F^S(y;C_R) dy = 1,$$

then by rearranging Eq.'s (53) and (54) one can get

$$N_A^T / N_A^L = 1 / \int_0^1 [V^L / (V^L + V^S \exp(-m_y \theta))] F(y;C_R) dy \quad (55)$$

and

$$N_A^T / N_A^S = 1 / \int_0^1 [V^S / (V^L \exp(m_y \theta) + V^S)] F(y;C_R) dy \quad (56)$$

Using the growing size distribution of clusters of asphaltene particles Eq.'s (55) and (56) 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. Also by substituting Eq.'s (53) or (54) into Eq. (49), 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 Eq.'s (42), (50), (51), and (52) the total volume fraction of asphaltene in the liquid phase,  $\phi_A^L$ , in equilibrium with the solid phase can be derived in the following form:

$$\phi_A^L = \int_0^1 d\phi_y^L = \int_0^1 [y V_A^L / (V^L + V^S \exp(-m_y \theta))] F(y;C_R) dy \quad (57)$$

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 stock tank oil and miscible solvent ( $V_A^T = V^T - \phi_B^L V^L$ ). Using the above Eq. (57), the onset of asphaltene deposition from a petroleum



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 precipitate from the mixture. This implies that if  $C_R < CRC$  asphaltene flocculation is possible and if  $C_R > CRC$  the amount of miscible solvents can 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,

$$w_{A,T} = \phi_A [\phi_A^L V^L] \text{ at CRC} \quad (58)$$

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,  $\phi_A^L$ , as given by Eq. (58), 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

$$w_{A,D} = w_{A,T} - \rho_A \phi_A^L V^L \quad (59)$$

Eq. (59) can be used in conjunction with the growing size distribution function of asphaltene clusters [Eq. (42)] for the calculation of the onset and the amount of asphaltene deposition.

## RESULTS AND DISCUSSION

The proposed model for prediction of heavy organics deposition from petroleum crudes 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 (flocs / aggregates). Utilization of the kinetic aggregation theory of diffusive 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 [8] is used to to perform vapor-liquid phase behavior data, including the flash calculations from which compositions of liquid mixture leaving the flash tank are calculated. In Table 1 the experimental composition and other properties of the 60 °F and 1 atm Stock Tank Oil derived from the live crude under study are reported. Table 2 also shows the properties of pseudo-components of the crude oil under study. Using the algorithm proposed by Manafi et al [8] and the experimental data of Tables 1 & 2 the results reported in Table 3 & 4 and Figures 1 & 2 are produced. Table 3 shows the comparison between the experimental and calculated bubble point data for the live oil. According to this table the predictions by Manafi, et al model [8] are in very good agreement with the experimental data. The results of differential liberation study of live oil at 65 °C shows the gas and liquid compositions, density, gas average specific gravity in Table 4. Overall, Tables 4 show that the experimental laboratory data is fairly in good agreement with calculated results. Figures 1 to 5 demonstrated in the following pages show the prediction results of live oil P/T diagram. Figures 1

agreement with calculated results. Figures 1 to 5 demonstrated in the following pages show the prediction results of live oil P/T diagram. Figures 1 and 2 will be very useful in describing the phase behavior of live reservoir oil.

### **TUNING THE DEPOSITION MODEL WITH LOW PRESSURE ORGANICS DEPOSITION DATA**

The parameters of the proposed model need to be tuned to some deposition data. The best and easiest way of producing deposition data is to use the stock tank oil and titrate it with the addition of a number of paraffin hydrocarbons at various concentrations and measure the amount of heavy organics deposits generated. In Figure 3 we report such data for the stock tank oil of the crude 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 experimental data for n-pentane is somehow scattered. However, in the average, the agreement between the experimental data and the tuned model is quite satisfactory considering the deposition data due to the three paraffin hydrocarbons.

