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An Investigation on Asphaltene Precipitation Potential for Light and Heavy Oils, During Natural Depletion

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Abstract

Asphaltene and wax deposition during production of many Iranian reservoirs has become a serious problem. In order to investigate the asphaltene precipitation behavior of various Iranian light and heavy oils and to predict their best method of prevention and/or curing the problem a comprehensive research study was launched. This article describes the precipitation potential of various reservoir oils, (8 samples, light and heavy) during their deposition. Three-phase equilibrium calculation of NGHIEM et al., is used. In the method pure asphaltene in the oil is considered as solid. The heavy part of the oil is split as precipitating and non-precipitating. The results of the study, which compares the onset and quantity of asphaltene precipitation of the oil samples revealed; a) the precipitation potential in the light oils depends strongly on the nature of asphaltene molecules in the oil which varies from one to another. b) Light oils behave in a more complicated fashion than heavy oils. c) The volatile oils were more unstable and the ratio of precipitation to the heavy fraction of the oil is highest. The paper describes the foregoing in detail.

1. Introduction and Literature Review

A great many of the hydrocarbon accumulations in the world, by themselves, are not economic to develop or produce. In many of the more prolific hydrocarbon basins, multiple reservoirs are encountered stacked one above the other. Conventional government regulations and good petroleum practice prescribe that the production of conventional oil or gas from distinct reservoirs or pools must remain segregated in the wellbore. As the Alberta Energy and Utilities Board explains, The nature of asphaltenes and their role in the production and processing of crude oils has been the topic of numerous studies. This is due to the fact that the economics of oil production can be seriously affected by the asphaltene deposition problem. From the other hand, it is estimated that there are above 60% of crude oils remaining underground after exploiting by the present technologies within the world's oilfields.

Asphaltene is one of the major compounds responsible for various and unwanted blockage cases in the petroleum industry. Chemically asphaltenes represent complex molecules of polar, polyaromatic hydrocarbon or non-hydrocarbon but high molecular weight fractions of crude oils. However, no clear chemical formula has been reported for asphaltenes yet. Speight et al [1] concluded that asphaltenes are difficult to define even when a standard method of precipitation is applied. By definition of asphaltene is that the portion of the crude oil that is insoluble in low molecular weight of n-alkanes but soluble in benzene or toluene [2-3]. Asphaltene is considered partly dissolved and mostly kept in finely dispersed colloidal suspension particles [4]. The other high molecular weight fraction namely non-polar resins is surrounding suspended asphaltene particles and hence stabilizes its suspension. The common belief is that asphaltenes stabilized by resins are small enough in size so that their transport do not pose any threat to permeability. The ratio of polar to non-polar components and the ratio of high to low molecular weight components control the solubility of asphaltenes and resins within the crude oil. If asphaltene flocculate in situ they deposit on the rock

surfaces through either adsorption or absorption. The deposition of such large particles constitutes the real threat of naturally occurring formation damage.

Asphaltene adsorption on rock surface has been documented and attributed to the polarity of asphaltene molecules [5-6]. The most significant factors influencing asphaltene deposition are considered to be composition of the crude oil [7-8], pressure and temperature [9-11] properties of asphaltene [8-10] and conditions of wellbore hole and pipeline into which the reservoir fluid is flowing [4].

Asphaltene deposition is sequential process of the following mechanisms: (a) contact and then adsorption of asphaltene aggregates with rock surface, (b) asphaltene flocculation and deposition [7, 11,12] defined the main factors controlling asphaltene adsorption on rock surfaces to be (1) chemical and natural structure of the rock surface, (2) asphaltene and resin content of the crude oil, (3) physicochemical properties of asphaltene and resins, (4) brine pH and composition, (5) pore shape/size, and distribution, (6) pressure and temperature conditions, (7) presence of asphaltene in oil in the form of colloidal micelle, and (8) finally the ability of hydrocarbon fraction of the crude to stabilize these micelle in the oil or even to dissolve them. These studies did not cover the age time effect on asphaltene adsorption.

The most important effect of asphaltene deposition in porous media is permeability reduction. The continuous nature of the permeability reduction in flow experiments has been widely observed in the previous studies [11, 13, 14]. However, two different views exist regarding the nature of this mechanism of permeability reduction. Among in the first group, Piro et al. [14] conducted a series of flow experiments to determine the rate of asphaltene adsorption on sandstone rocks. They have reached the conclusion that asphaltene adsorption is a continuous phenomenon under dynamic conditions in which the amount of absorbed asphaltene on rock surface increases as the flowing time increases. From those in the second group, Kamath et. al. [13] conducted a series of waterflooding experiments to evaluate the asphaltene deposition in both consolidated and unconsolidated sandpacks. They concluded that permeability reduction occurred due to two distinct mechanisms. One is the smaller pore throat blocking by larger size asphaltene particles. Second is the accumulation and adsorption of smaller size particles in larger pore throats causing a gradual reduction of pore throat radii. Later, Ali and Islam [15] systematized this theory. They proved also that a continuous asphaltene precipitation damaged rock permeability of carbonate

rocks at high flow rate. Ali and Islam [15] interpreted their gained experimental data that the continuous nature of asphaltene deposition comes from the combination of adsorption and hydrodynamic/mechanical trapping of asphaltene in rock pores.

