

Organic Deposition From Reservoir Fluids: A Thermodynamic Predictive Technique

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Summary. A molecular model is developed to predict onset and amount of organic deposition from reservoir fluids caused by variations in temperature and pressure and introduction of miscible solvents. The model is used successfully to predict the phase behavior and deposition regions of asphaltene in CO₂/oil mixtures.

Introduction

The compounds that constitute complex petroleum crudes, coal liquids, and similar substances are mutually soluble as long as a certain ratio of each kind of molecule (or particle) is maintained in the mixture. Variations in the mixture's temperature, pressure, or composition (such as addition of a miscible solvent) alter this ratio. Then the heavy and/or polar molecules may separate from the mixture either in the form of another liquid phase or as a solid precipitate. Hydrogen bonding and the sulfur- (and/or nitrogen)-containing segments of the separated molecules may start to aggregate (or polymerize) and to produce the irreversible asphaltene deposits that are insoluble in solvents. Development of predictive techniques of organic deposition to describe the behavior of large organic molecules in hydrocarbon mixtures calls for fundamental detailed analyses of such systems.

Major questions of interest in the oil industry are when and how much organics will flocculate out under certain conditions. Because petroleum crude generally consists of a mixture of aromatic and other hydrocarbons (resin, wax, and asphaltenes), each of the constituents of this system can be considered as a continuous or discrete mixture interacting with the other constituents as pseudopure components.¹ The theory of continuous mixtures, the statistical mechanical theory of monomer/polymer solutions, the concept of Hildebrand's solubility parameter, and the concept of pseudoizations are used here to analyze and predict the onset and amount of organic precipitation in petroleum crudes.

Because heavy organic particles in petroleum crudes have a wide range of size, or molecular weight, distribution, one may consider each crude family as a heterogeneous (polydisperse) polymer. Then, to predict the behavior of such compounds, one can assume that the properties of their fractions depend on their molecular weights. Mansoori and Jiang² initially proposed this treatment of heavy organics in petroleum fluids. In their proposed formulation, the Scott and Magat^{3,4} theory of polymer mixtures, which is the statistical thermodynamic model of the mixture of solvents and heterogeneous (polydisperse) polymers, was used. In this paper, the proposed model of Mansoori and Jiang is applied to predict asphaltene deposition from petroleum fluids. Similar calculations can be performed for deposition prediction of other organic macromolecules.

Asphaltene Deposition

The petroleum industry defines the asphaltene content of a crude as the normal-pentane-insoluble and benzene-soluble fraction of the crude.⁵⁻⁷ The exact chemical structure of asphaltenes is not known. On heating, they are not melted but decompose, forming carbon and volatile products above 300 to 400°C. They react with sulfuric acid to form sulfonic acids, as might be expected on the basis of the polyaromatic structure of these compounds. The color of dissolved asphaltene in benzene is deep red at low concentrations. At around 3 ppm asphaltene concentration in benzene, the solution is distinctly yellow.

While solutions to the problems associated with the deposition of nonasphaltic organic compounds from petroleum fluids are mostly understood, the asphaltene deposition problem remains a mystery. The devastating effect of asphaltene deposition in the economy of petroleum processing and oil recovery techniques is well recognized. Asphaltene deposition during oil production and processing is a very serious problem in many areas throughout the world.⁸⁻¹² The presence of asphaltene in petroleum crudes causes a number of severe technological problems. One such problem is the untimely precipitation of asphaltene in the petroleum reservoir; in the wells, tubings, and pipelines; and in the refinery components. Currently, mechanical and chemical cleaning methods are being improvised to remove asphaltene deposits and to maintain production, transportation, and processing of petroleum.

According to Long,⁷ asphaltenes are highly polydisperse and contain a broad distribution of polar groups in their structure. The average molecular weight of asphaltenes present in petroleum crudes is generally very high. Published molecular-weight data for petroleum asphaltenes range from about 500 to 500,000. The wide range of asphaltene size distribution suggests that asphaltenes are partly dissolved in oil and partly in colloidal state. The colloidal asphaltenes are believed to be dispersed and stabilized primarily by resin molecules present in oil that are adsorbed on asphaltene surface.¹³ The degree of dispersion of asphaltenes in petroleum oils depends on the chemical composition of the petroleum. In heavy and highly aromatic crude oils, the asphaltenes are well dispersed, but in the presence of an excess of petroleum ether and similar paraffinic hydrocarbons, they are coagulated and then precipitate.

In developing a comprehensive model of asphaltene deposition, we have considered a number of theoretical approaches, including colloidal solution theories,¹³ polydisperse polymer solution theories, continuous thermodynamics, and fractal aggregation theories.¹⁴ The theoretical technique proposed here is part of our continuing effort to develop a comprehensive model of asphaltene deposition.

Background of Proposed Model

The statistical mechanical theory of mixtures of high-molecular-weight polymer solutions was originally introduced by Meyer,^{15,16} who used hypothetical lattice cells, one of which may be filled with a segment of either a polymer or a solvent molecule, and discussed the theory qualitatively. Later, Flory^{17,18} and Huggins¹⁹ independently developed thermodynamic models of the lattice theory for homogeneous polymer solutions—i.e., the solution containing uniform polymer molecules in a solvent in which the partial molar entropies of mixing are obtained by use of the lattice theory. Furthermore, Flory applied his lattice theory to homogeneous chain-polymer solutions and used the van Laar's rule for calculation of the heat of mixing. Then, by combining the entropy and heat of mixing, he derived the expression of the partial molar free energy for the homogeneous polymer solutions. Later, Scott and Magat³ proposed a statistical mechanical method to derive expressions for partial molar free energies of heterogeneous polymer solutions. Their method was based on Huggins' theory, in which less restrictive assumptions were made than in Flory's theory. This makes

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the Scott and Magat theory more general for heterogeneous polymer/monomer solutions. For the heat of mixing, Scott and Magat used the Scatchard-Hildebrand formula.³

In this paper the Scott and Magat theory is used to present a statistical thermodynamic model for the predictions of the onset point and amount of asphaltene (or any other organic compound) deposition from petroleum crude under the influence of miscible solvents. In the proposed model, asphaltene is assumed to consist of many components of similar polymeric molecules so that a continuous distribution function can be used for it. A continuous gamma distribution function allows properties of asphaltene to be related to the molecular weight of asphaltene fractions. The adjustable parameters in this model are optimized with experimental titration data²⁰ of asphaltene deposition caused by addition of normal paraffin hydrocarbons. To demonstrate the applicability of the proposed model, it is used to predict the high-pressure phase behavior and the pressure-vs.-composition region of asphaltene deposition for CO₂/crude-oil mixtures.

Polydisperse Polymer Model of Organic Deposition

Hirschberg *et al.*²⁰ originally attempted to apply polymer theory to develop a model to predict asphaltene deposition. In their formulation of the problem, they assumed that asphaltene consisted of a uniform (homogeneous) component of petroleum crude. Mansoori and Jiang² applied the Scott and Magat heterogeneous polymer solution theory to formulate a continuous-mixture model to predict the onset point and amount of organic deposition from petroleum crude oil. The basic technique used in this report is the Mansoori and Jiang model.

In a heterogeneous polymer mixture, one may specify different fractions of the polymer according to their molecular weights. Assuming that asphaltene behaves as a heterogeneous polymer, the Scott and Magat theory can be used to calculate the chemical potential of the *i*th fraction of asphaltene, μ_{CAi} , in a mixture of asphaltene and a solvent as

$$\frac{(\mu_{CAi} - \mu_{CAi}^O)/RT}{RT} = \ln V_{fAi} + 1 - (N_{SAi}/\bar{N}_{SA})(1 - V_{fB}) - N_{SAi}V_{fB} + fN_{SAi}(V_{fB})^2, \dots \dots \dots (1)$$

where subscripts *Ai* and *B* = *i*th fraction of asphaltene and solvent, respectively, and superscript *O* = standard state. The volume fraction, V_{fi} , is defined by the volume, *V*, of a component divided by the total volume of a mixture, V_{mix} . Therefore, $V_{fAi} = V_{Ai}/V_{mix}$, $V_{fB} = V_B/V_{mix}$, and $(\sum V_{fAi}) + V_{fB} = 1$.