### **MODEL PREDICTIONS AT HIGH PRESSURES AND AT VARIOUS TEMPERATURES**

The proposed model also can be applied for predictions of the phase behavior and deposition region of heavy organics in the crude oil and its mixtures with miscible solvents at high pressures and different temperatures. In Figure 4 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 graph deposition occurs in the one-phase (liquid) region for this particular crude oil. In order to test the accuracy of the proposed model with the experimental data Table 5 is reported in which the pressures at which the onset of heavy organics depositions are observed are compared with the results of the predictions by the present model. Considering that 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. According to the above figures, the amount of heavy organics deposited from this particular crude first increases and then decreases as temperature increases.

On Figure 7 the size distribution of the heavy organics (in this case asphaltene) precipitated from the crude oil due to addition of n-C5 is reported. Figure 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. In this calculation, initial resin concentration in tank oil used is 0.0609 mole %. Figure 9 shows the molecular weight distribution of asphaltene in the original live oil. This distribution is a result of an extensive amount of calculations using the input data provided to us by the company.

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### **REFERENCES**

1. P.M. Lichaa and L. Herrera, "Electrical and Other Effects Related to the Formation and Prevention of Asphaltenes Deposition". Society of Petroleum Engineers Journal, paper no. 5304, 1975.
2. J. Escobedo, G.A. Mansoori, C. Balderas-Joers, L.J. Carranza-Becerra and M.A. Mendez-Garcia, "Heavy Organic Deposition During Oil Production from a Hot Deep Reservoir: A Field Experience". SPE Paper # 38989, p. 9, Proceedings of the 5th Latin American and Caribbean Petroleum Engineering Conference and Exhibition, Rio de Janeiro, Brazil, 30 August - 3 September 1997.
3. R.J. Cole and F.W. Jessen, "Paraffin Deposition". Oil and Gas Journal, v. 58, p. 87, 1960.
4. E.B. Hunt Jr., "Laboratory Study of Paraffin

