

A Solution Model for Predicting Asphaltene Precipitation

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ABSTRACT: Formation of asphaltene deposition during oil production, processing and synthesis is known as a fundamental problem of petroleum reservoir worldwide. Asphaltene is a petroleum fraction that can lead to increasing the operating costs in these industries. Variations in operational pressure, temperature and fluid composition are generally the significant cause of asphaltene precipitation. In this study, a regular solution model with liquid-liquid equilibrium criteria between asphaltene-rich phase and solvent-rich phase (maltene phase) is presented in order to calculate asphaltene precipitation. As a result, to achieve this objective, the Flory-Huggins (F-H) theory is applied and the definition of the interaction parameter in the traditional form of F-H model is modified. In this work, an empirical correlation is adapted using regular solution theory to predict the solubility parameters and eventually the DE (Differential Evolution) optimization strategy is applied to calculate optimum values of the justifiable parameters in the model. The results of the developed model are finally compared with the existing asphaltene precipitation data in various solvent ratios from the literature and it is shown that they are in acceptable agreement with the experimental data. Hence, the proposed model is capable of good prediction of asphaltene precipitation in a widespread range of the solvent ratios.

KEY WORDS: Asphaltene, Solvent ratio, Solution model, Differential evolution method, Modified Flory- Huggins model.

INTRODUCTION

Precipitation of heavy organic compounds from petroleum fluid can cause several serious issues. Therefore, it is necessary to develop accurate and simple model to investigate the conditions and the amount of asphaltene precipitation due to various factors.

Asphaltenes are the heaviest and most polar compounds of crude oil. They consist of highly dispersed mixture of molecules including polycyclic aromatic compounds, in which each aromatic cycle has few number of alkyl group. Asphaltenes can exist with

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different molecular weights and in various molecular structures. Asphaltenes are available as colloidal particles in crude oil and might be absorbed by resins dispersed as heavy polycyclic hydrocarbons in crude oil. Molecular weight of asphaltenes are generally between 1000 and several hundred thousand. Different factors control asphaltene precipitation such as temperature, pressure, properties of asphaltene etc.

Several precipitation and deposition models have been developed for understanding the behavior of asphaltenes in all different stages of production from formation to wellbore [1-3]. Asphaltene models can be divided to three main classes: real solution models, colloidal models and association Equation of State (EoS) models.

Real solution models are composed of two main assumptions: asphaltene is completely dissolved in crude oil and asphaltene precipitation and deposition phenomena are reversible. Solubility and solid models [4] are among the real solution models. Solubility models based on Flory-Huggins theory are widely used for predicting asphaltene precipitation [5]. This theory has been created for a mixture of polymers with very large molecules and solvents with smaller molecules [6]. *Hirschburg* [1] first applied solubility model in 1984. He used a thermodynamic approach for describing stability of asphaltene in equilibrium reversible solution with the basis of Soave equation of state [7]. To determine properties of liquid phase in *Hirschburg* model, first, Vapor-Liquid Equilibrium (VLE) calculation is performed. Later, Liquid-Liquid Equilibrium (LLE) was calculated using Flory-Huggins theory. Given that asphaltene precipitation phase does not affect Vapor-Liquid Equilibrium (VLE) which has been previously calculated, asphaltene has been considered as a pseudo liquid. Some researchers have proposed calculation of three-phase equilibrium using effect of asphaltene precipitation on gas phase [8]. A new model was formed by *Cimino et al.* [9] regarding expansion of the previous model by *Hirschburg* [1] in order to include thermodynamic polymeric solutions. In case this new modification is adjusted with experimental results, it can predict phase behavior of asphaltene well.

Solid models which were formed using cubic equations of state study asphaltene precipitation separately when solid phase composition (solid-liquid equilibrium) remains in the fluid phase. Solid models

may require several experimental and organized parameters for coordinating experimental data [10]. *Naghieh et al.* [4] presented a model based on theory of solid-liquid equilibrium in 1987 which considered asphaltene as a dense phase and assumed that the heaviest compounds of crude oil can be divided into sedimentary and non-sedimentary compounds. This model assumed that sedimentary compounds were asphaltenes.