The precipitation of asphaltene aggregates can cause such severe problems as reservoir plugging and wettability reversal. The adsorption of Asphaltene aggregates at oil–water interfaces has been shown to cause the steric stabilization of (W/O) petroleum emulsions. Consequently, the oil industry is in critical need of quantitative tools and thermodynamic data to predict asphaltene solubility and aggregation as a function of crude oil composition and reservoir temperature and pressure.

Generally speaking asphaltene both decreases the conventional oil production by deposition and also causes a high percent of oil remain underground. Asphaltenes are more likely found in heavy oil reservoirs in which there are more heavy components and therefore there is a higher risk of Asphaltene deposition. However, the weight percent of asphaltene does not indicate the existence of a problem situation. There have been cases in which in spite of their low asphaltene content a serious deposition problem was encountered. In Iran, different reservoirs suffer from the precipitation problem. The Bangestan group reservoir of Ahwaz and Marun oil fields, the Kupal, Ramshir and Zagheh fields can be mentioned as examples.

2. Thermodynamic models of Asphaltene precipitation

2.1. Polymer Solution Theory

Hirschberg et. al extended the Flory- Huggins polymer solution theory to model the Asphaltene solubility in crude oils. Many investigators [3] followed their work. In this approach, the crude is assumed to be a real solution, and the Flory-Huggins equations [16] are used to account for the nonideality of asphaltene species. A combination of VLE and LLE calculations along with polymer solution theory was used to calculate the precipitation. The micellar nature of Asphaltenes was neglected.

2.2. Thermodynamic Colloidal Model

This model was proposed by Leonaritis and Mansoori [10] based on statistical colloidal thermodynamics. They assumed that Asphaltene is partially soluble and

partially in colloidal suspension within the crude mixture. They also assumed that the insoluble suspended particles are stabilized by adsorbing resins onto their surface. Resins are necessary for the asphaltenes to exist as colloids. Many experimental observations using organic solvents and crudes have shown evidences of the reversibility of the Asphaltene association process which is different from the basic assumption of this model.

2.3. EOS Model

Nghiem et. al [17-20] used a thermodynamic model to predict the precipitation. They split the plus fraction of crude oil to a number of fractions and divided the heaviest residue into a non- precipitating and a precipitating pseudo component. The PR equation of state was used to calculate the asphaltene precipitation by assigning different values of binary interaction coefficient to the precipitating component with the light components. The calculations were performed using a three-phase flash calculation algorithm. Here, the micellar nature of Asphaltenes in the crudes was neglected.

2.4. Thermodynamic Micellization Model

This model was proposed by victorov and Firoozabai [21]. It describes that most of the asphaltene molecules exist as micelles in crude oil. When low carbon normal alkenes are mixed with crude, some asphaltene molecules exist as monomers and, due to low solubility of asphaltene monomers, precipitation may result. In this model, the micellar size and composition is fixed and the different steps of transformation of asphaltene monomers to asphaltene aggregates is discussed and a minimization of Gibb's free energy concept is used to calculate micellar size growth and amount of precipitation[22].

2.5. Governing Equations

The model used in the calculations, is based on the three-phase equilibrium between liquid, vapor and pure asphaltene as solid phase [19]. The fugacity of solid phase is calculated using the solid model as below:

$$\ln f_a = \ln f_a^* + \frac{v_a (p - p^*)}{RT} \quad (1)$$

In which f_a and f_a^* are the fugacities of asphaltene at pressures P and P^* respectively, v_a is the molar volume of pure Asphaltene, R is the universal gas constant and T is the absolute temperature. The values of f_a^* and v_a

are calculated at P^* and T using the empirical data of precipitation [18].

As asphaltene is the heaviest part of the mixture, the plus fraction is split to several pseudo groups, say, C_{31}^+ . This heaviest fraction itself is divided into two precipitating and non-precipitating parts. As discussed by Nghiem et al [17-19]. the two components have identical properties and acentric factors, but different binary interaction coefficients with the light components. The precipitating component has larger interaction coefficient with the light components. With larger interaction coefficient, it is more incompatible with the light components and tends to precipitate as the amount of light components in solution increases [17].

2.5.A. Three-phase Flash Calculations

To perform the three-phase flash calculations, the following equilibrium criteria are used:

$$\ln(f_i^v) = \ln(f_i^l), i = 1, \dots, nc \quad (2)$$

$$\ln(f_{nc}^l) = \ln(f_{nc}^a) = \ln(f_a) \quad (3)$$

Along with the above equations, the mass balance gives the following equations:

$$\sum_{i=1}^{nc} \frac{(k_{iv} - 1)z_i}{1 + F_v(k_{iv} - 1) + F_a(k_{ia} - 1)} = 0 \quad (4)$$

$$\sum_{i=1}^{nc} \frac{(k_{ia} - 1)z_i}{1 + F_v(k_{iv} - 1) + F_a(k_{ia} - 1)} = 0 \quad (5)$$

In which F_a and F_v are mole fractions of vapor and asphalt phases respectively and z_i is the composition of the oil. Using the above formula the composition of each phase can be calculated.

$$y_{il} = \frac{z_i}{1 + F_v(k_{iv} - 1) + F_a(k_{ia} - 1)} \quad (6)$$

$$y_{iv} = K_{iv} * y_{il} \quad (7)$$

$$y_{nca} = K_{nca} * y_{ncl} = 1 \quad (8)$$

The algorithm for performing three-phase flash calculation is shown in Figure 1 [18]. Solving equations 2 and 3 at the same time using iterative methods, gives the fugacity of each component in each phase [19]. For calculating the composition of each phase the equations 4 and 5 should be solved using Newton's iterative

algorithm. In three-phase flash calculation algorithm the stability of solid phase is investigated using the following stability criteria:

The asphaltene phase exists if

$$Ln f_{nc}^l \geq Ln f_a \quad (9)$$

And it doesn't exist if

$$Ln f_{nc}^l < Ln f_a \quad (10)$$

2.6. Modeling the Asphaltene Precipitation

The modeling of asphaltene precipitation was performed using winprop module of computer modeling group (CMG) software. Eight oil samples were used for modeling. The samples include two volatile oil sample, three light conventional oil and three heavy oil samples. The available data for these samples mostly included saturation pressure at a constant temperature, the API of stack tank oil, the weight percent of precipitate in the stack tank and measured weight percent of precipitation at different pressures for all the samples. Here, the previous asphaltene test results undergone in Iranian scientific/academic sources were used. The measuring pressures in table 4 has been selected such that the behaviour of different oils can be best described using a few points. The parameters used for tuning of the model were volume shift parameters of the pseudo components, asphaltene molar volume and binary interaction coefficients of precipitating component with the light hydrocarbons up to C5.

2.7. Results and Discussion

The composition of eight used oil samples in this study is presented in Table 1. It shows that many of these oil samples contain carbon dioxide, nitrogen, and hydrogen sulphide. The characteristics of these oil samples were measured such as API gravity, bubble point pressure, and temperature of measurement and listed in Table 2. the asphaltene content of these eight samples was measured and reported in Table 3. Table 4 presents the pressure at which the data points were attained.

A schematic diagram of all phases of used algorithm of three phase flash calculations is shown in Fig. 1.

The CMG software was used for modeling the eight oil samples and the results were graphically presented in Figs 2-7 for oil samples 1 to 7, respectively. These figures presented both the experimental and simulation results and indicate good matching of the attained simulation results with experimental ones.

Comparison of the behaviour of samples 1 through 5 is plotted in Fig. 8 while the similar comparison of oil samples # 4 through 8 are compared in Fig 9, respectively.

The onset pressures for light crude samples are plotted versus API in Fig. 10 and similar results is shown in Fig. 11 for heavy crude samples, respectively.

2.8. Conclusions

1- Despite the fact that heavy oils are more reliable of having high potential for precipitation, the precipitation process strongly is depended on the nature of the asphaltene molecules, the amount of resins, and the interaction between light and heavy components.

2- The onset of precipitation begins at a pressure above bubble point and the amount of precipitates riches to a maximum at the saturation pressure. After that it decreases as the pressure decreases.

3- For very light oils of same precipitation potential, the amount of precipitation is more than heavy oils compared to their plus fraction contents. This is due to the higher instability of thermodynamic equilibrium and lower solubility of asphaltene in light oils.

4- For volatile oils, since the saturation pressure at reservoir temperature is high, the onset pressure of precipitation of undersaturated reservoirs containing volatile oil is expected to be higher than heavy oils, which denotes a higher necessity to check the asphaltene behaviour of this type of oils.

5- The onset pressure for both light and heavy oils increases as the API of oil increases.

Nomenclature:

f_a	fugacity of precipitated asphaltene
f_a^*	fugacity at reference pressure
f_{ij}	fugacity of fraction i in phase j
F_i	mole fraction of phase i
K_{ij}	equilibrium ratio of fractions i and j
n_c	number of oil composition
P	pressure
p^*	reference pressure
R	universal gas constant
T	absolute temperature
z_i	composition of crude oil

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Table 1- Composition of oil samples used in modeling

Oil No. Comp.	1	2	3	4	5	6	7	8
N2	0.23	0.08	0.30	0.57	0.48	0.001	1.02	1.01
CO2	8.53	7.39	1.980	2.46	2.53	0.0051	2.8	1.32
H2S	0.01	0.05	2.1	0	0	0	0.48	0.64
C1	21.62	7.48	30.34	36.37	37.92	0.5815	25.32	31.31
C2	20.8	13.1	15.94	3.47	4.02	0.097	6.65	4.32
C3	4.82	6.93	5.40	4.05	4.53	0.056	4.23	4.85
IC4	1.35	0.77	1.11	0.59	0.45	0.032	1.02	0.23
NC4	3.47	3.82	3.5	1.34	1.53	0.03	2.3	1.25
IC5	1.68	1.68	1.25	0.74	0.98	0.0244	0.88	0.38
NC5	2.11	3.58	2.17	0.83	0.83	0.032	0.71	0.81
C6	2.53	4.99	4.43	1.62	1.22	0.022	0.41	0.67
C7+	32.76	50.13	31.48	47.96	45.51	0.119	54.18	53.21

Table 2- The Characterizations of oil samples

Oil No.	1	2	3	4	5	6	7	8
S.T. API	34	30	34	16	14.1	16.4	36	26
P.b (psi)	3900	1100	2160	2380	2420	2200	3100	2800
Temperature (F)	195	220	200	210	200	220	190	230

