



SPE 27070

Modeling and Prevention of Asphaltene and Other Heavy Organic Deposition in Oil Wells

G.Ali Mansoori, U. of Illinois at Chicago

SPE Member

This paper was prepared for presentation at the III Latin American/Caribbean Petroleum Engineering Conference held In Buenos Aires, Argentina, 27-29 April 1994.

ABSTRACT

Well-head production of petroleum can be significantly affected by flocculation, deposition, and plugging of asphaltene, paraffin/wax, and/or diamondoid inside the well. The economic implications of such a formation damage are tremendous. In this paper a comprehensive mechanism and predictive model for such compounds in the oil wells is presented. This model is based on the macromolecular theory of polydisperse polymer and colloidal solutions, kinetics of aggregation, electrokinetic transport phenomena, and phase behavior of multicomponent mixtures.

One question of interest in the oil industry is "when" and "how much" heavy organics will flocculate out under certain conditions. Since a petroleum crude generally consists of a mixture of hydrocarbons and heavy organics it may be necessary to look at this problem from a more fundamental point of view than it has been the practice in the past. In this paper the author presents the cause and effect mechanisms of such depositions and introduces mathematical models to be used for preventive measures in various cases of petroleum production, transportation, and processing.

With the application of the proposed models a number of predictive case studies are made. It is shown that with proper plannings in the production scheme, consideration of the characteristics of the producing petroleum, injection fluid, well casing, and the reservoir it is possible to choose a formation-damage-free production scheme.

References and illustrations at end of paper

INTRODUCTION

The need for understanding the nature of heavy organics (asphaltenes, asphalts, bitumens, resins, diamondoids) present in crude oil and their role in the production and processing of petroleum is well recognized around the world as manifested by the extensive related research and experimental activities underway at various research centers¹⁻⁴. It appears certain that the trend in the oil industry, worldwide, will be and has already started towards the exploration, drilling, production and processing of lower quality crude and use of secondary and tertiary methods for recovering more oil from existing reservoirs. Gas injection, re-injection and miscible flooding of oil reservoirs is an economically viable technique. One of the most common problems in such recovery processes is the possibility of poor reservoir volumetric sweep efficiency because of channeling and viscous fingering. This may be caused by the large difference between the mobilities of the displacing and displaced fluids. Blending or introduction of a miscible fluid in petroleum, in general, will produce a number of alterations in its flow and phase behavior as well as the reservoir rock and conduit characteristics. One such alteration is the heavy organic precipitation, which ultimately affects the productivity of a reservoir in the course of oil production or flow rate of the oil in a conduit (well or pipeline). In most such circumstances heavy organic precipitation may result in plugging or wettability reversal in the conduit and reservoir⁵⁻⁸.

MECHANISMS OF DEPOSITION

Understanding the mechanism of the heavy organic deposition would result in more economical, environmentally sounder, and speedier oil production,

transportation, and processing technologies. The kind and amount of depositions of heavy organics from petroleum fluids vary depending on the hydrocarbons present in oil and the relative amounts of each family of heavy organics⁶⁻¹⁰. Four different effects (mechanisms) are recognized for such depositions. One or more of these mechanisms would describe the organic depositions that may occur during oil production, transportation or processing.

I. Polydispersivity Effect

The degree of dispersion of heavy organics in oil depends upon the chemical composition of petroleum^{10,11}. The ratio of polar/non-polar and light/heavy molecules and particles in petroleum (Figure 1) are the factors primarily responsible for maintaining the stability of the polydisperse oil mixture. Deposition of heavy organics can be explained by an upset in the polydisperse balance of oil composition.

Any change in temperature, pressure, and composition, such as addition of a miscible solvent to oil as demonstrated by Figure 2, may destabilize the polydisperse oil. Then the heavy and/or polar fractions may separate from the oil mixture into another liquid phase or into a solid precipitate. Segments of the separated fractions which contain sulfur, nitrogen, oxygen and/or hydrogen bonds could start to flocculate and as a result produce the irreversible heavy organic deposits which may be insoluble in solvents.

II. Colloidal Effect

Some of the heavy organics (specially asphaltenes) will separate from the oil phase into an aggregate (large particles) and then will remain suspended in oil by some peptizing agents, like resins, which will be adsorbed on their surface and keeping them afloat as demonstrated by Figure 3. Stability of such steric colloids is considered to be a function of concentration of the peptizing agent in the solution, the fraction of heavy organic particle surface sites occupied by the peptizing agent, and the equilibrium conditions between the peptizing agent in solution and on surface of heavy organic particles. The amount of peptizing agent adsorbed is primarily a function of its concentration in the oil¹¹⁻¹⁸.