- Deposition". *Journal of Petroleum Technology*, v. 225, p. 1259, 1962.
5. C. Lhioreau, J. Briant and R. Tindy, "Influence de la Pression sur la Flocculation des Asphaltenes". *Revue Inst. Francais Pet.*, v. 22, p. 797, 1967.
  6. D.A. Shock, J.D. Sadbury and J.S. Crockett, "Studies of the Mechanism of Paraffin Deposition and Its Control". *Journal of Petroleum Technology*, v. 7(9), p. 23, 1955.
  7. Juan H. Pacheco-Sanchez and G.A. Mansoori, 1998, "In Situ Remediation of Heavy Organic Deposits Using Aromatic Solvents". SPE Paper # 38966, p. 13, Proceedings of the 68th Annual SPE Western Regional Meeting, Bakersfield, CA, 11-15 May, 1998.
  8. H. Manafi, G.A. Mansoori and S. Ghotbi, "Phase Behavior Prediction of Petroleum Fluids with Minimum Characterization Data". *Journal of Petroleum Science and Engineering*, v. 22, pgs. 67-93, 1999.
  9. R.L.Scott and M. Magat, "Thermodynamics of High Polymer Solutions". *J. Chem. Phys.*, v. 13, p. 172; R.L. Scott, *J. Chem. Phys.* v. 13, p. 178, 1945.
  10. Smoluchowski, V.M., "Drei Vortraege ueber Diffusion, Brownsche Molekular Bewegung und Koagulation von Kolloidteilchen". *Physikalische Zeitschrift*, v. 17, p. 593, 1916.
  11. F.J. Nollenstein, *J. Inst. Petrol. Technol.*, v. 10, p. 311, 1924.
  12. J. Swanson, *J. Phys. Chem.*, v. 46, p. 141, 1942.
  13. P.A. Witherspoon and Z.A. Munir, *Producers Monthly*, v. 24, p. 20, 1960.
  14. J. P. Dickie and T. F. Yen, *Analls Chem.*, v. 39, p. 1847, 1967.
  15. K.J. Leontaritis and G.A. Mansoori, "Asphaltene Flocculation During Oil Recovery and Processing: A Thermodynamic-Colloidal Model". SPE Paper #16258, Proceedings of the 1987 SPE Symposium on Oil Field Chemistry, Society of Petroleum Engineers, Richardson, TX, 1987.
  16. S. Kawanaka, S.J. Park, and G.A. Mansoori, "Organic Deposition from Reservoir Fluids". *SPE Reservoir Engineering Journal*, pgs. 185-192, May 1991.
  17. S.J. Park and G.A. Mansoori, "Aggregation and Deposition of Heavy Organics in Petroleum Crudes". *International Journal of Energy Sources*, v. 10, pgs.109-125, 1988.
  18. G.A. Mansoori, "Modeling of Asphaltene and Other Heavy Organics Depositions". *J. Petroleum Science & Engineering*, v. 17, pgs. 101-111, 1997.
  19. Botet, R. and Jullien, R., "Size Distribution of Clusters in Irreversible Kinetic Aggregation". *Journal of Physics A: Math. Gen.*, v. 17, pgs.2517-2530, 1984.
  20. Flory, P.J., "Principles of Polymer Chemistry". Cornell University Press, Ithaca, N.Y. 1953.
  21. Stockmayer, W. H., *Journal of Chemical Physics*. v. 11, p.45, 1943.
  22. Ernst, M.H., Hendriks, E.M., and Ziff, R.M., *Journal de Physique Letters*, v. 45, p. L211, 1984.
  23. Jullien, R., Kolb, M., and Botet, R., "Scaling Properties of Growth by Kinetic Clustering of Clusters". *Kinetics of Aggregation and Gelation* edited by F. Family and D.P. Landau, pgs. 101-109, 1984.
  24. Leyvraz, F. and Tschudi, H.R., "Singularities in the Kinetics of Coagulation Process", *Journal of Physics A: Math. Gen.*, v. 14, p. 3389, 1982.; *ibid*, *Journal of Physics A: Math. Gen.*, v. 15, p.1951, 1981.
  25. Ernst, M. H. and Hendriks, E. M., "Smoluchowski's Equation with Surface Interaction and Exponents in the Cluster Size Distribution". *Kinetics of Aggregation and Gelation* edited by F. Family and D.P. Landau, pgs. 225-228, 1984.
  26. Ziff, R. M., "Aggregation Kinetic via Smoluchowski's Equation". *Kinetics of Aggregation and Gelation* edited by F. Family and D.P. Landau, pgs. 191-199, 1984.
  27. Leyvraz, F., "Critical Exponents in Smoluchowski Equations of Coagulation". *Kinetics of Aggregation and Gelation* edited by F. Family and D.P. Landau, pgs. 201-204, 1984.
  28. Meakin, P., "Formation of Fractal Clusters and Networks by Irreversible Diffusion-limited Aggregation". *Physical Review Letter*, v. 51(13), pgs.1119-1122, 1983.
  29. Kolb, M., Botet, R., and Jullien, R., "Scaling of Kinetically Growing Clusters". *Physical Review Letter*, v. 51(13), pgs.1123-1126, 1983.
  30. Allain, C. and Joughier, B., *J. Phys. (Paris) Lett.*, v. 44, p. L421, 1983.

**Table 1. Experimental Stock Tank Oil  
Composition at T=60 °F and P=1 atm**

Component	Mole %
N2	0.0001
CO2	0.0015
CH4	0.4581
C2	0.1206
C3	0.2395
iC4	0.1463
nC4	0.5033
iC5	0.3793
nC5	0.6353
C6	1.4158
C7	5.3281
C8	6.3504
C9	4.6747
C10	2.9178
C11	3.5286
C12+	3.300
MW	438.18
Density (lb/cu. ft)	43.731
T <sub>c</sub> (K)=887.809, P <sub>c</sub> (atm)=11.71, Acen. factor=0.88656	
Molar volume=396.4953 (cc/mol)	

**Table 2. Properties of Pseudo components**

Component	BP(F)	$\rho$ (g/cc)	MW(g/mol)	T <sub>c</sub> (F)	P <sub>c</sub> (psia)	$\omega$
C6	147.0	0.685	84	452.2	468.7	0.281
C7	197.5	0.722	96	512.6	449.4	0.328
C8	242.0	0.745	107.0	563.7	427.0	0.368
C9	288.0	0.764	121.0	614.8	401.0	0.408
C10	330.5	0.778	134.0	660.1	374.5	0.445
C11	369.0	0.789	147.0	699.9	349.8	0.477
C12+	979.8	0.958	558.0	1262.1	130.9	1.076