The segment number of the *i*th fraction of asphaltene, N_{SAi} , is defined by the ratio of molar volume, V_{AiM} , of the *i*th fraction of asphaltene over the molar volume, V_{MB} , of a solvent, $N_{SAi} = V_{MAi}/V_{MB} = M_{Ai}/(\rho_{mAi}V_{MB})$, where ρ_{mAi} = mass density of the *i*th fraction. The segment number of the solvent is assumed to be unity. The mass density of the *i*th fraction of asphaltene is almost independent of the *i*th fraction molecular weight, M_{Ai} , because of the assumption of the uniformity of segments of asphaltene, and it is equal to the average mass density of asphaltene, $\bar{\rho}_m$. As a result, $\rho_{mAi} = \bar{\rho}_m$ and $N_{SAi} = M_{Ai}/(\bar{\rho}_m V_{MB})$.

The average segment number, \bar{N}_{SA} , of asphaltene may be defined by

$$\bar{N}_{SA} = \sum x_{Ai} N_{SAi}, \dots \dots \dots (2)$$

where x_{Ai} = mole fraction of the *i*th fraction of asphaltene with respect to the total asphaltene; i.e., $\sum x_{Ai} = 1$. Furthermore, the parameter *f* in Eq. 1 is defined by (see Appendix A)

$$f = 1/N_c + V_{MB}[(\delta_A - \delta_B)^2 + 2k_{AB}\delta_A\delta_B]/RT, \dots \dots \dots (3)$$

where N_c = coordination number between two successive segments in an asphaltene molecule (N_c has a value³ between 3 and 4), k_{AB} = interaction parameter between asphaltene molecule and asphaltene-free crude oil, δ_A = average solubility parameter of asphaltene, and δ_B = solubility parameter of asphaltene-free crude. It is assumed that the molecular interaction parameter between asphaltene and asphaltene-free crude oil, k_{AB} , is linearly proportional to the average molecular weight of asphaltene-free oil, M_B :

$k_{AB} = a + b\bar{M}_B$, where *a* and *b* are two independent constants. The solubility parameter, δ , is defined with respect to the square root of the molar internal energy change of vaporization, ΔU_v , over the molar volume:

$$\delta = (\Delta U_v/V_M)^{1/2}, \dots \dots \dots (4)$$

Eq. 3 is formulated with respect to average solubility parameter of asphaltene so that the available (average) experimental solubility parameter data²⁰ of asphaltene can be used in the present model.

By using the above equations and the principle of phase equilibria, one can derive an expression for calculating the asphaltene concentration in a solution. This corresponds to the asphaltene concentration in a solution in equilibrium with the asphaltene content of a precipitated phase.

Phase-Equilibrium Calculation

To perform phase-equilibrium calculation, one needs to equate chemical potentials of every asphaltene fraction in the liquid phase, μ_{CAi}^L , and the solid phase, μ_{CAi}^S :

$$\mu_{CAi}^S = \mu_{CAi}^L; \quad i = 1, 2, \dots \dots \dots (5)$$

Provided that Eq. 1 is valid for every fraction of asphaltene in the liquid and solid phases, Eq. 5 will take the following form:

$$\ln V_{fAi}^S + 1 - (N_{SAi}/\bar{N}_{SA})(1 - V_{fB}^S) - N_{SAi}V_{fB}^S + f^S N_{SAi}(V_{fB}^S)^2 =$$

$$\ln V_{fAi}^L + 1 - (N_{SAi}^L/\bar{N}_{SA}^L)(1 - V_{fB}^L) - N_{SAi}^L V_{fB}^L + f^L N_{SAi}^L (V_{fB}^L)^2, \dots \dots \dots (6)$$

In Eq. 6, the molar volumes of the *i*th fraction of asphaltene in both phases are assumed identical; $V_{MAi}^S = V_{MAi}^L = V_{MAi}$. Furthermore, because $V_{MB}^S = V_{MB}^L = V_{MB}$, then $N_{SAi}^S = N_{SAi}^L = N_{SAi}$. Now if we assume that the solid phase is free of the solvent—i.e., $V_{fB}^S = 0$ —Eq. 6 will take the following form:

$$V_{fAi}^L/V_{fAi}^S = \exp(N_{SAi}\theta), \dots \dots \dots (7)$$

$$\text{where } \theta = (1/\bar{N}_{SA}^L - 1/\bar{N}_{SA}) + (1 - 1/\bar{N}_{SA}^L)V_{fB}^L - f^L(V_{fB}^L)^2, \dots \dots (8)$$

Eq. 7, in conjunction with a continuous distribution function for asphaltene, can be used to calculate the total volume fraction of asphaltene in a liquid mixture in equilibrium with a solid phase.

Continuous Model of Asphaltene

To calculate the total volume fraction of asphaltene in a liquid mixture in equilibrium with a solid phase, we need to assume a molecular-weight-distribution function for the continuous asphaltene components. The molecular-weight-distribution function of asphaltene can be defined as follows:

$$F(M_{Ai}) = (1/n_A)(dn_{Ai}/dM_{Ai}), \dots \dots \dots (9)$$

$$\text{where } \int_0^\infty F(M_{Ai})dM_{Ai} = 1,$$

and where M_{Ai} = molecular weight of the *i*th fraction of asphaltene, dn_{Ai} = differential of the number of moles of the *i*th fraction of asphaltene whose molecular weight is in the range of M_{Ai} to $M_{Ai} + dM_{Ai}$, and n_A = total number of moles of asphaltene.

The expression for the average segment numbers of asphaltene in a given phase, Eq. 2, can be defined by using the continuous distribution function of asphaltene.

$$\bar{N}_{SA} = \int_0^\infty N_{SAi}F(M_{Ai})dM_{Ai}, \dots \dots \dots (10)$$

Upon partial deposition of asphaltene from a petroleum crude caused by the introduction of a miscible solvent, two phases (one liquid and one solid) will form. As a result of the mass balance for the *i*th fraction of asphaltene between the original crude oil *C*, solid phase *S*, and solvent-rich liquid phase *L*, one can write

$$dn_{Ai}^C = dn_{Ai}^S + dn_{Ai}^L, \dots \dots \dots (11)$$

$$\text{and } F^C(M_{Ai})n_A^C = F^S(M_{Ai})n_A^S + F^L(M_{Ai})n_A^L, \dots \dots \dots (12)$$

where $dn_{Ai}^C = VC dV_{fAi}^C / V_{MAi}$, $dn_{Ai}^S = VS dV_{fAi}^S / V_{MAi}$, $dn_{Ai}^L = VL dV_{fAi}^L / V_{MAi}$, $VC = VS + VL$, and $V_A^C = W_{Ai} / \bar{\rho}_m$. VC , VS , and VL = total volumes of the crude oil, solid phase, and liquid phase, respectively. W_{Ai} = total weight of asphaltene in the crude oil, and $\bar{\rho}_m$ = mass average density of asphaltene.