Table 3 – Asphaltene weight percent at the stack tank

Oil No.	1	2	3	4	5	6	7	8
S.T. Asph. wt%	2.3	2.8	1.7	18	8	11.5	3.2	12.5

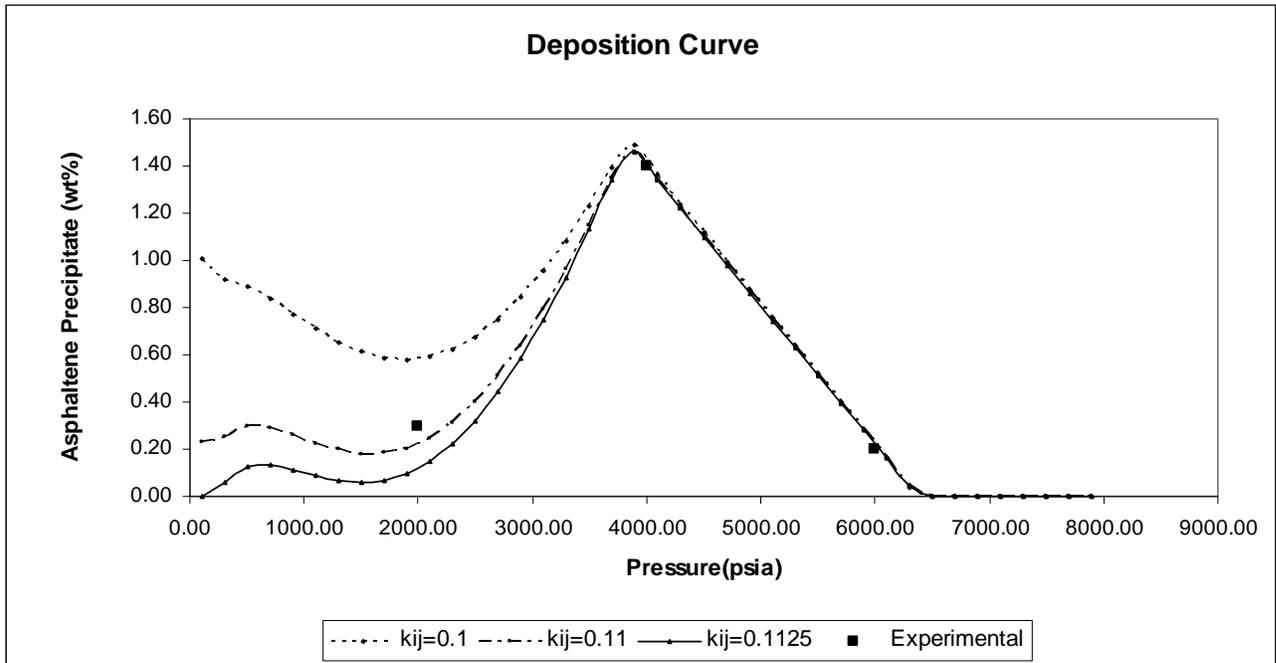


Figure 2- Precipitation curve for oil No. 1