**Table 3. Comparison of experimental vs. calculated bubble point pressures of live oil**

Temperature (°C)	Saturation Pressure (PSIG)	
	Experiment	Calculated
21	3200.0	3201.7
55	3734.0	3733.7
65	3848.7	3842.2
70	3855.0	3866.1
80	3902.0	3897.0
90	3917.0	3918.1

**Table 4. Differential liberation study of live oil at 65 °C**

Comp.	P [Kgf/cm <sup>2</sup> ] 240		180	
	<u>Liquid</u> Pred	<u>Vapor</u> Pred(Exp)	<u>Liquid</u> Pred	<u>Vapor</u> Pred (Exp)
N2	0.044	0.124	0.044	0.124
CO2	0.078	0.100	0.072	0.105
CH4	50.687	93.896 (95.11)	42.681	93.985 (95.15)
C2	2.768	2.653	2.751	2.787
C3	1.798	1.151	1.908	1.183
iC4	0.468	0.218	0.515	0.216
nC4	1.224	0.493	1.361	0.485
iC5	0.474	0.145	0.537	0.136
nC5	0.663	0.182	0.758	0.169
C6	0.937	0.177	1.082	0.182
C7+	40.950	0.820	48.210	0.351
MW	195.310	18.100 (17.328)	227.84	17.9 (17.260)
Spec. Grav (with Air)		0.624 (0.598)		0.617 (0.596)
Density (lb/cu. ft)	40.599	9.82	41.147	7.545

**Table 5: Onset of Heavy Organics Depositions at Various Temperatures and Pressures**

T (°F)	Expt'l P (PSIG)	Predicted P (PSIG)
158	no deposit observed	no deposit predicted
176	4,200.	3,900.
194	4,500	3,950.

Figure 1: Detailed composition of live oil P/T diagram predicted by the Model due to Manafi, et al [8]

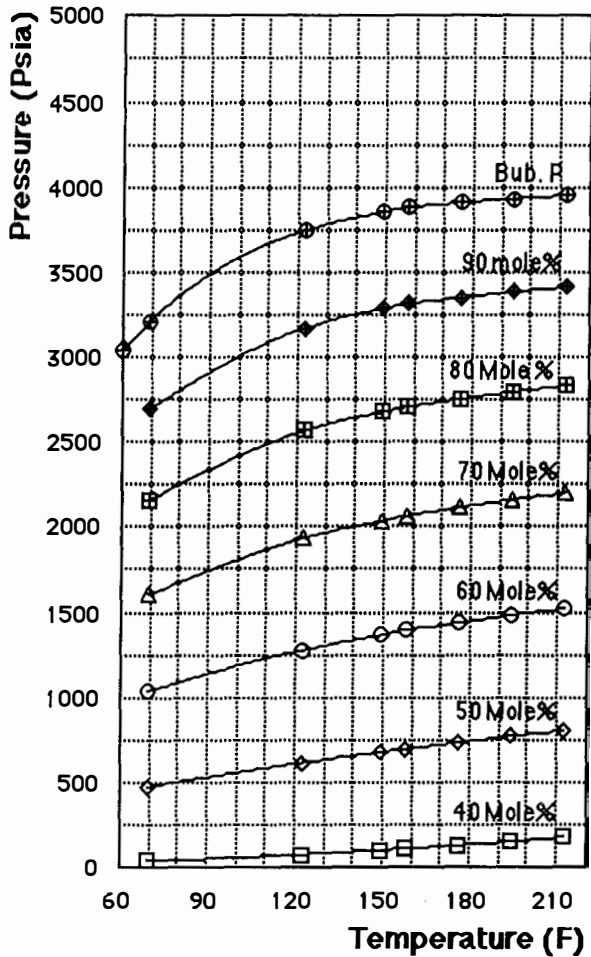


Figure 2: Overall P/T diagram for the Live Oil Predicted by the Model due to Manafi, et al [8]