Eq. 7, which is valid for a given fraction of asphaltene, can be written in the following differential form when a differential fraction of asphaltene is considered in the context of its continuous model:

$$dV_{fAi}^L / dV_{fAi}^S = \exp(N_{sAi}\theta) \quad (13)$$

By joining Eqs. 9 and 11 through 13, the following expressions can be derived:

$$FL(M_{Ai}) = \{VL / [VL + VS \exp(-N_{sAi}\theta)]\} (n_A^C / n_A^L) FC(M_{Ai}) \quad (14)$$

$$\text{and } FS(M_{Ai}) = \{VS / [VL \exp(N_{sAi}\theta) + VS]\} (n_A^C / n_A^S) FC(M_{Ai}) \quad (15)$$

$$\text{Because } \int_0^\infty FL(M_{Ai}) dM_{Ai} = 1 \text{ and } \int_0^\infty FS(M_{Ai}) dM_{Ai} = 1,$$

by rearranging Eqs. 14 and 15, one can get

$$n_A^C / n_A^L = 1 / \int_0^\infty \{VL / [VL + VS \exp(-N_{sAi}\theta)]\} FC(M_{Ai}) dM_{Ai} \quad (16)$$

$$\text{and } n_A^C / n_A^S = 1 / \int_0^\infty \{VS / [VL \exp(N_{sAi}\theta) + VS]\} FC(M_{Ai}) dM_{Ai} \quad (17)$$

Provided that the asphaltene distribution functions are available, Eqs. 16 and 17 can be used to calculate the total number of moles of asphaltene in the separated solid, n_A^S , and liquid, n_A^L , phases. Also by substituting Eq. 14 or 15 into Eq. 10, the expression of the average segment numbers, \bar{N}_{sA}^L or \bar{N}_{sA}^S , in a phase can be obtained.

Eqs. 9 and 11 through 13 can be used to derive the total volume fraction of asphaltene in the liquid phase, V_{fA}^L , in equilibrium with the solid phase:

$$V_{fA}^L = \int_0^\infty dV_{fAi}^L = \int_0^\infty \{(M_{Ai} / \bar{M}_A) V_A^C / [VL + VS \exp(-N_{sAi}\theta)]\} \times F(M_{Ai}) dM_{Ai} \quad (18)$$

All the terms in Eq. 18 are already defined except $V_A^C = W_{Ai} / \bar{\rho}_m = VC - V_{fA}^L VL$, which is the total volume of asphaltene in the crude oil. With Eq. 18, the onset of asphaltene deposition from a petroleum crude and the amount of asphaltene in a liquid mixture in equilibrium with a solid phase can be calculated. Appendix B describes the special case²⁰ when the asphaltene is considered to consist of a homogeneous compound.

Calculation and Discussion

With the total volume fraction of asphaltene in the liquid phase, V_{fA}^L given by Eq. 18, the amount of asphaltene in the liquid phase in equilibrium with the solid phase will be $\rho_A V_{fA}^L VL$. Therefore, the amount of asphaltene deposited will be given by

$$W_{Ad} = W_{Ai} - \rho_A V_{fA}^L VL \quad (19)$$

where W_{Ai} = total amount of asphaltene in the crude oil. Because the amount of asphaltene precipitated at the onset of deposition is zero, the total amount of asphaltene, W_{Ai} , can be calculated from the asphaltene composition of the liquid phase at the onset: $W_{Ai} = \rho_A (V_{fA}^L VL)_{\text{onset}}$.

To proceed with the calculation, the continuous molecular-weight-distribution function of asphaltene is represented by the gamma distribution function:

$$F(M_{Ai}) = [(M_{Ai} - M_{A0})^{\alpha-1} / \Gamma(\alpha) \beta^\alpha] \exp[-(M_{Ai} - M_{A0}) / \beta] \quad (20)$$

TABLE 1—DATA FOR TANK OIL 1

Composition ²⁰ (mol%)	
Methane	0.10
Ethane	0.48
Propane	2.05
i-Butane	0.88
n-Butane	3.16
i-Pentane	1.93
n-Pentane	2.58
Hexanes	4.32
Heptanes-plus	84.50
Average molecular weight ²⁰	221.5
Specific gravity ²⁰	0.873
Average mass density of asphaltene,* g/cm ³	1.2
Average molecular weight of asphaltene*	4,800.0
Initial molecular weight of asphaltene ⁷	500.0**
Coordination number of asphaltene ³	3.5**
Asphaltene solubility parameter, ²⁰ MPa ^{0.5}	20.04(1 - 1.07 × 10 ⁻³ T)

*Personal communication with A.F.D. van Bergen and L.N.J. Jong, Koninklijke/Shell E&P Laboratorium, Amsterdam, April 4, 1986.
**Assumed value.

TABLE 2—PROPERTIES OF C₆ AND C₇₊ PSEUDOCOMPONENTS

	C ₆	C ₇₊
Critical temperature, K	506.6	771.2
Bubblepoint temperature, K	337.0	585.0
Molecular weight	84.0	249.9
Critical pressure, kPa	3272.8	1692.1
Acentric factor	0.281	0.639
Density, g/cm ³	0.685	0.868

$$\text{where } \alpha = (\bar{M}_A - M_{A0})^2 / \eta, \beta = \eta / (\bar{M}_A - M_{A0}), \Gamma(\alpha) = \int_0^\infty t^{\alpha-1}$$

$$\times \exp(-t) dt,$$

and M_{A0} , \bar{M}_A , and η are the initial value, mean value, and the variance of the gamma distribution function, respectively. The choice of gamma function is rather arbitrary and other equally versatile distribution functions may also be used.

To illustrate the application of the proposed model for the asphaltene-deposition predictions, the data of a tank oil (Oil 1, Sample 1 of Ref. 20) are used. Table 1 shows the data for this tank oil. In the present calculation, hexanes and heptane-plus fractions are assumed to be two distinct pseudocomponents. Their properties (Table 2) are calculated on the basis of their average molecular weights.²¹⁻²³ The Benedict-Webb-Rubin (BWR) equation of state (EOS), along with the Lee-Kesler²⁴ correlation, is used to calculate molar volumes and solubility parameters of asphaltene-free oils.

Four adjustable parameters (a , b , W_{Ai} , and η) in the proposed model are to be determined at this stage. These parameters are calculated by minimizing the differences between the experimental titration data with n-pentane and n-decane²⁰ and the results of the predictive model. Table 3 gives results of the calculations of these parameters. The experimental titration data for n-heptane was not used in this calculation because it did not seem to conform with the other titration data, as was demonstrated in an earlier publication.¹³

The calculated adjustable parameters in the model are used to predict the onsets and the amounts of asphaltene depositions, and the predictions are compared with the experimental data in Table 4. According to Table 4, all the onsets and amounts of deposition data (except in the n-heptane case) are in good agreement with the experimental data. Fig. 1 shows the predictions of onsets and amounts of asphaltene deposition vs. volumes of different n-paraffin

TABLE 3—MODEL PARAMETERS*

Interaction parameter, k_{AB}	$-7.8109 \times 10^{-3} + 3.8852 \times 10^{-6} \bar{M}_B$
Total amount of asphaltene, W_{Ai} , wt% of tank oil	4.0234
Variance of distribution function, η	4.9223×10^6

*Parameters are calculated by minimizing the differences between the experimental titration data of n-pentane and n-decane²⁰ and the predictive model.

solvents added to the tank oil. According to Fig. 1, the trend of the deposition predictions for different n-paraffins are consistent with their molecular weights. This indicates that the amount of asphaltene deposited for the same volume of n-paraffin solvents added to the tank oil decreases as the n-paraffin molecule gets bigger. This observation is reported in Fig. 2 along with the available experimental data.