III. Aggregation Effect

A concentration variation of a peptizing agent (such as resins) in oil will cause its adsorbed amount on surface of heavy organic particles to change. The peptizing agent

concentration in oil may drop to a point at which its adsorbed amount would not be high enough to cover the entire surface of heavy organic particles as shown by Figure 4. This may then permit the heavy organic particles to come together (irreversible aggregation), grow in size (see Figure 5), and flocculate. The nature and shape of the resulting aggregates will determine their effect on the behavior of the petroleum fluids^{11, 19-22}. For example, the irreversible aggregates of asphaltene are considered to follow an aggregation growth pattern¹⁹ shown by Figure 6

IV. Electrokinetic Effect

When the oil is flowing in a conduit (porous media, well, pipeline, etc.) there is an additional effect (electrokinetic effect) to be considered in the deposition of its heavy organic constituents^{18,23,24}. This is because of the development of an electrical potential difference along the length of the conduit due to the motion of charged particles. This electrical potential difference could then cause a change in the charged and colloidal particles further down the conduit, the ultimate result of which is their untimely deposition and plugging of the conduit as shown by Figure 7. The factors influencing this effect are the electrical and thermal characteristics of the conduit, flow regime, flowing oil properties, characteristics of the polar heavy organics and colloidal particles, and blending of the oil. Depending on the operation and the kind of heavy organic present in oil one or more of the effects described above will cause heavy organic depositions^{8,18}. In what follows a number of mathematical models will be presented to deal with heavy organic deposition from petroleum fluids.

MODELING OF HEAVY ORGANIC DEPOSITION FROM PETROLEUM FLUIDS

Solution of the heavy organic deposition problem calls for detailed analyzes of heavy organic containing oils from the microscopic standpoint and development of molecular models which could describe the behavior of heavy organics in hydrocarbon mixtures. From the available laboratory and field data it is proven that the heavy organics which exist in oil generally consist of very many particles having molecular weights ranging from a few hundred to several hundred thousands²⁵⁻²⁹. As a result distribution-function curves are used to report their molecular weight distribution. Most of the heavy organics present in the oil deposit due to the first order phase transitions from liquid to solid state. However, this is not generally the case for asphaltene particles. The high affinity of asphaltene

particles to association with one another, their absorpsivity to resins, and their extensively wide range of size distribution suggest that asphaltenes are partly dissolved and partly in colloidal state (in suspension) in oil peptized (or stabilized) primarily by resin molecules that are adsorbed on asphaltene surface^{4,8,11}. As a result, a realistic molecular model for the interaction of asphaltene and oil should take into account both the solubility in oil of one segment and suspension characteristic (due to resins) of another segment of the molecular weight distribution curve of asphaltene. Four different stochastic models are proposed which are based on molecular-level interaction theories of particles (monomers, polymers, and colloids) dissolved or suspended in oil. A combination of these four models is general enough to predict the heavy organic deposition from oil wherever it may occur during oil production, transportation, and processing.

A. Solubility Model of Interaction of Heavy Organics and Oil

It is generally assumed that two factors are responsible for maintaining the mutual solubility of the compounds in a complex mixture such as the petroleum crude: They are the ratio of polar to nonpolar and the ratio of the high to low molecular weight molecules in oil^{8,10,11}. Of course polar and nonpolar compounds are basically immiscible, and light and heavy molecules of the same kind are partially miscible depending on the differences between their molecular weights. However, in the complex mixture of petroleum crude or coal liquids and the like all these compounds are probably mutually soluble so long as a certain ratio of each kind of molecule is maintained in the mixture. By introduction of a solvent into the mixture this ratio is altered. Then the heavy and/or polar molecules separate from the mixture either in the form of another liquid phase or to a solid precipitate. In order to formulate the necessary model for prediction of the onset of migration and the equilibrium amount of deposition of heavy organics one can take advantage of the theories of polymer solutions. Because heavy organic particles have a wide range of size, or molecular weight, distributions one may consider them as heterogeneous polydisperse polymers and assume their fractional properties to be dependent on their molecular weights. According to the heterogeneous polymer solution theory the chemical potential, μ_{Ai} , of the i^{th} fraction of a heavy organic in a solvent (crude oil) is^{3,10}

$$\frac{(\mu_{Ai} - \mu_{Ai}^{\circ})}{RT} = \ln \phi_y + 1 - (m_y / \langle m_y \rangle) (1 - \phi_B) - m_y \phi_B + f m_y \phi_B \quad (1)$$

Subscripts A_i and B refer to the i^{th} fraction of heavy

organic and solvent, respectively, and superscript \circ stands for a standard state. To perform phase equilibrium calculations one needs to equate chemical potentials of every heavy organic fraction in the liquid phase, μ_{Ai}^L , and the solid phase^{30,31}, μ_{Ai}^S ;

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

The molecular weight distribution function of heavy organics can be defined as^{3,10}

$$F(M_{Ai}) = (1/N_A) (dn_{Ai} / dM_{Ai}) \quad (3)$$

where M_{Ai} is the molecular weight of the i^{th} fraction of heavy organic, dn_{Ai} is the differential of the number of moles of the i^{th} fraction of heavy organic whose molecular weight is in the range of M_{Ai} to $M_{Ai} + dM_{Ai}$, and N_A is the total number of moles of heavy organic. Then the total volume fraction of heavy organic in the liquid phase, ϕ_A^L , in equilibrium with the solid phase can be derived in the following form^{3,10}:

$$\phi_A^L = \int_0^{\infty} d\phi_{Ai}^L = \int_0^{\infty} [(M_{Ai} / \langle M_A \rangle) V_A^C / (V^L + V^S) \times \exp(-m_{Ai} \theta)] F(M_{Ai}) dM_{Ai} \quad (4)$$

V_A^C is the total volume of heavy organic in the crude oil ($V_A^C = V_B^C - \phi_B^L V^L$). Using this equation the onset of heavy organic migration from a petroleum crude and the amount of heavy organic remaining in a liquid mixture in equilibrium with a non-aggregated solid phase can be estimated.