In solid model of *Chung* [3] presented in 1992, asphaltenes were assumed as a uniform pseudo component and all other compounds were considered solvent. This made direct calculation of asphaltene solubility possible due to its simplicity but it did not include the effects of pressure, which is an important factor in stability of asphaltene.

The basis of colloidal models [2] is thermodynamic and colloidal science. This model assumes that asphaltenes are available in crude oil as solid particles in colloidal suspension which have been stabilized by the resins absorbed on their surface. With respect to association equation of state model, that there are hypotheses as follows [11]:

Asphaltene molecules are available in mass of crude oil as small molecules and flocculate in precipitation phase. Asphaltene precipitation is thermodynamically reversible. Association EoS model combines relations of physical-chemical effects of association of asphaltene molecules with each other, which requires awareness of size, composition, molecular weight and interaction coefficients of combining agents [12]. Association equations of state model can be applied for modeling asphaltene precipitation. In the past decades, few precipitation models have been created according to asphaltene precipitation calculation. For example, *Wang & Civian's* [13] model can simulate formation of risk due to asphaltene deposition in horizontal and vertical reservoirs of wells during recycling crude oil. In deposition model, deposition level, line and connection of pore opening were presented and regeneration of porosity and permeability was included in the simulator. *Leontaritis's* [2] model was the first model which predicted asphaltene deposition in a new area of well head along with the following hypotheses:

Production ratio is constant; transient flow time can be neglected; asphaltene deposition occurs around well head; risk formation area is constant. The results of this model were not satisfactory when asphaltene

was solved in oil during recycling crude oil. Asphaltene precipitation has an important effect on oil production in primary recovery (i.e. pressure reduction), secondary recovery (i.e. flood) and tertiary recovery (i.e. CO₂ injection) [14]. Asphaltene precipitation reduces relative permeability of oil and increases chance of risk formation and effects of plugging. Therefore, to simulate behavior of asphaltene precipitation process, it is important to prevent or at least to reduce problems of asphaltene precipitation during oil production according to optimal production strategy. In recent years, different studies for prediction of asphaltene precipitation have been carried out using solution theory, including researches conducted by *Nourbakhsh et al.* [15], *Pazuki et al.* [16], *Vafaie-sefti et al.* [17] and *Mohammadi et al.* [18].

In this study, correlation of the new interaction parameter and *Flory-Huggins* [5] theory was used for predicting asphaltene precipitation. This correlation was considered as function of molecular weight, solvent ratio and molar volume. To calculate optimum values of the current quantities of the model, DE optimization strategy [19] was used and this equation was applied for predicting the amount of asphaltene precipitation. Finally, the accuracy of the proposed model was approved by comparing the results with the experimental in a widespread range of solvent ratios.

THEORITICSL SECTION

Modeling of asphaltene precipitation

In this work, equilibrium between two phases is taken into account: the asphaltene and solvent rich phase. This approach involves direct calculation of the solubility parameters for asphaltene and solvent by two empirical correlations.

The models which apply the solubility parameter concept estimate any interactions through an assumption that petroleum is composed of two bulk phases, the asphaltenes and the deasphalted (oil). Any changes in the phase equilibria of this two-component system are caused by changes in the solubility parameter of either of the two pseudo-components [20].

According to the equilibrium condition and the following equation, the maximum volume fraction of dissolved asphaltene in the oil phase is shown.

$$\Delta\mu_a^{\text{oil}} = \Delta\mu_a^{\text{asph}} \quad (1)$$

$$\ln \phi_a^{\text{oil}} + \left(1 - \frac{\vartheta_a^{\text{oil}}}{\vartheta_s^{\text{oil}}}\right) \phi_s^{\text{oil}} + \chi \phi_s^{\text{oil}2} = \quad (2)$$

$$\ln \phi_a^{\text{asph}} + \left(1 - \frac{\vartheta_a^{\text{asph}}}{\vartheta_s^{\text{asph}}}\right) \phi_s^{\text{asph}} + \chi \phi_s^{\text{asph}2}$$

$$\ln \phi_a^{\text{oil}} = \left(\frac{\vartheta_a^{\text{oil}}}{\vartheta_s^{\text{oil}}} - 1\right) - \frac{\vartheta_a}{RT} \left[(\delta_a - \delta)^2 + 2l_{as} \delta_a \delta_s \right] \quad (3)$$