Fig. 3 shows the predicted distribution functions of asphaltenes in the original petroleum crude (Tank Oil 1) and in the solid and liquid phases (after 5 cm³ of n-heptane is added to the tank oil). Fig. 4 is similar to Fig. 3 except that in this case 20 cm³ of n-heptane is added to the tank oil. In the calculations in Figs. 3 and 4, the molar distribution of asphaltene in the original petroleum crude is expressed by the gamma distribution function (Eq. 20). Then, the molar distributions of asphaltene in the liquid and solid phases (resulting from addition of the miscible solvent to the crude oil) are defined by $n_A^{FL}(M_{Ai})$ and $n_A^{FS}(M_{Ai})$, respectively. According to Figs. 3 and 4, the fractions of asphaltene with higher molecular weights tend to deposit sooner than the lower-molecular-weight fractions. Figs. 5 and 6 show the molar distributions of

precipitated asphaltenes and remaining asphaltenes in the solvent-rich liquid phase with different n-paraffins as miscible solvents along with the distribution of asphaltene in the original petroleum crude (Tank Oil 1). According to Figs. 3 through 6, the distribution of the precipitated asphaltene tends toward the original crude oil distribution as the amount of the added miscible solvent increases. Also, the distribution of the precipitated asphaltene tends toward the original crude oil distribution as the molecular weight of the added miscible solvent decreases. The trend of the distributions of the remaining asphaltene in the liquid phase reported in Fig. 6 are opposite to that of the solid phase. According to these figures, the proposed continuous model suggests that the nature of asphaltenes caused by the introduction of different solvents in the solvent-rich liquid and the precipitated solid phases is not the same. This prediction is consistent with the experimental observations of different investigators as to the variations in the nature of asphaltenes that are precipitated because of the introduction of different miscible solvents in a crude oil.^{7,11,25}

To demonstrate the applicability of the proposed model for prediction of the pressure/composition region of asphaltene deposi-

TABLE 4—EXPERIMENT* vs. PREDICTION FOR ONSET AND AMOUNT OF ASPHALTENE DEPOSITION FROM TANK OIL

Dilution Ratio (cm ³ diluent/g tank oil)	n-C ₅		n-C ₇		n-C ₁₀	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
1.35						OF
1.40				OF	OF	
1.90	NT	OF				
2.22			OF			
5	—	3.31	1.53	1.52	1.34	1.30
10	3.61	3.67	1.82	2.28	1.45	1.53
20	3.79	3.75	1.89	2.43	1.50	1.45
50	3.87	3.73	1.87	2.29	—	1.13

*Experimental titration data (wt% tank oil) are taken from Ref. 20.
 NT=onset of asphaltene deposition not determined.
 OF=onset of flocculation.

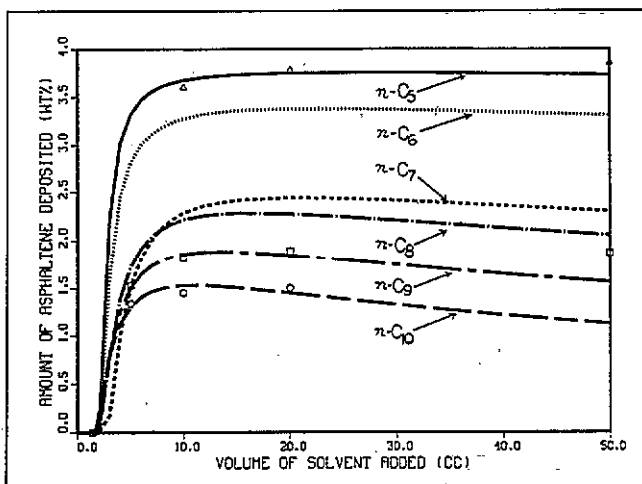


Fig. 1—Prediction of amount of asphaltene deposition from Tank Oil 1 vs. volume of six different n-paraffin solvents. Experimental asphaltene deposition data²⁰ caused by addition of n-pentane, n-heptane, and n-decane are shown by Δ , \square , and \circ , respectively.

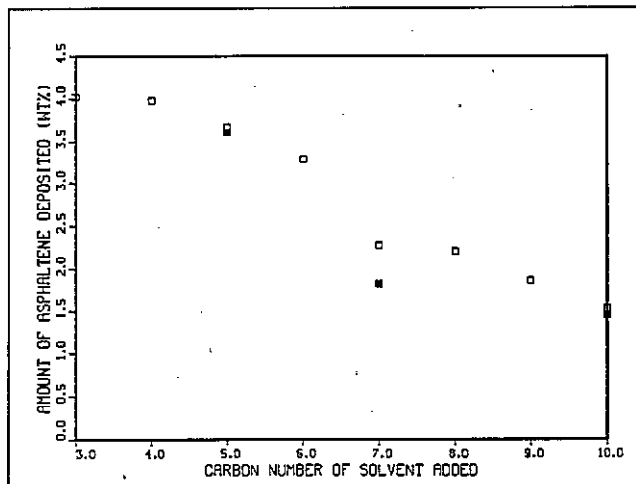


Fig. 2—Effect of n-paraffin solvent chain length on amount of asphaltene deposition. Volume of all the n-paraffin solvents added is 10.0 cm³. Experimental data²⁰ are shown by \blacksquare and predictions by \square .

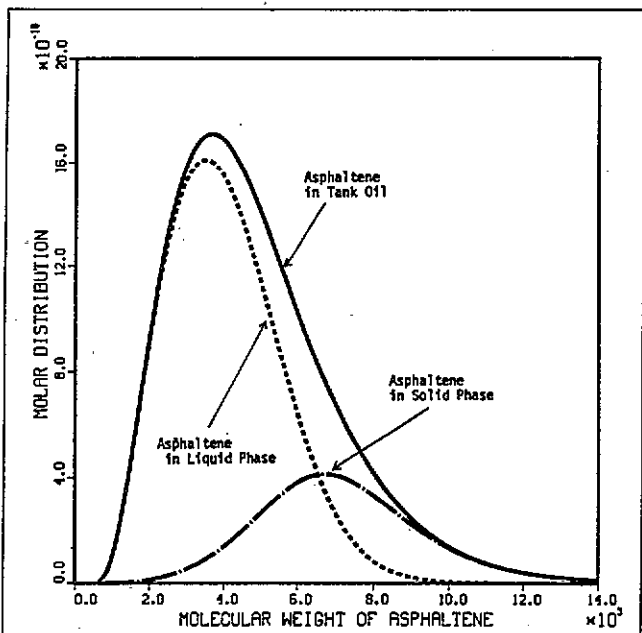


Fig. 3—Relations between molar concentration distributions of asphaltene in different phases in equilibrium resulting from the addition of a given amount of miscible solvent (5.0 cm³ n-heptane) to 1 g of tank oil.

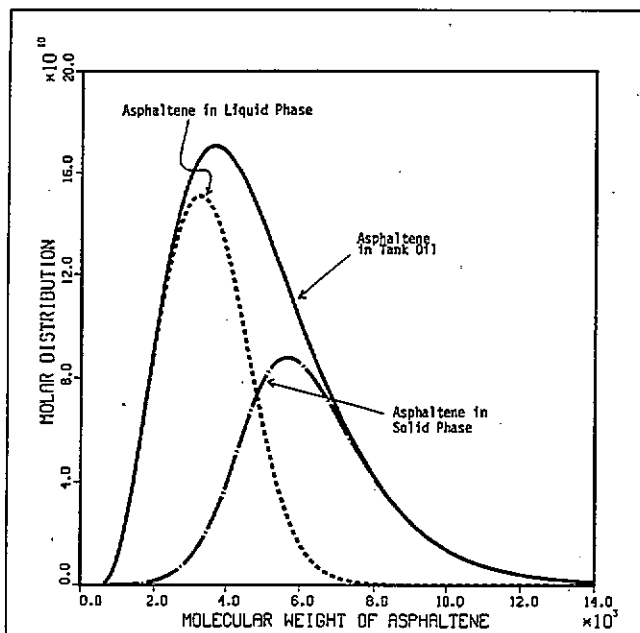


Fig. 4—Relations between molar concentration distributions of asphaltene in different phases in equilibrium resulting from the addition of a given amount of miscible solvent (20.0 cm³ n-heptane) to 1 g of tank oil.