B. Suspension Model of Interaction of Asphaltene and Oil

This model is based on the assumption that heavy organics in oil exist as particles suspended in oil. The causes of suspension vary with the kind of heavy organic particle^{5,8,11-13,18}. For example, asphaltene suspension is assumed to be caused by resins which are adsorbed to the surface of asphaltenes and keeping them afloat because of the repulsive forces between resin molecules in the solution and the adsorbed resins on the asphaltene surface¹⁸ (see Figure 3). Stability of such a suspension is considered to be a function of concentration of resins in the solution, the fraction of asphaltene surface sites occupied by resin molecules, and the equilibrium conditions between the resins in solution and on the asphaltene surface.

Utilization of this model requires the calculation of resin chemical potential and the resin adsorption on asphaltene particle surface and the related Langmuir

constants. The resin content of an oil mixture at its critical point is given the name critical resin concentration, $(\Phi_R)_{crit}$. When the temperature of the reservoir is too high to permit the determination of the critical resin concentration in the oil with a given solvent, the following expression is used to extrapolate $(\Phi_R)_{crit}$ to the reservoir temperature¹⁸:

$$\{(\Phi_R)_{crit}\}_{T_2} = \{(\Phi_R)_{crit}\}_{T_1} \times (\alpha)^{[(T_2 - T_1)/T_2 T_1]} \quad (5)$$

where α is a constant determined from the experimental data. The amount of resins adsorbed is primarily a function of their concentration in the liquid state (the oil). So, for a given system (i.e., fixing the type and amount of oil and asphaltenes) changing the concentration of resins in the oil will cause the amount of resins adsorbed on the surface to change accordingly. This means that one may drop the concentration of resins in the oil to a point at which the amount of resins adsorbed is not high enough to cover the entire surface of asphaltenes. This may then permit the asphaltene particles to come together (irreversible aggregation), grow in size, and flocculate.

C. Kinetics of Aggregation of Heavy Organics

A FRACTAL aggregation model is developed, which is capable of predicting the onset and amount of asphaltene deposition from petroleum crudes under the influence of miscible solvents^{21,22}. This model is based on the fact that resins play a key role in the solubilization of asphaltenes because they reduce asphaltene aggregation. In other words, the degree of solubility of asphaltenes in the oil depends on the peptizing role of resins with respect to asphaltenes (i.e., the change of resin concentration in the oil due to the addition of a miscible solvent). By utilizing the kinetic theory of FRACTAL aggregation into the theory of heterogeneous polymer solutions, it is possible to describe properly the growing mechanism of asphaltene aggregates, the growing size distributions of asphaltene, and the geometrical aspect of asphaltene aggregation in oil due to several factors^{21,22}. One 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 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 asphaltene clusters would stick rigidly to each other.

That is, a cluster A_i of mass m_i colliding with a cluster A_j 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^{21,22}.



where K_{ij} is a concentration-independent kinetic (or collision) kernel which describes the aggregation mechanism. 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

$$R_{ij} = K_{ij} C_i C_j; \quad C_i = n_i / N_0 \quad (7)$$

where n_i is the number of clusters of mass m_i (containing i asphaltene particles of unit mass m). Since the population of the resulting cluster k ($k=i+j$) increases by all collisions between i - and j -clusters and decreases when a k -cluster combines with another cluster, then $C_k(t)$ will satisfy^{21,22}

$$\frac{\partial C_k(t)}{\partial t} = (1/2) \int_0^k K(k-x, x) C(x, t) C(k-x, t) dx - C_k(k, t) \int_0^\infty k(k, x) C(x, t) dx \quad (8)$$

A major advantage of this coagulation equation is that many analytic results can be obtained from it. The kinetic theory of FRACTAL aggregation process can be utilized in order to describe properly the growing size distribution of clusters of asphaltene particles due to the influence of miscible solvents^{19,21,22}. The analytic equation for the "reduced" size distribution of clusters of asphaltene molecules can be shown as^{21,22}:

$$F(y; C_R) = (1-2w)^{1-2w} y^{-2w} \exp[-(1-2w)y] / \Gamma(1-2w) \quad (9)$$

where $y = m / \langle m \rangle$ and $w = w(C_R)$. Utilization of the kinetic aggregation of diffusive clusters has enabled us to relate the concentration of resin in a mixture of oil and a miscible solvent with the growing size distribution of clusters of asphaltene particles^{19,21,22,32-34}.