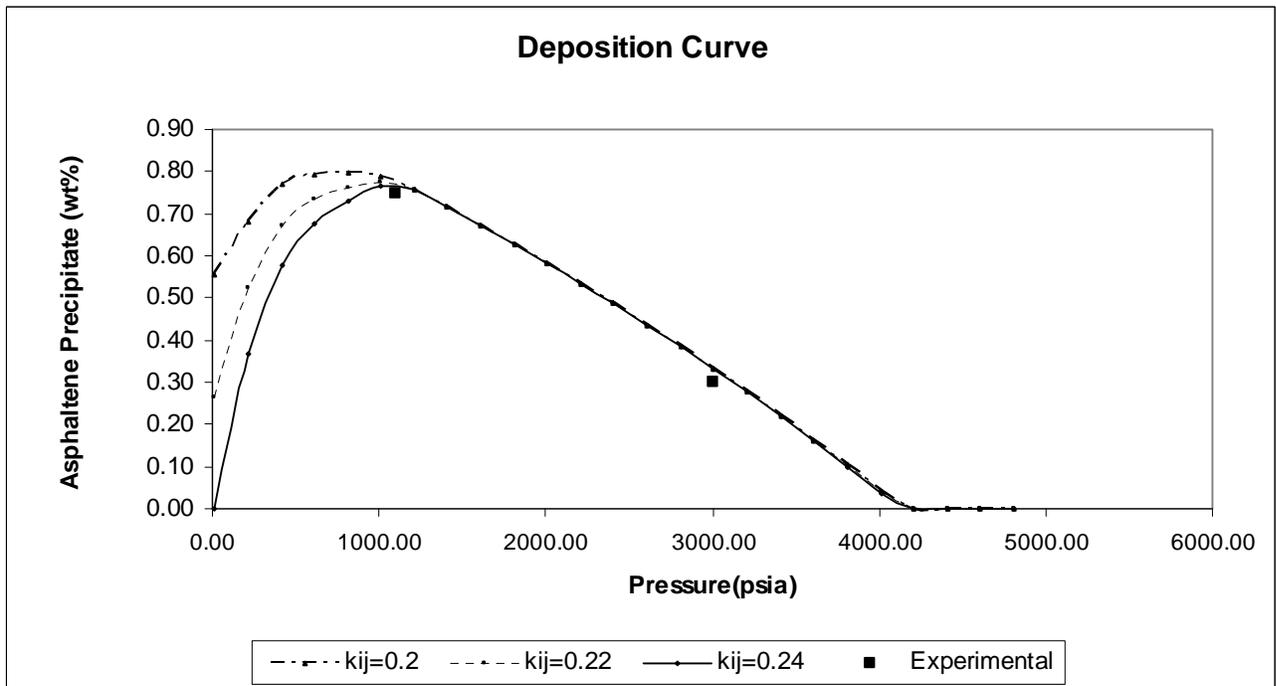


Figure 3- Precipitation curve for oil No. 2

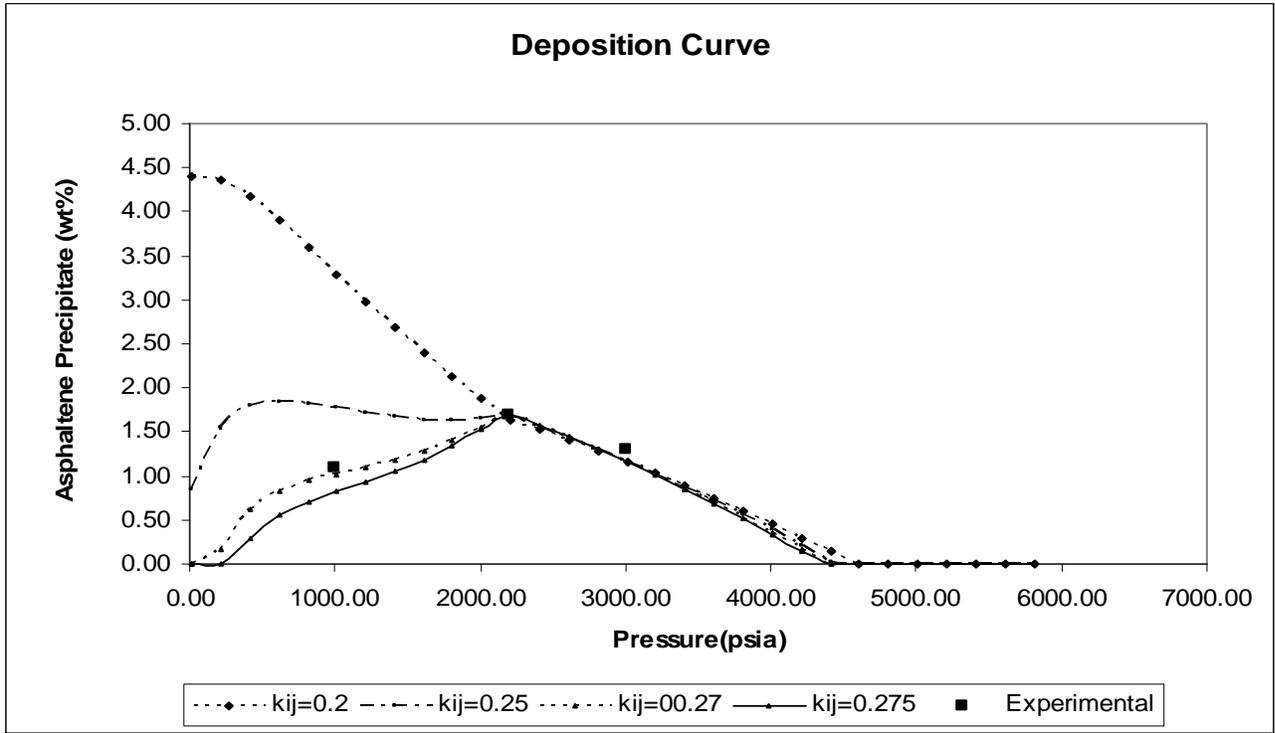


Figure 4- Precipitation curve for oil No. 4

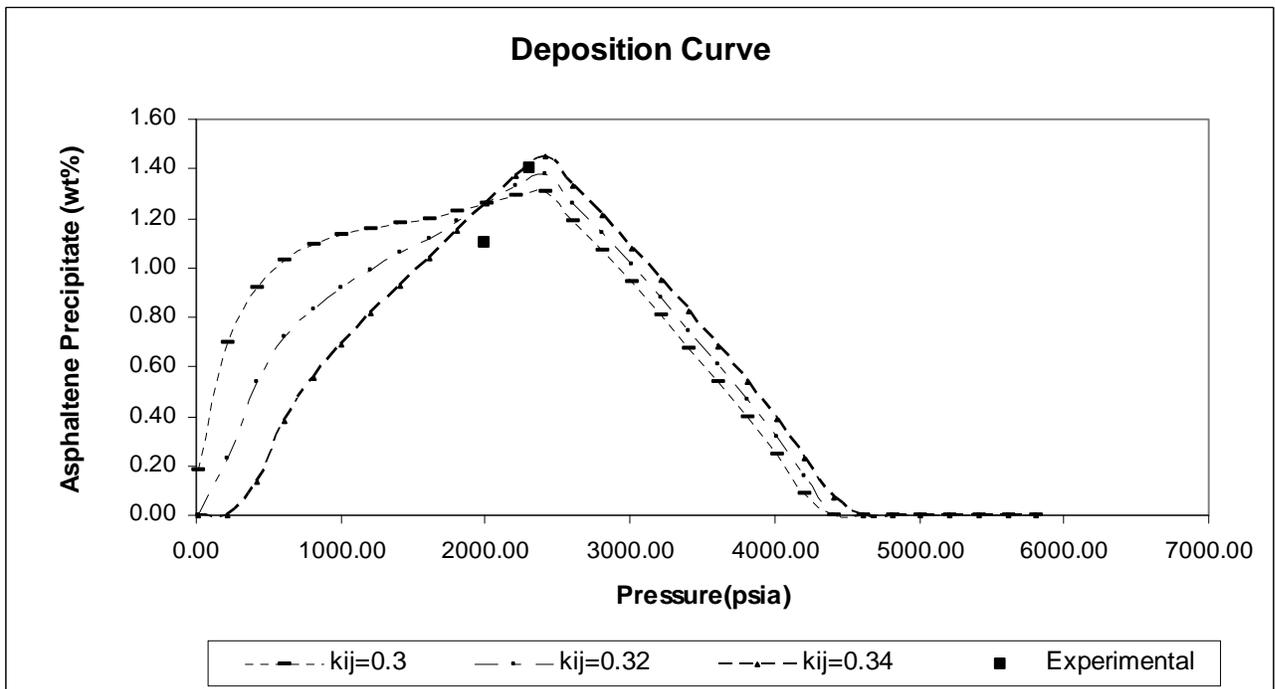