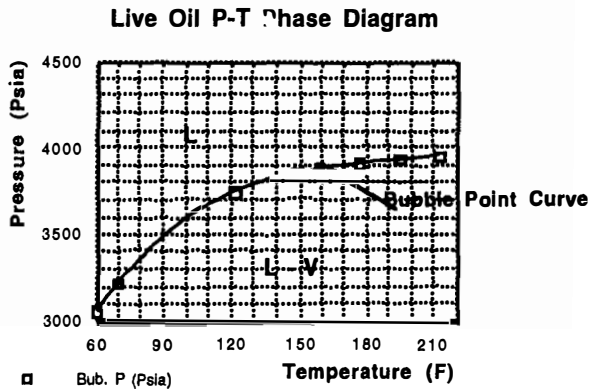


Figure 3: Comparison of low pressure (stock tank oil) deposition data with the model calculations due to the addition of n-pentane, n-hexane and n-heptane as miscible solvents.

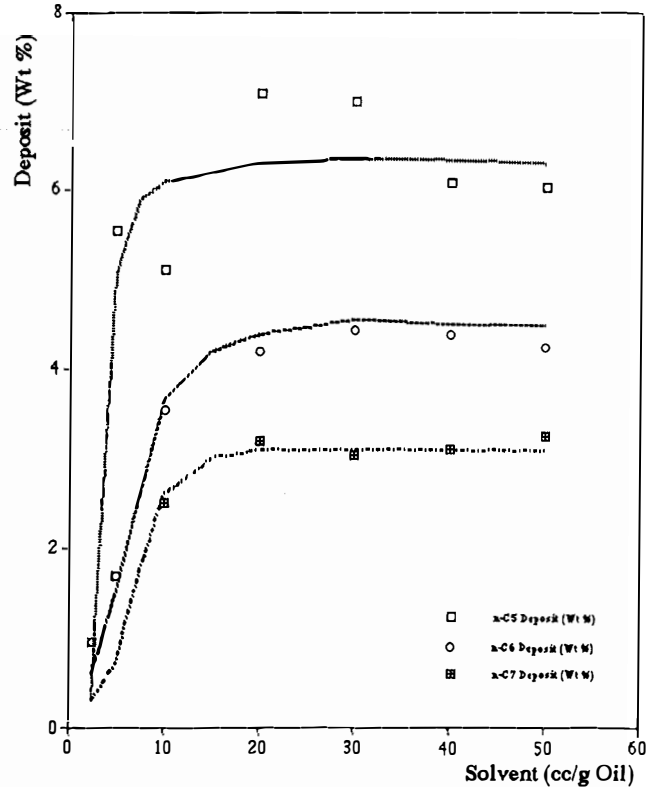


Figure 4: Heavy organics deposition envelope which contains lower and upper pressure bounds of deposition region at different temperatures and pressures

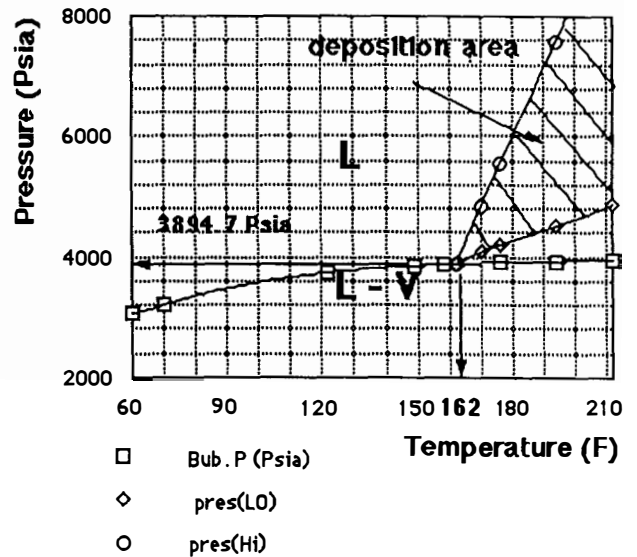


Figure 5: The pressure dependence of the amount of heavy organics deposition for live oil mixture at T=194 °F (90 °C)