D. Electrokinetic Deposition of Particles in the Well and Pipeline

This model deals with heavy organic flocculation caused by the streaming potential generated by the flow of oil containing charged solid particles^{8,18}. It has been

proven experimentally^{13,23} that charged suspended particles, such as asphaltene colloids, present in solutions will flocculate out when placed under the influence of an electrical field. Furthermore, in general, if the streaming potential generated during flow of oil through reservoir pores or well tubings and pipes is large enough, it could assist in flocculating asphaltenes and other charged particles due to electrodeposition^{8,13,18,23}.

As the oil enters the flow conduit (well or pipeline) asphaltene particles begin to get attached to the wall where a phase separation occurs leaving the two phases oppositely charged (e.g., the asphaltene phase positively and the oil phase negatively charged, for the case of Figure 8). As the oil continues to flow downstream more phase separation occurs and the charge difference between the two phases grows. Hence, a potential field is set up between the wall and the bulk phase and also between the inlet and exit of the conduit. The transfer of charged asphaltene particles with the flow of oil is equivalent to a net current or a "streaming current" and therefore to a potential difference. This potential difference opposes the mechanical transfer of charge. For the system shown in figure 8, where the particles are positively charged, the potential is set up as negative upstream and positive downstream, if it is to oppose the flow of the charged asphaltene particles. This potential difference causes the particles to tend to flow backwards or one may say it causes asphaltene particle upflow diffusion or back-conduction. The charge transfer due to back-conduction is called "leak current".

At equilibrium, when the asphaltene particles tend to remain stationary because of the two opposing forces, the potential difference is called streaming potential. For example, the streaming potential corresponding to the turbulent flow in a pipe is¹⁸:

$$E = 4.95 \times 10^{-3} \left[\frac{16}{3} \epsilon \zeta \frac{1}{r_p} \right] \left[\frac{d^{0.75} L \rho^{0.75}}{\mu^{0.75} k} \right] u_{\text{avg}}^{0.75} \quad (10)$$

where μ is viscosity of the medium, ζ is the zeta potential of asphaltene particles, L is length of the pipe, ϵ is permittivity of oil, r_p is radius of the particle, and u is the electrophoretic velocity of the particle. By application of the streaming potential equation it is possible to determine the flow conditions under which charged heavy organic deposition and plugging of pipes and wells would occur.

DISCUSSION AND CONCLUSION

Depending on the kinds of heavy organics present in crude oil and the operations which the crude oil goes through in its production, transportation, and processing one or more of the models presented in this report could

be used for deposition prediction. While the paraffin deposition is mostly due to lowering the temperature of the crude, asphaltene and resin depositions are due to variety of causes as mentioned above. However, since all the heavy organics and hydrocarbon families of the crude are polydisperse compounds the phenomena of heavy organic precipitation will be more complex than the case of precipitation of a monodisperse heavy organic.

By utilizing the above mentioned mechanisms and models a comprehensive package of computer programs and database, named ASPHRAC, has been developed by the author which calculates various properties of petroleum fluids containing heavy organics. This package is based on the following principles: Statistical mechanical mixing rules and conformal solution equations of state, polydisperse polymer solution theories, polydisperse thermodynamics and various continuous mixture phase equilibrium algorithms, electrokinetic phenomena, transport phenomena, colloidal solution theory, and FRACTAL kinetics of aggregation theories. This package is general enough to predict the heavy organic-oil-wall interaction problems wherever they may occur during oil production, transportation or processing. The emphasis of the package is on the prediction of the behavior of asphaltenes, resins, and paraffin-waxes and their role in the production, transportation, and processing of natural and synthetic hydrocarbons. This package can be utilized for:

(i). Reservoir and production engineering in oil recovery simulation studies and design of well completions and surface facilities.

(ii). Research and process engineering in the design and performance evaluation of crude, bitumen, and heavy oil related facilities and processes.

(iii) Petroleum engineering and refining processing in the design of cost-effective anti-foulants for heavy organic fouling mitigation in various processes, estimation of wettability reversal³⁵ of surfaces due to asphaltene deposition.

This package is already tested for the following cases with success:

a. Prediction of the onset, amount, size distributions, and re-dissolving conditions of asphaltenes, resins, and other heavy organics due to: (i) Introduction of high pressure miscible gaseous or liquid solvents. (ii) Changes of composition, pressure, temperature, and well bore effects.

b. Prediction of the onset and amount of heavy organic precipitation in pipeline transport when blended with miscible fluids (such as NGL) at different blending ratios, temperatures, and flow conditions.

c. Design and selection of anti-foulants to improve heavy organic dispersivancy and, as a result, to prevent heavy organic fouling in processing equipment.

The kind of input data which may be used in the package are: Bottom-hole (and/or stock-tank oil) sample(s) composition data, oil aromaticity, oil paraffin, resin, asphaltene and diamondoid content, characterization data for C7+ fraction of oil, onset of deposition and amount of heavy organic titration data, chromatography (GC, HPLC and GPC) data of oil fractions. In what follows examples of the utility of this package is presented for various organic deposition studies.