Figure 5- Precipitation curve for oil No. 5

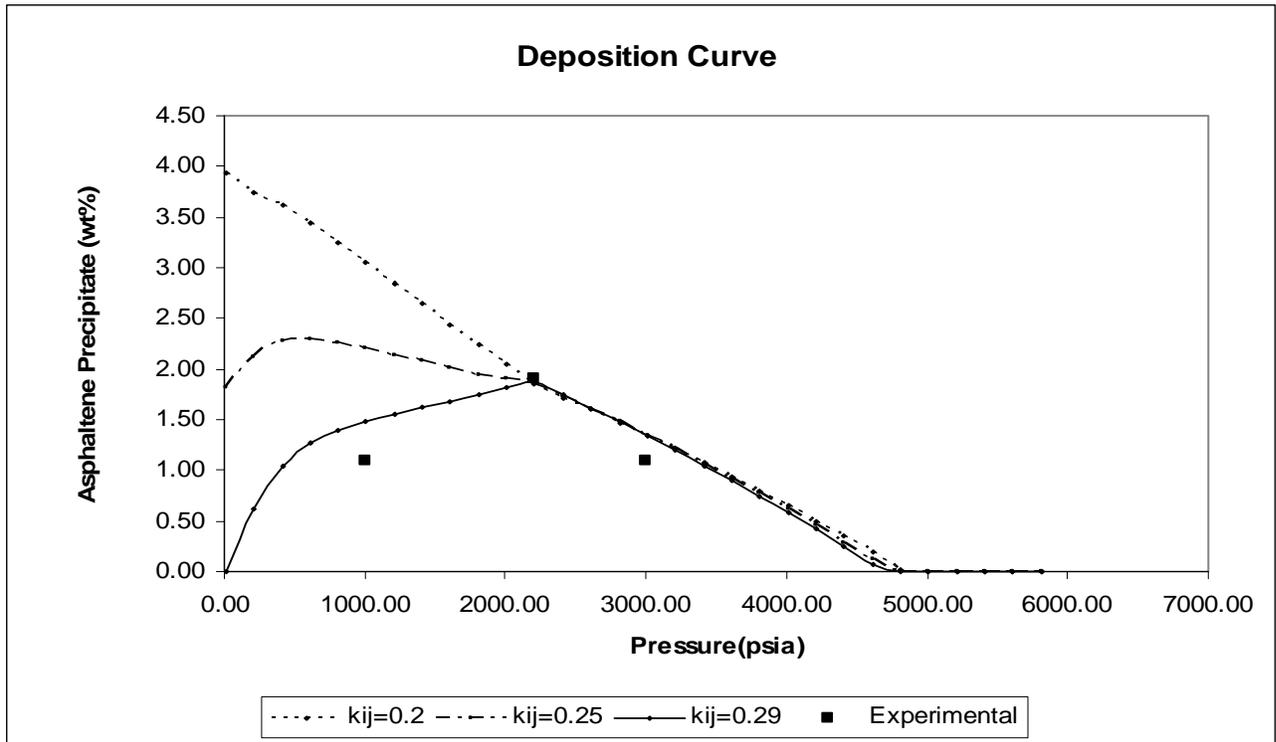


Figure 6- Precipitation curve for oil No. 6

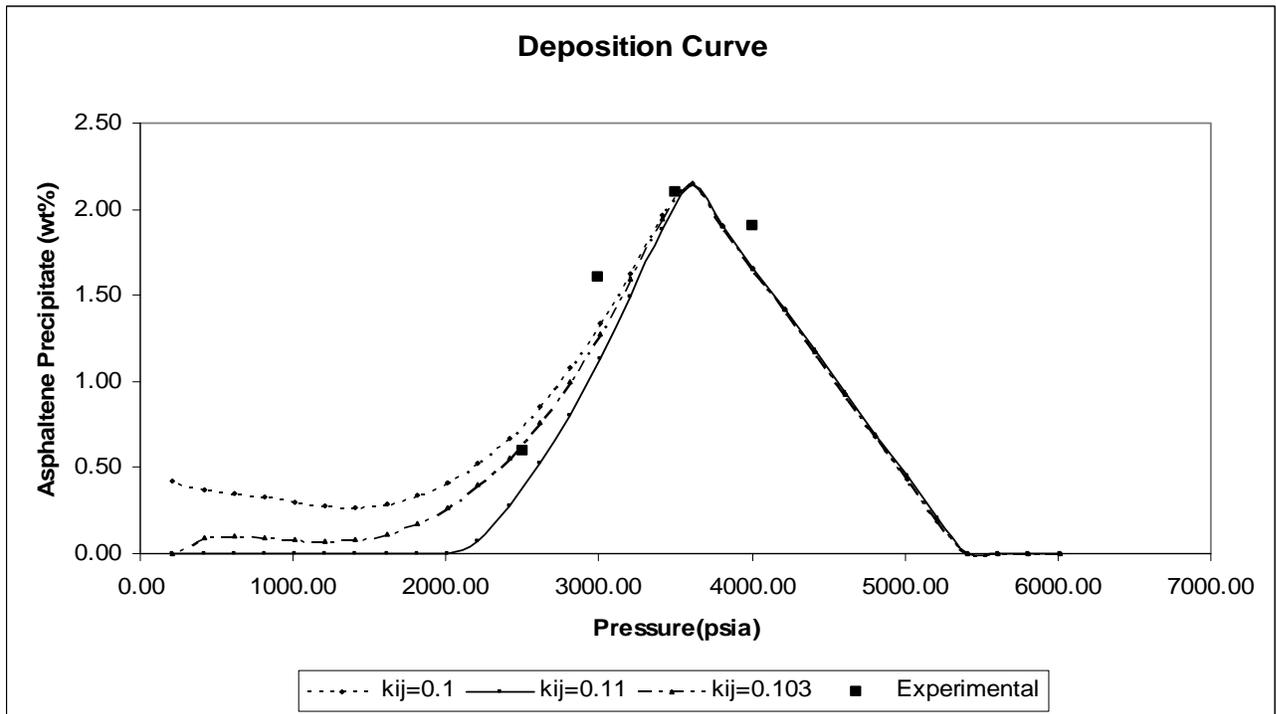