Using the volume fractions of asphaltene and solvent phase, the precipitated weight percent of asphaltene can be written as:

$$W_a = \frac{(1 - \phi_a^{\text{oil}}) \left(\frac{MW^{\text{oil}}}{\vartheta^{\text{oil}}}\right)}{(1 - \phi_a^{\text{oil}}) \left(\frac{MW^{\text{oil}}}{\vartheta^{\text{oil}}}\right) + \phi_a^{\text{oil}} \left(\frac{MW^{\text{asph}}}{\vartheta^{\text{asph}}}\right)} \quad (4)$$

In aforementioned equation γ , ϕ , ϑ , x , a and s are the activity coefficient, volume fraction, molar volume, mole fraction, asphaltene and solvent, respectively.

The original form of F-H model is not accurate enough to calculate and predict the asphaltene precipitation. Therefore, a modified version of F-H model is herein used. In fact, this model is modified by the interaction parameter (l_{as}). Within the frame of the original Flory- Huggins theory, this parameter was supposed to be constant and first calculated by the empirical correlation. From a qualitative point of view, the F-H interaction parameter is a reflection of the polymer/solvent affinity [21]. A number of investigators have tried to understand the impact of the interaction parameter in predicting the phase behavior of asphaltene compounds, and some different empirical and theoretical modifications have been conducted to modify F-H model in various systems; e.g. *Kawanaka et al.* [22], *Mansoori* [23], *Pazuki & Nikookar* [16], and *Nourbakhsh et al.* [15]. Further analysis in terms of the F-H theory generally shows that the accuracy of the final results considerably depends on the interaction and solubility parameters. Various experimental study and mathematical models to deal with the predictability of asphaltene behavior can be considerably found in the literature [24- 26].

In all models which employ the interaction and solubility parameter concept, there are a number of adjustable parameters which have to be tuned to obtain best fits between experiment and model. Even though

the models are based on thermodynamic concepts, they remain empirical because of the number of parameters used in the calculations.

In this study, the interaction parameter is considered according to the following equations:

$$l_{as} = a_0 + a_1F + a_2F^2 + a_3F^3 \quad (5)$$

$$F = \frac{(1 + SR)MW_a \left(\frac{v_a^{oil}}{v_s^{oil}} \right)}{SR MW_s \left(1 + \frac{v_a^{oil}}{v_s^{oil}} \right)} \quad (6)$$

Where SR, ϑ and MW are the solvent ratio, molar volume and molecular weight, respectively. In order to establish a solution model capable of accurately predicting asphaltene precipitation in different condition this investigation proposes Eqs. (5&6) based on the strong dependence of the interaction parameter towards molecular weight and concentration.

The adjustable parameters in Eq. (5) are determined using the Differential Evolution (DE) optimization method by minimizing the following objective function:

$$OF = \frac{100}{N} \sum_i^N \left| \frac{w_a^{cal} - w_a^{exp}}{w_a^{exp}} \right| \quad (7)$$

Where N is the number of experimental data.

In this communication, the DE method was applied to calculate the optimum values.

Calculation of the Solubility Parameter Using Empirical Correlation

In present work, correlation (8) has been applied to evaluate the solubility parameter of asphaltene as follows [18]:

$$\delta_a = 20.04 \left\{ 1 - 1.07 \times 10^{-3} (T - 273.15) \right\} \quad (8)$$

Where T and δ_a are in K and MPa^{0.5}, respectively.

The Calculation of the solubility Parameter For Asphaltene

Another important parameter for the calculation of asphaltene precipitation is the solvent solubility parameter. Therefore, the correlation (9) was used to calculate this parameter in the following form [27]:

$$\delta = 0.500765 (T_B)^{0.982382} \left(\frac{SG}{MW} \right)^{0.482472} \quad (9)$$

Where T_B , SG and MW are average boiling point (K); specific gravity at 20°C (refer to water density at 4°C) and molecular weight (g/mol), respectively.

Differential Evolution (DE) optimization method

Today, using algorithms for solving hard optimization problems is of special significance. The DE [19] algorithm is one of the best and most successful algorithms presented for solving optimization problems. Simulation results have demonstrated that this algorithm is an effective method for solving the stochastic resource constrained project scheduling problem.