The biggest challenge of the ASPHRAC package has been the case of asphaltene and resin deposition. This is because of the irreversibility, complexity and multi-effect nature of such depositions. Asphaltene particles are highly polydisperse as it is shown by the example of Figure 9. According to this figure, by addition of different amounts of n-pentane to a crude oil containing asphaltene different polydisperse kinds and amounts of asphaltenes will be deposited from the solution which are also different from the original asphaltene present in the oil (before adding n-pentane). One of the necessary information for miscible gas injection of an oil reservoir is the knowledge about the PX phase diagram of the crude plus miscible injectant at the temperature of the reservoir. Experimental measurement of such data in the absence of any solids deposition is rather routine, even though expensive, in the present day production research laboratories. However, simultaneous measurement of the vapor/liquid phase diagram and the onset boundary of heavy organic deposition (solid/liquid and solid/vapor phase equilibrium) would be a very costly undertaking. With the application of a comprehensive deposition computational package which incorporates all the effects discussed above it is possible to produce such a gas/liquid/solid phase diagram. As an example the predicted phase diagram of a crude oil plus carbon dioxide along with the experimental phase equilibrium data³⁶ are reported in Figure 10. Asphaltene deposition from petroleum fluids is partly due to solubility effect and partly due to colloidal phenomena. Asphaltene particles have the tendency to aggregate together in an irreversible fashion, grow in size and form new and larger particles. They have the affinity to adsorption of resins, and other charged species present in the oil. They also are electrokinetically active by causing electrostatic charge development and being affected by stronger electrostatic charges.

In order to demonstrate the effect of electrokinetics on

asphaltene deposition we have produced Figures 11-13 for a particular crude mixed with a miscible injectant (MI) at various proportions, temperatures, and pressures. Each set of these figures consist of two parts. Part (a) of each figure is the vapor/liquid/solid (asphaltene) phase diagram showing the boundaries of each phase on a PX diagram and indicating the onset of deposition of asphaltene in a stationary state. Part (b) of each figure consists of the dynamic QP phase diagram for various MI/crude proportions at a certain length of the conduit (well or pipeline). The function Q is defined as

$$Q = U_{avg}^{1.75} d^{0.75} / k \quad (10)$$

whose variation versus pressure demonstrates the dynamic effect of average crude velocity, U_{avg} , inside the well (or pipe), the effect of well (or pipe) diameter, d , and the effect of crude conductivity, k , on the onset of deposition of asphaltene. On these figures the region above each curve of constant MI/crude proportion is the asphaltene deposition region, while the region under each figure is representative of the flow without deposition. To avoid asphaltene deposition the flow condition must remain under the appropriate curves. In constructing these diagrams it has been necessary to take advantage of the various models of heavy organic deposition presented in this report. Similar calculations can be performed on every crude prone to heavy organic deposition. According to these figures with proper plannings in the production scheme, consideration of the characteristics of the producing petroleum, injection fluid, well casing, and the reservoir it is possible to choose a formation-damage-free production scheme.

It should be pointed out that most of the organic deposition problems, except for asphaltene, are reversible. This means by changing the pressure, temperature, or composition in the crude system it is possible to re-dissolve the deposits back into the solution. Asphaltene deposition, on the other hand, is an irreversible phenomenon which will not generally re-dissolve itself in the crude upon changes of condition inside the crude system. This is, of course, due to aggregation of asphaltene particles upon separation from petroleum crude.

ACKNOWLEDGEMENTS

The author would like to thank Mr. Joel Escobedo, Mr. Anand Janardhan, Dr. Sang J. Park, Dr. Kosta Leontaritis, Mr. Saido Kawanaka, Dr. Tsang S. Jiang, and Dr. Pin-Chan Du for their helpful discussions and comments. This research is supported in part by UNDP, MUCIA, ARCO Oil & Gas Company, Petrobras, and Nova Huski Research Corp.