tion at high pressures under the influence of a miscible gas (CO₂ in the present example), the phase behavior (vapor/liquid/solid equilibria) of Tank Oil 1 in contact with CO₂ at different pressures and at 24°C was predicted and is shown in Figs. 7 and 8. Fig. 8 is an expanded scale of the region of Fig. 7 where the asphaltene precipitation occurs. In this calculation, it is assumed that there is no asphaltene in the gas phase and that the asphaltene content of the liquid phase has no effect on the vapor/liquid equilibrium of the CO₂/oil system. A flash calculation²⁶ for CO₂/asphaltene-free oil was performed to compute the composition of the liquid phase leaving the flash tank. Then, the present model was applied to the mixture of asphaltene and the liquid phase leaving the flash tank. The dashed area in Fig. 8 is the predicted region of asphaltene depo-

sition from Tank Oil 1. According to this figure, the asphaltene deposition begins in a region where the mole fraction of CO₂ entering the flash tank is about 0.984. In these calculations, every gram of tank oil was assumed to be prediluted with 0.98 cm³ of n-decane before CO₂ was injected into the system. For <0.98-cm³ n-decane predilutions, the model did not predict any precipitation, consistent with the experimental observations.²⁰ In Fig. 9, the pressure dependence of asphaltene precipitation in a mixture of CO₂ and asphaltene-free crude oil are reported. According to this figure, the amount of asphaltene deposited decreases as pressure increases. This trend of asphaltene depositions at different pressures is consistent with experimental observation.²⁰

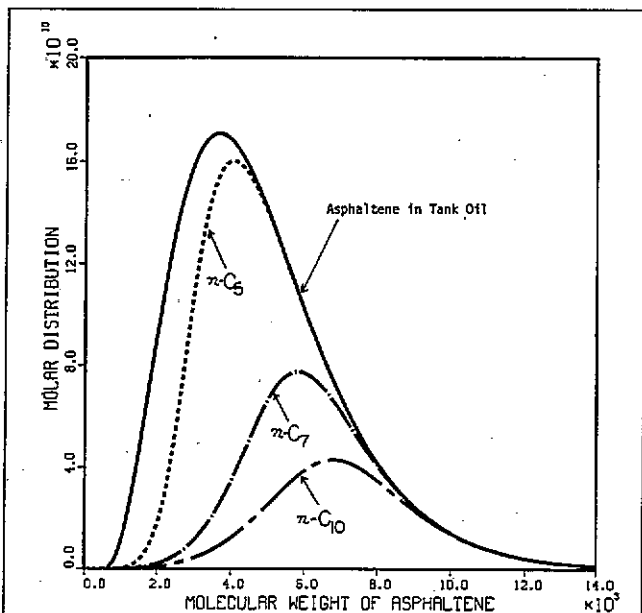


Fig. 5—Comparison of molar concentration distributions of asphaltene in the solid phase for different precipitating solvents. Volume of all precipitating solvents added is 10.0 cm³.

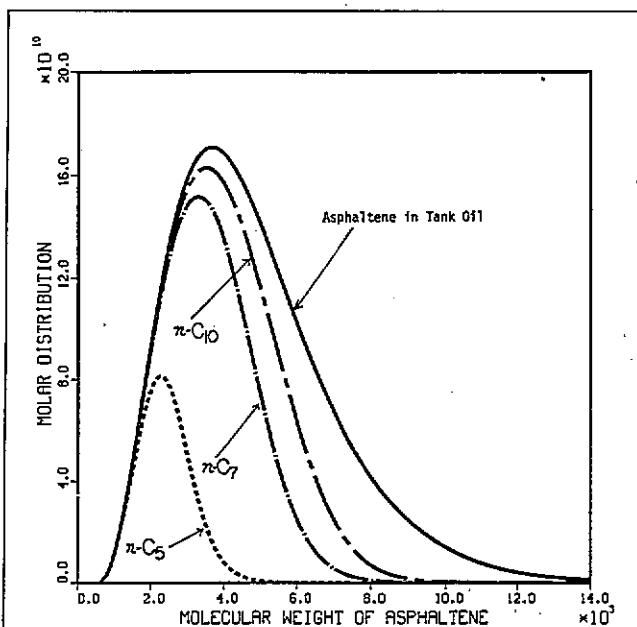


Fig. 6—Comparison of molar concentration distributions of asphaltene in the liquid phase for different precipitating solvents. Volume of all precipitating solvents added is 10 cm³.

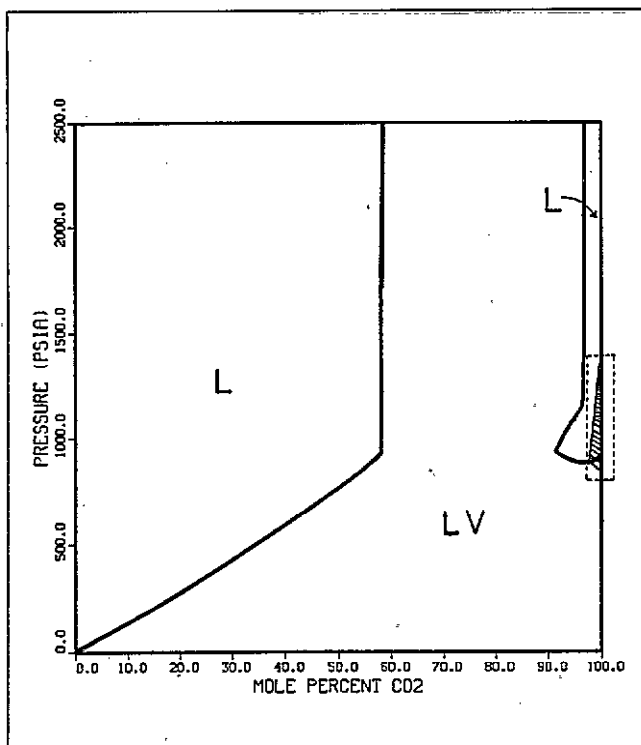


Fig. 7—Phase diagram for mixtures of oil and CO₂. Region L is the homogeneous liquid phase area and LV is the liquid/vapor phase-equilibrium area. Asphaltene precipitation occurs inside the dashed area.

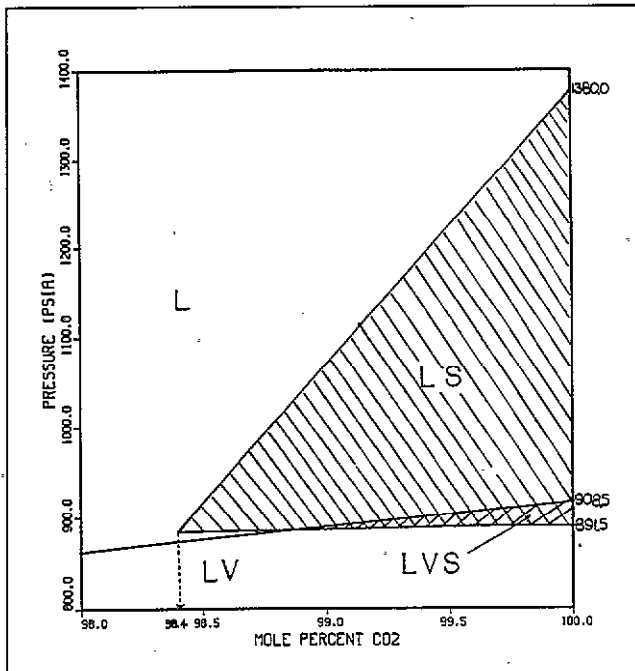


Fig. 8—Phase diagram for oil/CO₂ mixtures. Expanded scale version of Fig. 7 in the regions where asphaltene deposition occurs. Region L is the homogeneous liquid-phase area, LV is the liquid/vapor phase-equilibrium area, LS is the liquid/solid (asphaltene) phase-equilibrium area, and LVS is the liquid/vapor/solid (asphaltene) phase-equilibrium area. Asphaltene precipitation occurs in the LS and LVS areas.

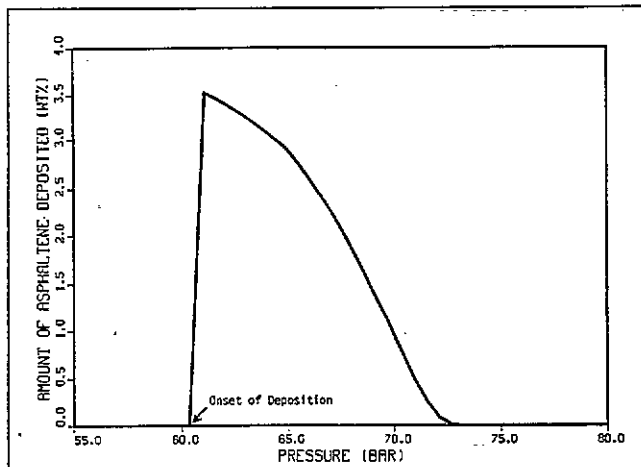


Fig. 9—Pressure dependence of the amount of asphaltene deposition for a given oil/CO₂ mixture with known composition ($x_{CO_2} = 0.99$).