Optimization methods are used to achieve optimum values in mathematical modeling. One of the major problems of traditional optimization algorithms is their convergence to local optimum. In fact, there is no guarantee for these optimization methods to find the global optimum solution. Therefore, the population-based search algorithms have been assumed to achieve the global optimum. There are some optimization methods such as the Evolution Strategies (ES), the Genetic Algorithms (GA) and the Differential Evolution (DE) that have been developed to overcome the problem of traditional methods [28].

The DE has been designed based on the random and direct search method [19] in order to find a function's true global optimum. In fact, GA uses a binary coding for representing problem parameters. But, DE uses real coding of floating point numbers. The mutation operator here is addition instead of the bit-wise flipping used in GA. Moreover, the DE uses non-uniform crossover and tournament selection operators to make new solution strings. Investigations have shown that the DE is an effective and robust evolutionary optimization method. In the DE method depending on the conditions a range of changes is considered for parameters. Then, the DE method Checks whether the parameters of trial vector are within the bounds. If an estimation of this trial vector is outside of the bounds, therefore, that vector will be removed. Otherwise, the DE method tries to find a value with minimum error form the experimental data [29-31].

RESULTS AND DISCUSSION

In this research, the amounts of asphaltene precipitation was calculated for the oil sample from

Table 1: The chemical composition and PVT properties of oil sample (1) [15].

Component	Mole Percent
C ₁ -C ₃	0.22
i-C ₄	0.22
n-C ₄	0.93
i-C ₅	0.48
n-C ₅	0.48
n-C ₆	6.84
C ₇ ⁺	90.83

^aAsphaltene wt. %=13, Molecular weight of the oil=316. Specific gravity of the oil (at 60/60 °F)=0.943

Table 2: The optimum adjusted parameters for each solvent.

Solvent	ndp	a ₀	a ₁	a ₂	a ₃
n-Pentane	8	-0.04073	1.3540E-07	-6.9800E-06	2.2260E-07
n- Hexane	8	-0.03105	2.5730E-05	-1.7535E-06	1.0018E-08
n-Heptane	8	-0.02796	9.7313E-04	-8.1395E-05	2.1842E-06

southwest of Iran in different solvents (n-pentane, n-hexane and n-heptane). Chemical composition and properties of this oil sample are given in Table 1. To model the amounts of asphaltene precipitation, a modified form of F-H model was applied. In fact, the modified model was performed such that there were parameters like the interaction parameter (I_{as}), asphaltene and solvent solubility parameters in Eq. (3). The interaction parameter can be regarded as one of the most important and key parameters in increase of model accuracy to determine the amounts of asphaltene precipitation. In this work, it was attempted to make required modifications in the interaction parameter (I_{as}) so as to increase ability of the model in predicting the weight percent of the precipitated asphaltene by necessary effective changes. The present model was proposed based on the parameters effective on asphaltene precipitation such as solvent ratio, molecular weight, and molar volume of asphaltene and solvent. Considering that the proposed correlation was a third-degree linear relation, as a result, there was a series of constant coefficients (a_0 , a_1 , a_2 , a_3) in this relation which would be obtained by the experimental values of asphaltene precipitation and optimization method. Table 2 demonstrates optimal values of (a_0 , a_1 , a_2 , a_3) evaluated from DE method for different solvents used in the interaction parameter equation. In fact, the precision of

the proposed model in prediction of asphaltene precipitation can be increased by the coefficients reported in Table 2. As mentioned above, the amounts of asphaltene precipitation depends on molecular weight, solvent ratio and molar volume. Effects of these factors with each other are considered as a coefficient called the ratio factor (F) according to Eq. (6). In Figs. (1-3), the impact of different values of the Solvent Ratio (SR) on the ratio factor can be observed. As it is shown, when the ratio of solvent increases for different solvents, the ratio factor decreases; however, after a certain solvent ratio, it could be seen that more increase of the solvent ratio would not make special changes in the amounts of this factor. In the present work, this modified model using the interaction parameter equation proposed by Pazuki *et al.* defined based on molecular weight of asphaltene to molecular weight of crude oil ratio in form of polynomial function was finally tested [16] (This is called MFH1 in this paper). The Calculated amount of asphaltene precipitation using both approaches along with the experimental data is demonstrated in Table 3. It has to be noted that, in both MFH1 approach and our model, the solubility parameters were calculated from the equations proposed in this study. As demonstrated in Table 3, the results show that the proposed model could easily predict the amounts of asphaltene precipitation with acceptable accuracy.