REFERENCES

1. Lichaa, P.M. : "Asphaltene depotition problem in Venezuela crudes - usage of asphaltenes in emulsion stability", *Can. Pet. Technology, J.* (June, 1977) Oil and Sands, 609-624.
2. David, A. : "Asphaltene flocculation during solvent stimulation of heavy oils," *AICHE Symp. Ser.*, 1973, 69 (127) 56.
3. Mansoori, G.A. and Jiang, T.S. : "Asphaltene deposition and its role in enhanced oil recovery miscible gas flooding" , *Proceedings of the the 3rd European Conference on Enhanced Oil Recovery, Rome, Italy, April 1985.*
4. Mansoori G.A. : "Asphaltene Deposition : An economic challenge in heavy petroleum crude utilization and processing" , *OPEC Review*, 1988, 103-113.
5. Leontaritis, K.J. and Mansoori, G.A. : "Asphaltene deposition: a survey of field experiences and research approaches", *Journal of Petroleum Science and Engineering*, 1988, 1, 229-239.
6. Addison, G.E. : "Identification and treating of downhole organic deposits", paper SPE 18894, Presented at the 1989 Production Operations Symposium, Oklahoma City, OK, 627-632.
7. Newberry, M.E. and Barker, K.M. : "Formation damage prevention through the control of paraffin and asphaltene deposition", 1985; paper SPE 13796.
8. Escobedo, J. and Mansoori, G.A. : "Heavy organic deposition and plugging of wells (analysis of Mexico's experience);" *Proceedings of the II LAPEC, March, 1992, paper SPE 23696, Society of Petroleum Engineers, Richardson, TX.*
9. Garcia H.F., Silva L.P., Lopez A.N.: "Causas que originan la depositacion del material asfaltico en pozos del area Cretacica Chiapas-Tabasco", *Revista del Instituto Mexicano del Petroleo*, Sept 1989, 17-25.
10. Kawanaka, S. Park, S.J. and Mansoori, G.A. : "Organic deposition from reservoir fluids" *SPE Reservoir Engineering Journal*, May 1991, 185-192
11. Kawanaka S., Leontaritis, K.J., Park, S.J. and Mansoori, G.A. : "Thermodynamic and colloidal models of asphaltene flocculation", in "Oil Field Chemistry" *ACS Symposium Series # 396, 1989, Chapter 24,* American Chemical Society, Washington, D.C.
12. Ray, R.B., Witherspoon, P.A., and Grim, R.E. : "A study of the colloidal characteristic of petroleum using the ultracentrifuge", *J. of Phys. Chem.*, 1957, 61, 1296-1302.
13. Katz, D. L. and Beu, K. E. : "Nature of asphaltic substances," *Ind. Eng. Chem.*, 1945, 37, 195.
14. Witherspoon, P. A. and Winniford, R. S. : "The asphaltic components of petroleum," in *Fundamental Aspects of Petroleum Geochemistry*, (Eds.) Nagy, B. and Columbo, U. , Elsevier, New York (1967) 264-297.
15. Dickie, J. P. and Yen, T. F. : "Macrostructure of asphaltic fractions by various instrumental methods," *Analytical Chemistry*, 1967, 39 (14) 1847-1852.
16. Rogacheva, O. V., Rimaev, R. N., Gubaidullin, V. Z. and Khakinov, D. K. : "Investigation of the surface activity of the asphaltenes of petroleum residues," *Colloid J.*, 1980, 42, 490.
17. Nellensteyn, F. J. : "The colloidal structure of bitumens" in "the Science of Petroleum" A. E. Dunstan (Ed.), vol. IV, Oxford Univ. Press, London , 1983.
18. Leontaritis, K.J. and Mansoori, G.A. : "Asphaltene flocculation during oil recovery and processing: a thermodynamic-colloidal model", paper SPE 16258, *Proceedings of the 1987 SPE Symposium on Oil Field Chemistry, Society of Petroleum Engineers, Richardson, TX.*
19. Janardhan, A.S. and Mansoori, G.A. : "Fractal nature of asphaltene aggregation", *Journal of Petroleum Science & Engineering*, 1993, Vol 9, 17-27.
20. Mukhametzyanov, I. Z. and Kuzeev, I.R. : "Fractal structure of paramagnetic aggregates of petroleum pitches". *Colloid. J. , USSR*, 1991, 53 (4): 644-648.
21. Park, S.J. and Mansoori, G.A. : "Aggregation and deposition of heavy organics in petroleum crudes", *International Journal of Energy Sources*, 1988, 10, 109-125.
22. Park, S.J. and Mansoori, G.A. : "Orgainc deposition from heavy petroleum crudes (a FRACTAL aggregation theory approach)", *Proceedings of the UNITAR/UNDP 4th International Conference on Heavy Crudes and Tar Sands, Edmonton, Alberta, August 1988.*
23. Lichaa, P.M., Herrera, L. : "Electrical and other

effects related to the formation and prevention of asphaltene deposition problem in Venezuela", 1975, paper SPE 5304.

24. Del Guzman, M.; Dominguez, E.J.M. Garcia, E.J.L. : "Estudio termogravimetrico de un asfaltero"; Revista del Instituto Mexicano del Petroleo, July 1985, XVII, # 3.

25. Leontaritis, K.J. and Mansoori, G.A. : "Fast crude-oil heavy component characterization using combination of ASTM, HPLC, and GPC methods", International Journal Petroleum Science & Technology, 1989, 2, 1-12.

26. Chom, L.G. and Mansoori, G.A., (Editors) : "C7+ fraction characterization", Advances in Thermodynamics, 1988, Vol. I, Taylor & Francis Pub. Co., New York, N.Y.

27. Long, R. B. : "The concept of asphaltene," The Advances in Chemistry Series, 1981, # 195, 17.

28. McKay, J. F., Amend, P. J., Cogswell, T. E., Harsberger, P. M., Erickson, R. B., and Latham, D. R. : "Petroleum asphaltenes: chemistry and composition," The Advances in Chemistry Series # 170, 1978, 128-142.

29. Mazee, W. M. : "Physical and chemical properties of petroleum waxes," J. Inst. Petrol. London, 1958, 44(419) 401.

30. Du, P.C. and Mansoori, G.A. : "A continuous mixture computational algorithm for reservoir fluids phase behavior", paper SPE 15082, Proceedings of the 1986 California Regional Meeting of SPE, Society of Petroleum Engineers, Richardson, TX.