Figure 7- Precipitation curve for oil No. 7

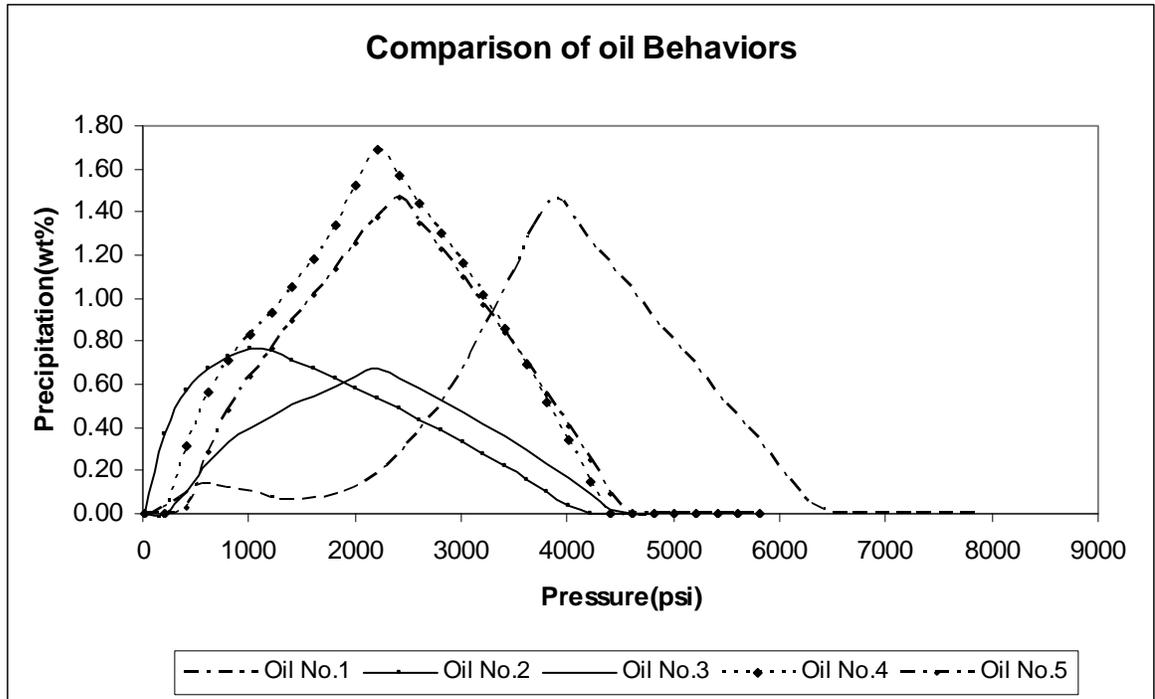


Figure 8- Comparison between phase behaviors of oil samples

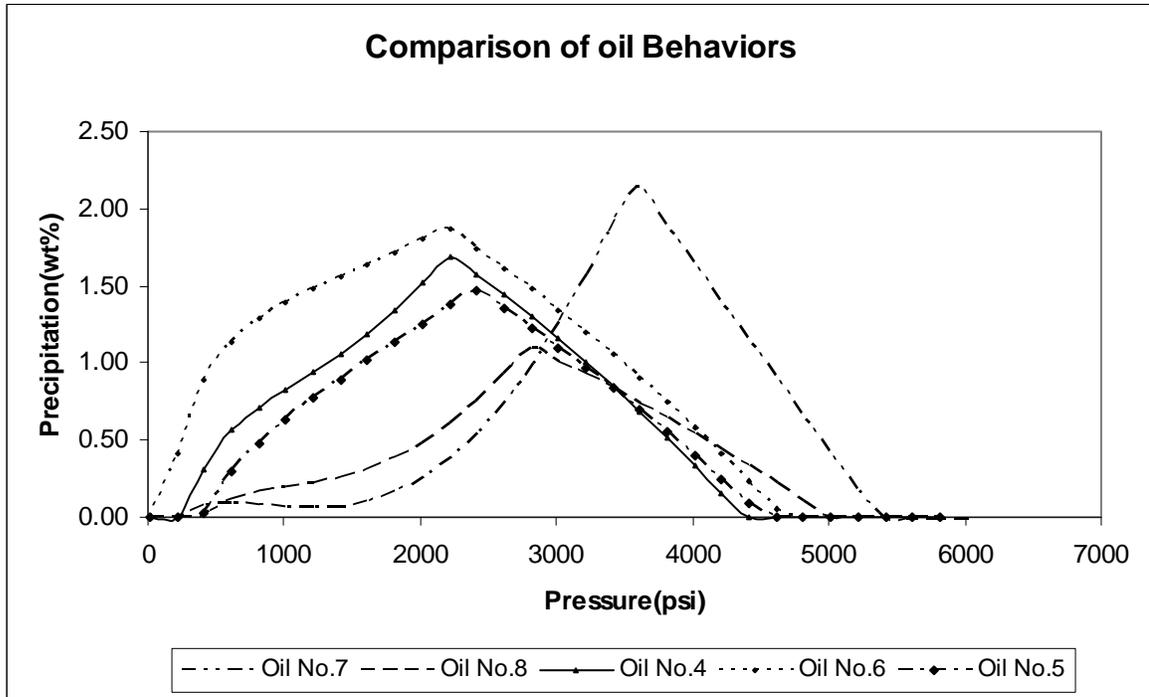


Figure 9- Comparison between phase behaviors of oil samples