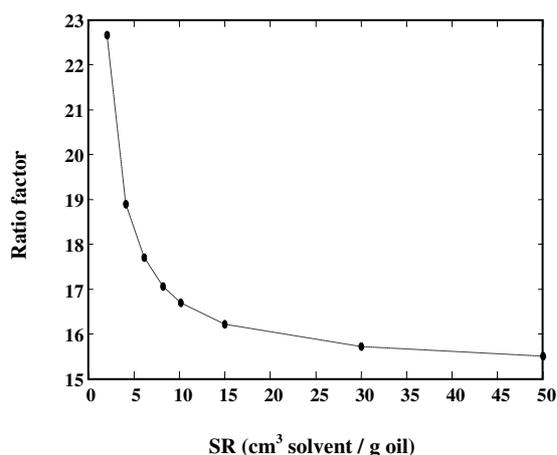


Fig. 1: Ratio factor versus solvent ratio for n-C₅.

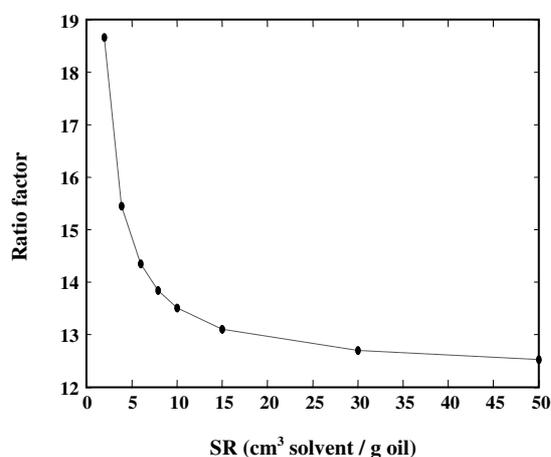


Fig. 2: Ratio factor versus solvent ratio for n-C₆.

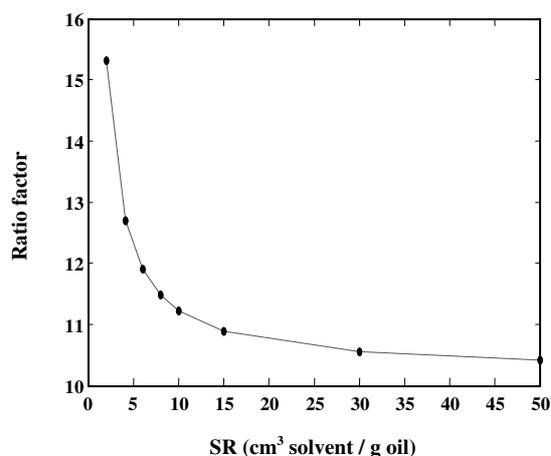


Fig. 3: Ratio factor versus solvent ratio for n-C₇.

According to the indicated results in the above table, the weight percent of asphaltene precipitation increases as Solvent Ratio (SR) arises. Owing to SR enhancement, solubility difference between asphaltene and solvent which is one of the major factors leading to the asphaltene formation increases. The Absolute Average Deviation (AAD%) values of the proposed model results from the experimental data are shown in Table 4. The results indicate that the average absolute errors of the proposed model predictions are between 1.44 and 3.25% for various types of solvents.

In order to measure the precision and validity of proposed correlations as a reliable predictive tool, the tuned coefficients were used for the data of another oil sample reported in the literature [15, 32]. The comparison of the predicted weight percent of precipitated asphaltene for different solvents (n-C₅, n-C₆ and n-C₇) against the experimental data from oil sample (2) are shown in Figs. (4–6). As it can be seen, the predictions are in good agreement with the experimental values

CONCLUSIONS

1- In this work, asphaltene precipitation in crude oil was calculated using the proposed thermodynamic model based on the modified F-H theory and new equations for calculating effective parameters in the model.

2- The parameters of the proposed model include molecular weight, molar volume and solvent ratio which have a strong impact on the accuracy of the results.