31. Du, P.C. and Mansoori, G.A. : "Continuous mixture computational algorithm of reservoir fluid phase behavior applicable for compositional reservoir simulation", paper SPE 15953, Proceedings of the 1986 Eastern Regional Meeting of SPE and Proceedings of the 9th SPE Symposium on Reservoir Simulation, Society of Petroleum Engineers, Richardson, TX.

32. Crickmore, P. J. and Hruska, C. : "FRACTAL geometry, the Korcak law and asphaltene precipitation", Fuel, 1993, 68: 1488-1489.

33. Lin, Jiunn-Ren, Lian, Hsienjen, Sadeghi, K. M. and Yen, T. F. : Asphalt colloidal types differentiated by Korcak distribution. Fuel, 1991, 70: 1439-1444.

34. Raghunathan, P. : "Evidence for fractal dimension in asphaltene polymers from electron spin relaxation measurements", Chemical Physics Letters, 182 (Aug.

1991): 331-335.

35. Kim, S.T.; Boudh- Hir, M.E. and Mansoori, G.A. : "The role of asphaltene in wettability reversal", Proceedings of the 1990 Annual Convention of the Society of Petroleum Engineers, paper SPE 20700.

36. Monger, T. G. and Khakoo, A. : "The phase behavior of CO₂ - Appalachian oil systems," paper SPE 10269 presented at the 1981 Annual Fall Technical Conference and Exhibition San Antonio, Texas, Oct. 5-7, 1981.



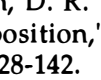
Figure 1: Microscopic level composition of a petroleum crude containing heavy organics. In here — and ~ represent the paraffinic molecules, ● represents the aromatic molecules, ○ represents the resin molecules and  represents the asphaltene molecule



Figure 2: Flocculation and precipitation of the heavy components of a petroleum crude due to the introduction of a miscible solvent

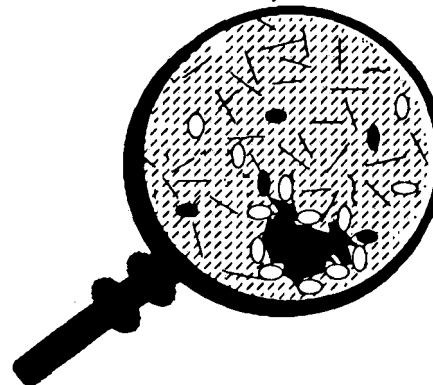


Figure 3: Steric colloidal phenomena



Figure 4: Migration of peptizing molecules (shown by black arrows) from the surface of heavy organic particles due to the change in their chemical-potential-balance between the bulk oil phase and the surface phase. This causes the potential for aggregation (white arrows) of heavy organic particles due to development of free active sites on their surfaces, and their eventual flocculation as shown below



Figure 5: Flocculation and deposition (arrow) of very large heavy organic particles



Figure 6: A possible growth pattern for asphaltene aggregates



Figure 7: Electrokinetic deposition in a pipeline

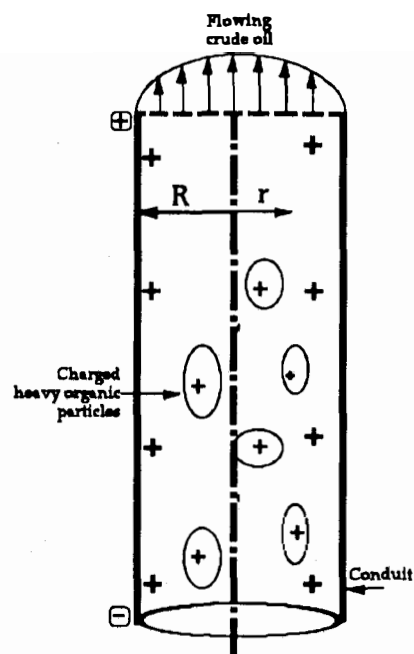


Figure 8: Schematic representation of the streaming potential generated by the flow of oil containing charged particles

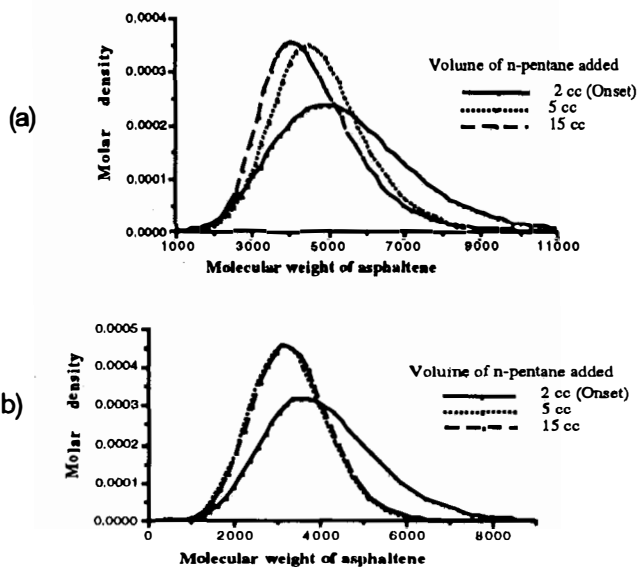


Figure 9: Molecular weight distributions of asphaltene particles as calculated by ASPHRAC in the precipitate phase (a) and in the oil phase (b) after additions of different amounts of n-pentane to the crude oil. For this particular crude oil 2 cc of n-pentane per gram of oil was needed to observe the onset of asphaltene deposition.