The proposed model generally is applicable for predicting organic deposition (asphaltene, wax, diamantine, etc.) from reservoir fluids under the influence of a miscible solvent at various temperatures, pressures, and compositions. In applying this theory, it may be necessary to use a multiparameter concentration-distribution function to account for various families of precipitating organic compounds in the reservoir fluid.

Nomenclature

- a, b = constants
- f = parameter defined in Eq. 3
- F = distribution function of asphaltene with respect to molecular weight
- F_a = acentric factor

- ΔH = enthalpy change
- ΔH_p = partial enthalpy change
- k = interaction parameter
- M = molecular weight
- n = total mole number
- N_c = coordination number between two successive segments in asphaltene molecules
- N_s = segment number
- p = pressure
- R = universal gas constant
- T = temperature, °C
- ΔU^v = molar internal energy change of vaporization
- V = total volume
- V_f = volume fraction
- V_M = molar volume
- W_{At} = total weight of asphaltene in petroleum crude oil
- W_{Ad} = weight amount of asphaltene deposited from petroleum crude oil
- x = mole fraction
- α = parameter in gamma distribution function
- β = parameter in gamma distribution function
- δ = solubility parameter
- η = variance of gamma distribution function
- μ_c = chemical potential
- ρ = density

Subscripts

- A = asphaltene
- A_i = i th fraction of asphaltene with respect to molecular weight
- A_0 = initial value of continuous distribution function of asphaltene
- B = mixture of asphaltene-free crude oil and solvent
- c = critical property
- C = original petroleum crude oil
- f = fraction

- i, j = component identifications
- m = mass
- mix = mixture

Superscripts

- E = excess
- L = solvent-rich liquid phase
- O = standard state
- S = solid phase
- = average property over continuous distribution function of asphaltene

Acknowledgments

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Appendix A—Derivation of Eq. 3

The expression for f given by Eq. 3 is more general than the expression originally proposed by Scott and Magat,³ $f=1/N_c+kV_{MB}(\delta_A-\delta_B)^2/RT$. To derive Eq. 3, we may start with the van der Waals EOS for mixtures:

$$p=RT/(V_{Mmix}-b_{mix})-a_{mix}/V_{Mmix}^2 \quad (A-1)$$

where $a_{mix}=\sum_i \sum_j x_i x_j a_{ij}$ and $b_{mix}=\sum_i \sum_j x_i x_j b_{ij}$. The reason for the choice of the van der Waals EOS is its simplicity and the fact that van der Waals mixing rules for a_{mix} and b_{mix} are quite accurate.²⁷ Because

$$(\partial U/\partial V_M)_T=T(\partial p/\partial T)_{V_M}-p=a_{mix}/V_{Mmix}^2 \quad (A-2)$$

for the van der Waals EOS, then

$$\Delta U_v = \int_{V_M}^{\infty} (a_{mix}/V_{Mmix}^2) dV_M = a_{mix}/V_{Mmix} \quad (A-3)$$

Therefore, the solubility parameter is given by

$$\delta \equiv (\Delta U_v/V_M)^{1/2} = a_{mix}^{1/2}/V_{Mmix} \quad (A-4)$$

where ΔU_v = internal energy change of vaporization. The combining rule for parameter a_{ij} is

$$a_{ij} = (1-k_{ij})(a_{ii} a_{jj})^{1/2} \quad (A-5)$$

where a_{ii} = energy parameter of pure Component i . The interaction parameter for $i=j$, $k_{ij}=0$, is nonzero when $i \neq j$. By combining Eqs. A-1 through A-5 and using the volume fraction $V_{fi} = x_i V_{Mi}/V_{Mmix}$, one can get

$$\delta_{mix}^2 = \sum_i \sum_j x_i x_j (1-k_{ij})(a_i a_j)^{1/2} / V_M^2 = \sum_i \sum_j (1-k_{ij}) V_{fi} V_{fj} \delta_i \delta_j \quad (A-6)$$

It can be also shown that the molar excess internal energy change of mixing is

$$\Delta U_{mix}^E = -\Delta U_{Vmix} + \sum_i x_i \Delta U_{vi} = -V_{Mmix} \sum_i \sum_j (1-k_{ij}) V_{fi} V_{fj} \delta_i \delta_j + V_{Mmix} \sum_i V_{fi} \delta_i^2 \quad (A-7)$$

Assuming that the molar excess volume change of mixing is zero at constant pressure, we can obtain the excess enthalpy change of mixing with

$$\Delta H_{mix}^E = (\sum_i n_i) (\Delta U_{mix}^E - \Delta(pV_M)_{mix}^E) = (\sum_i n_i) \Delta U_{mix}^E \quad (A-8)$$

The partial molar excess enthalpy change of mixing for Component l is

$$\Delta H_{pl}^E = (\partial \Delta H_{mix}^E / \partial n_l) = V_{Ml} [\sum_i \sum_j (1-k_{ij}) V_{fi} V_{fj} \delta_i \delta_j - 2 \sum_i (1-k_{il}) V_{fi} \delta_i \delta_l + \delta_l^2] \quad (A-9)$$

For a binary system, the partial molar excess enthalpy change of mixing for Component B can be reduced to

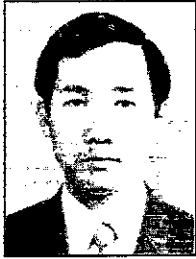
$$\Delta H_{pB}^E = V_{MB} (V_{fA})^2 [(\delta_A - \delta_B)^2 + 2k_{AB} \delta_A \delta_B] \quad (A-10)$$

According to the Scott and Magat theory, parameter f^L consists of two terms: a term $(1/N_c)$ resulting from entropy of mixing and a term $\{\Delta H_{pB}^E/[RT(V_{fA})^2]\}$ resulting from the heat of mixing:

$$f^L = 1/N_c + \Delta H_{pB}^E/[RT(V_{fA})^2] \quad (A-11)$$

By substituting Eq. A-10 into Eq. A-11, we derive the expression for f^L in Eq. 3.

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Appendix B—Special Case of a Homogeneous Asphaltene Model

When asphaltene is considered as a single (homogeneous) compound, the segment numbers are all identical ($\bar{N}_{sA} = \bar{N}_{sA}^L = \bar{N}_{sA}^S = N_{sA}$), the molecular weight is equal to the average molecular weight ($M_A = \bar{M}_A$), and the distribution function is $F(M_{Ai}) = \delta_D(M_{Ai} - \bar{M}_A)$, where δ_D is the Dirac delta function ($\delta_D = \infty$ when $M_{Ai} = \bar{M}_A$ and $\delta_D = 0$ when $M_{Ai} \neq \bar{M}_A$). Then Eq. 17, the total volume fraction of asphaltene in the liquid phase in equilibrium with the solid phase, will reduce to

$$V_{fA}^L = \exp[(N_{sA} - 1)V_{fB}^L - N_{sA} f^L (V_{fB}^L)^2], \dots \text{(B-1)}$$

$$\text{where } V_{fB}^L = 1 - V_{fA}^L. \dots \text{(B-2)}$$

Furthermore, the term $1/N_c$ in Eq. 3 disappears for the case of a homogeneous chain polymer of uniform molecular weight in a single uniform solvent. With $k_{AB} = 0$ and the $1/N_c$ term in Eq. 3 removed, after some manipulations, the total volume fraction of asphaltene in the liquid phase in equilibrium with the solid phase for a homogeneous model can be obtained as²⁰

$$V_{fA}^L = \exp[-1 + V_{MA}/V_{Mmix} - V_{MA}(\delta_A - \delta_{mix})^2/RT], \dots \text{(B-3)}$$

where δ_{mix} is defined as the solubility parameter of the crude oil mixture: $\delta_{mix} = V_{fA}^L \delta_A + V_{fB}^L \delta_B$.