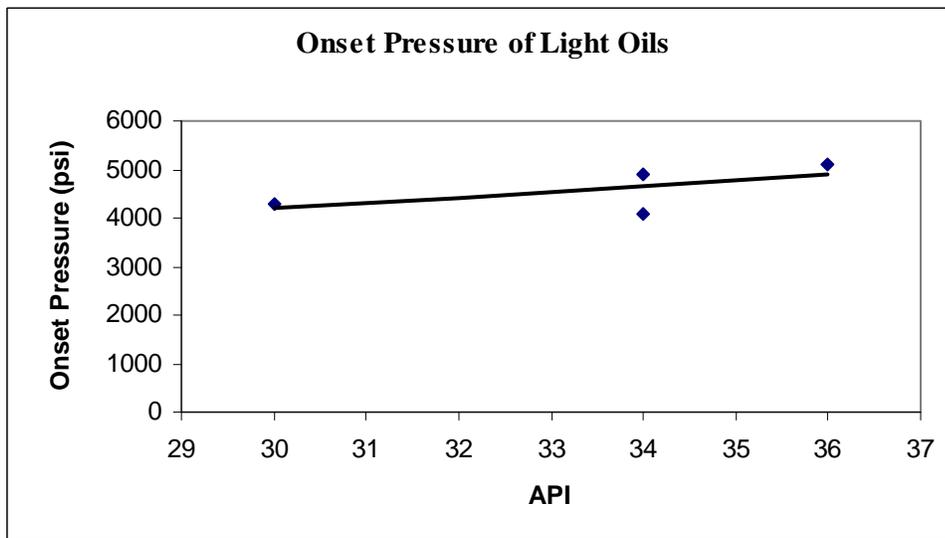


Figure 10- Onset Pressure of Light oils versus API

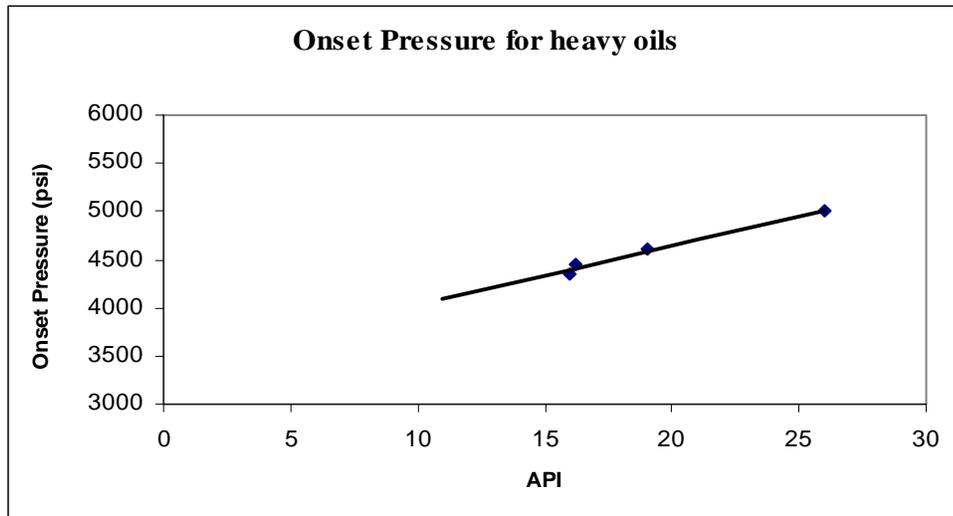


Figure 11- Onset Pressure of Heavy oils versus API