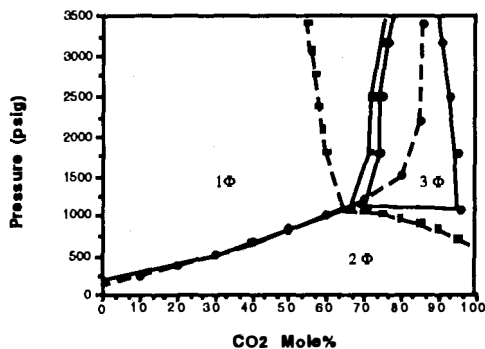


Figure 10: Phase diagram for mixtures of Brookhaven oil and carbon dioxide at 317 K. Region 1 Φ is the homogeneous liquid phase area, 2 Φ is the liquid-vapor phase equilibrium area, and 3 Φ is the solid-liquid-vapor phase area. The region to the right of the vertical hollow square tick marks and to the top of the horizontal hollow square tick marks is the predicted 3 Φ region. The 3 Φ region bounded by the solid dots is the experimentally observed³⁶ deposition region.

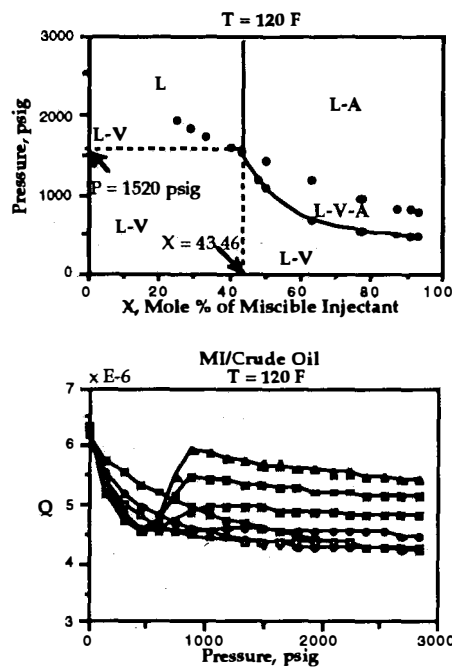


Figure 12: Static (PX) and dynamic (PQ) phase diagrams of the crude oil of Figure 11 mixed with the same miscible injectant (MI) but at 120° F and at various proportions and pressures.

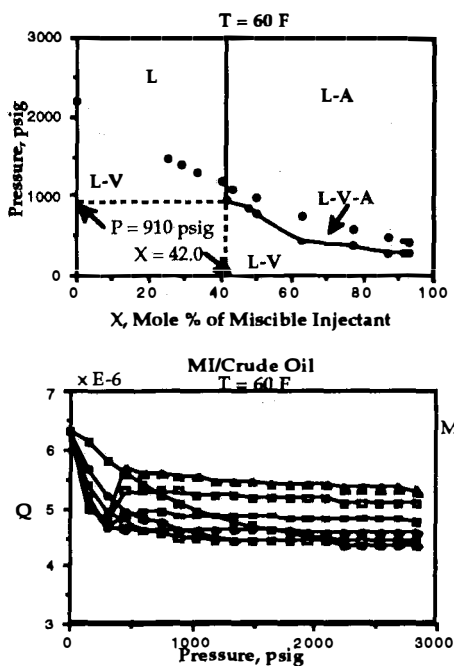


Figure 11: Static (PX) and dynamic (PQ) phase diagrams of a crude oil mixed with a miscible injectant (MI) at 60° F but at various proportions and pressures.

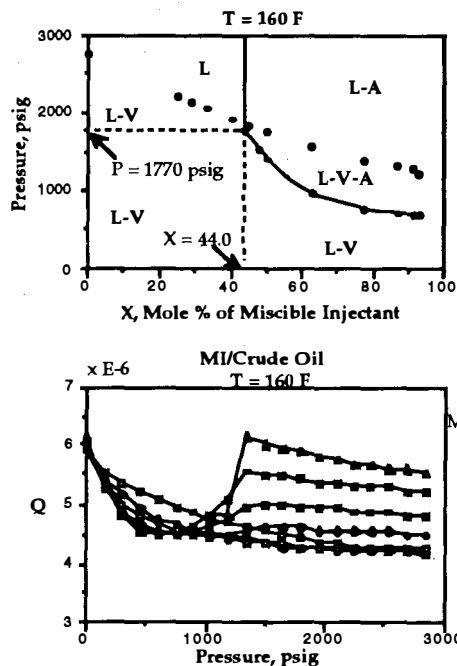


Figure 13: Static (PX) and dynamic (PQ) phase diagrams of the crude oil of Figure 11 mixed with the same miscible injectant (MI) but at 160° F and at various proportions and pressures.