SI Metric Conversion Factors

atm	× 1.013 250*	E+05	= Pa
bar	× 1.0*	E+05	= Pa
°F	(°F - 32)/1.8		= °C
psi	× 6.894 757	E+00	= kPa
°R	°R/1.8		= K

*Conversion factor is exact.

SPERE

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Table 1. Data of the tank oil no.1 under study

The compositions of the tank oil¹⁹

Compound	mole %
Methane	0.10
Ethane	0.48
Propane	2.05
i-butane	0.88
n-butane	3.16
i-pentane	1.93
n-pentane	2.58
Hexanes	4.32
Heptane-plus	84.50
Average molecular weight of tank oil ¹⁹	221.5
Specific gravity of tank oil ¹⁹	0.873
Average mass density of asphaltene ²³ (g/cm ³)	1.2
Average molecular weight of asphaltene ²³	4800.0
Initial molecular weight of asphaltene ³	500.0 (assumed value)
Coordination number of asphaltene ¹²	3.5 (assumed value)

The solubility parameter (δ_A) of asphaltene¹⁹ [MPa^{0.5}]

$$\delta_A = 20.04 (1 - 1.07 \times 10^{-3} T), \quad T \text{ is in } ^\circ\text{C}$$

Table 2. Properties of C₆ AND C₇₊ pseudocomponents

	C ₆	C ₇₊
Critical temperature (°K)	506.6	771.2
Bubble point temperature (°K)	337.0	585.0
Molecular weight	84.0	249.9
Critical pressure (atm)	32.3	16.7
Acentric factor	0.281	0.639
Density (g/cc)	0.685	0.868

Table 3. Parameters in the model

Interaction parameter	$K_{AB} = -7.8109 \times 10^{-3} + 3.8952 \times 10^{-5} \langle M_B \rangle$
Total amount of asphaltene (wt% of tank oil)	$w_{AT} = 4.0234$
Variance of the distribution function	$\sigma = 4.9223 \times 10^6$

The above parameters are calculated by minimizing the differences between the experimental titration data of n-pentane and n-decane¹⁹ and the present predictive model.

Table 4. The experiment vs. prediction for the onset and amount of asphaltene deposition from the tank oil

Dilution Ratio (cm ³ diluent/g tank oil)	n-C ₅		n-C ₇		n-C ₁₀	
	EXP ^a	CAL ^a	EXP	CAL	EXP	CAL
1.35						O.F
1.40				O.F	O.F	
1.90	N.T ^b	O.F ^c				
2.22			O.F			
5	-	3.31	1.53	1.52	1.34	1.30
10	3.61	3.67	1.82	2.28	1.45	1.53
20	3.79	3.75	1.89	2.43	1.50	1.45
50	3.87	3.73	1.87	2.29	-	1.13

The experimental titration data (wt% tank oil) are taken from the Ref.19.

a; EXP, experimental values; CAL, calculated values.

b; N.T denote that Onset of asphaltene deposition is not determined.

c; O.F denote the Onset of flocculation.

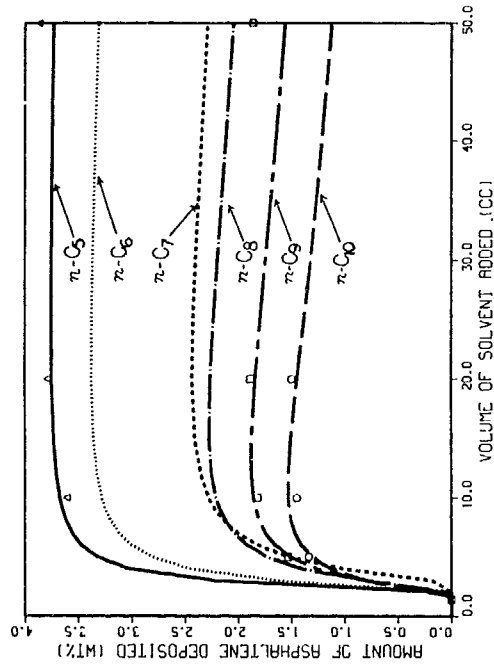


Fig. 1—The prediction of the amount of asphaltene deposition from Tank Oil No. 1 vs. the volume of six different n-paraffin solvents. The experimental asphaltene deposition data (Ref. 19) due to n-pentane, n-heptane, and n-decane additions are shown by Δ , \square , \circ , respectively.

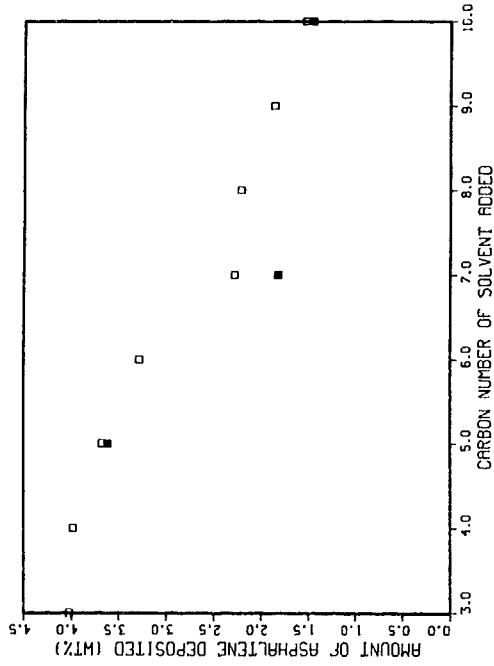


Fig. 2—Effect of n-paraffin solvent chain length on the amount of asphaltene deposition. The volume of all the n-paraffin solvents added is 10.0 cc. Experimental data (Ref. 19) are shown by \blacksquare and the predictions are reported by \square .

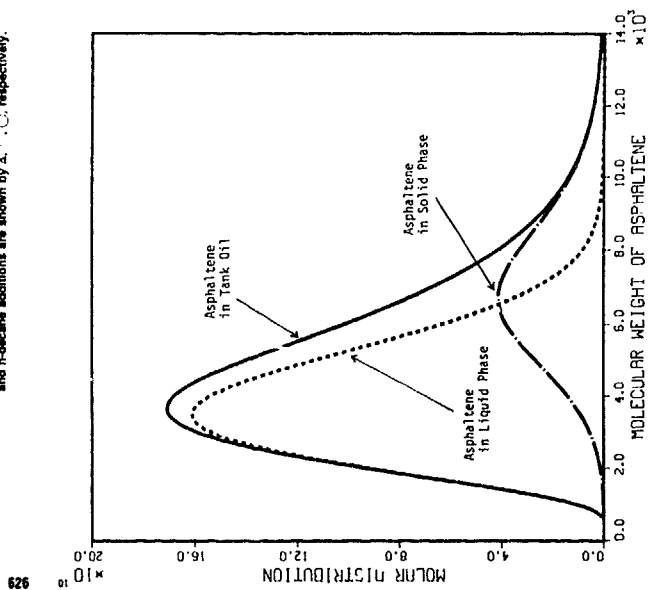


Fig. 3—Relations between molar concentration distributions of asphaltene in different phases in equilibrium resulting from the addition of a given amount of the miscible solvent (5.0 cc n-heptane) to 1 gram of the tank oil.