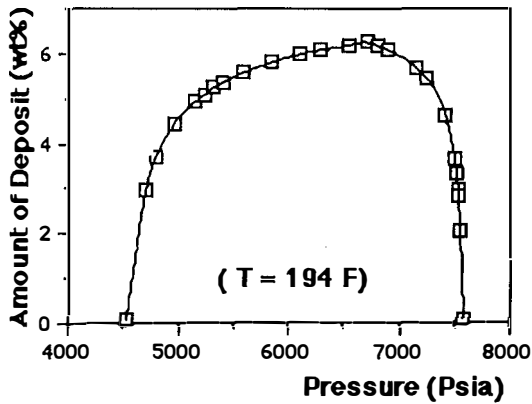


Figure 6: Trends of amount of asphaltene deposited from live oil as the temperature and pressure change

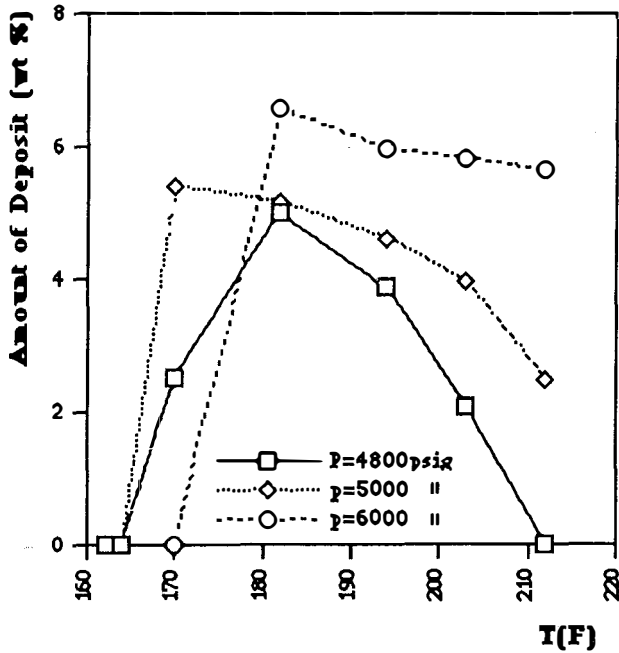


Figure 7: Size distribution of asphaltene precipitated from the crude oil due to addition of nC5

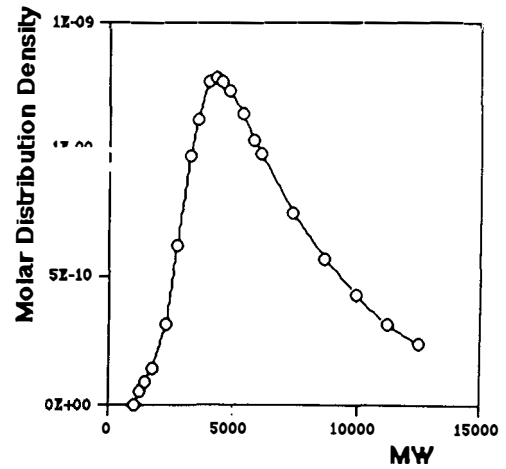


Figure 8: Growing average molecular weight of asphaltene flocs / aggregates as a function of the volume of n-C5 precipitating solvent added

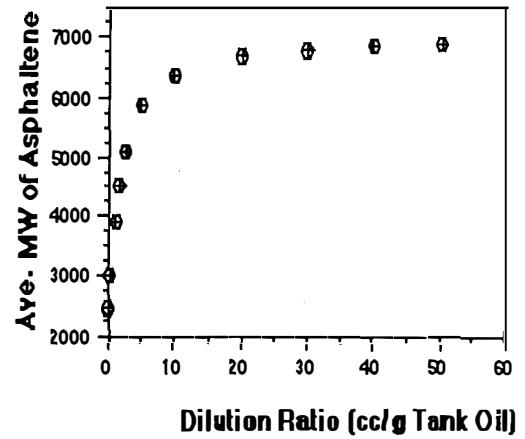


Figure 9: Molecular weight distribution of asphaltene in the live crude oil