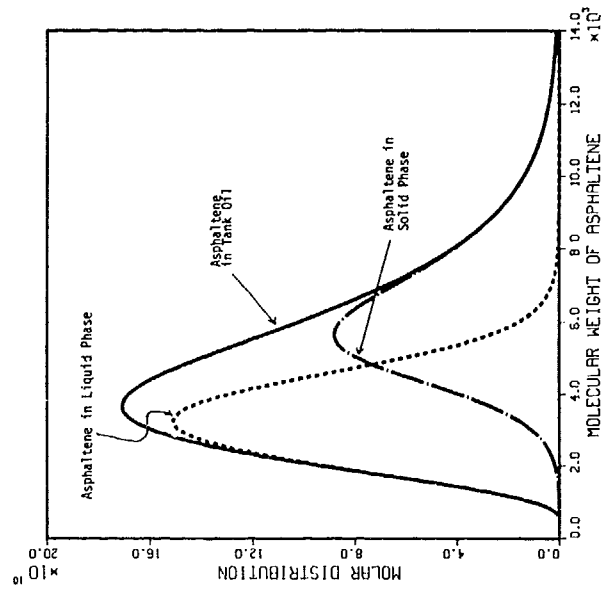


Fig. 4—Relations between molar concentration distributions of asphaltene in different phases in equilibrium resulting from the addition of a given amount of the miscible solvent (20.0 cc n-heptane) to 1 gram of the tank oil.

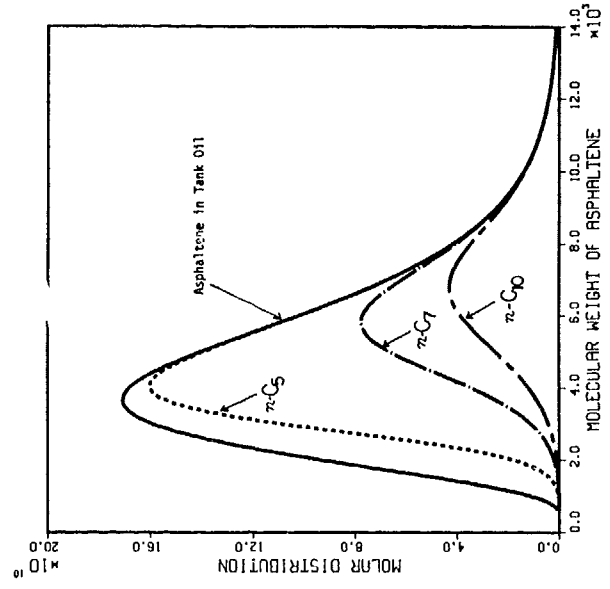


Fig. 5—Comparison of molar concentration distributions of asphaltene in the solid phase for the different precipitating solvents. The volume of all precipitating solvents added is 10.0 cc.

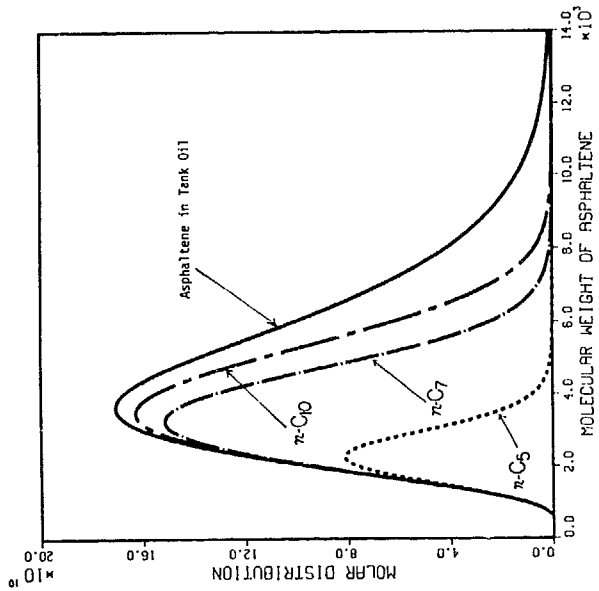


Fig. 6—Comparison of molar concentration distributions of asphaltene in the liquid phase for different precipitating solvents. The volume of precipitating solvents added is 10 cc.

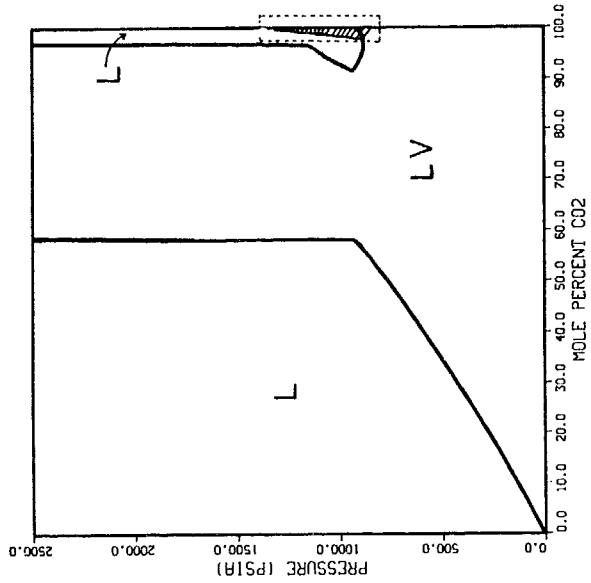


Fig. 7—Phase diagram for mixtures of oil and carbon dioxide. Region L is the homogeneous liquid phase area and LV is the liquid-vapor phase equilibrium area. Asphaltene precipitation occurs inside the dashed area.

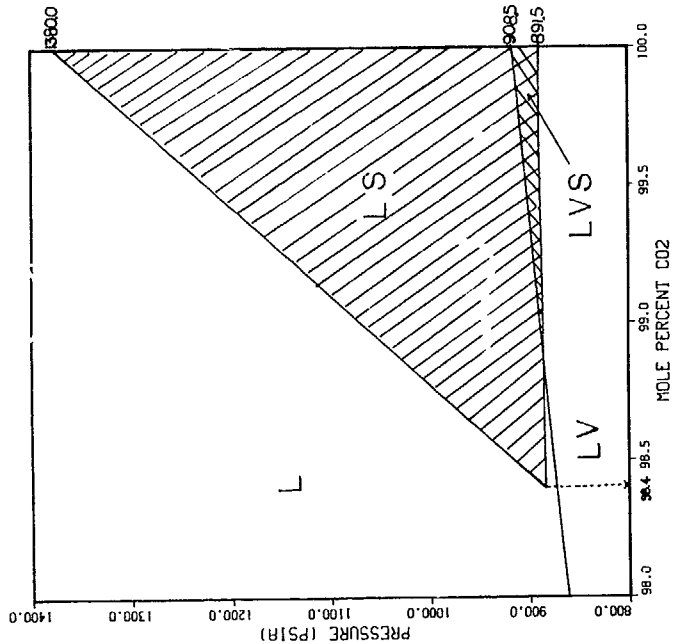


Fig. 8—Phase diagram for mixtures of oil and carbon dioxide. This figure is the expanded scale version of Fig. 7 in the regions where asphaltene precipitation occurs. Region L is the homogeneous liquid phase area, LS is the liquid-solid (asphaltene) phase equilibrium area, LVS is the liquid-vapor-solid (asphaltene) phase equilibrium area, and LV is the liquid-vapor phase equilibrium area. Asphaltene precipitation occurs in the LS and LVS areas.

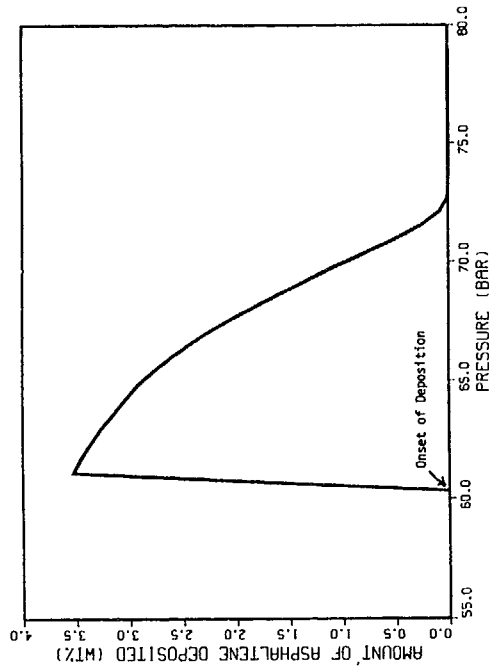


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