3- The adjustable parameters were tuned using precipitation data of an oil sample from the southwest of Iran. The desired coefficients were found such that the weight percent of precipitated asphaltene were accurate enough using the proposed model considering definition of the objective function in the optimization method.

4- The validity and capability of this modified model for estimating asphaltene precipitation was finally compared with different experimental data reported in the literature. The results demonstrate that the proposed model would be able to accurately predict the amounts of asphaltene precipitation using the average molecular weight without further tuning.

Nomenclature

a_0, a_1, a_2, a_3	Adjustable Parameters
ϑ	Molar Volume, cm ³ /gmole

Table 3: Comparison between the calculated asphaltene precipitations and the experimental data [15] of oil sample.

Solvent	Solvent Ratio	Asphaltene Precipitation (W _a)		
		Experimental	Our Model	MHF1 Model
n- C ₅	2	14.05	13.95	16.48
	4	14.18	14.07	16.48
	6	15	15.53	16.48
	8	16.49	16.52	16.48
	10	17.82	17.12	16.48
	15	19.1	18	16.48
	30	19.08	18.98	16.48
	50	18.67	19.38	16.48
n- C ₆	2	9.14	9	13.71
	4	12.54	12.4	13.71
	6	13.05	13.3	13.71
	8	13.71	13.67	13.71
	10	14.02	13.89	13.71
	15	14.47	14.14	13.71
	30	14.68	14.38	13.71
	50	14.27	14.47	13.71
n- C ₇	2	7.41	7.32	10.68
	4	9.48	9.4	10.68
	6	10.54	10.68	10.68
	8	11.65	11.31	10.68
	10	12.04	11.64	10.68
	15	10.68	12.01	10.68
	30	12.75	12.29	10.68
	50	12.44	12.36	10.68

Table 4: Comparison among absolute average deviations.

Type of Oil	ndp ^a	Solvent	AAD% Our Model	AAD% MHF1 Model
Oil sample (1)	8	n-C ₅	2.41	11.24
	8	n-C ₆	1.44	10.29
	8	n-C ₇	3.25	13.47

^aNumber of experimental data points. ^b $\%AAD = \frac{100}{ndp} \sum_i \frac{|Calculated(i) - Experimental(i)|}{Experimental(i)}$

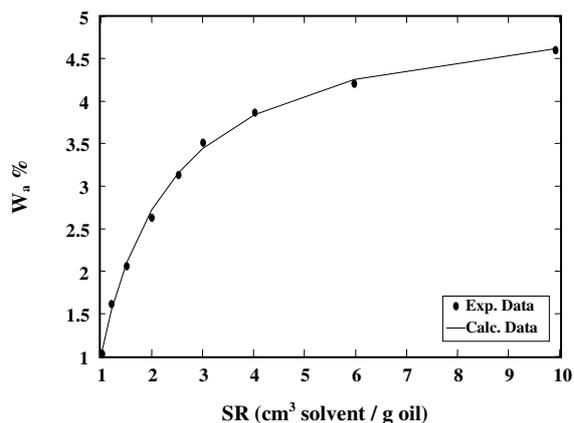


Fig. 4: Comparison between the weight percent of asphaltene precipitation obtained from the proposed model and the experimental data in different ratio of *n*-C5, oil sample (2) (%AAD=2.12)

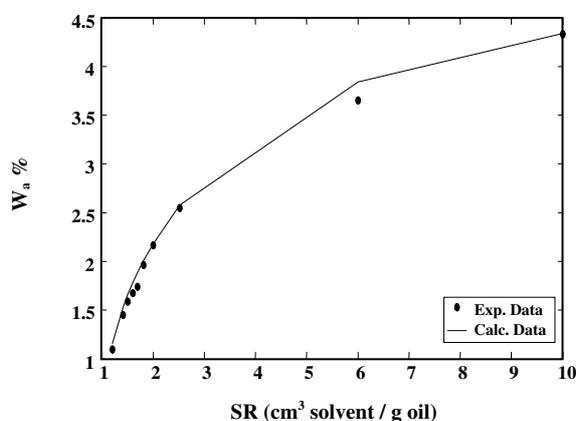


Fig. 5: Comparison between the weight percent of asphaltene precipitation obtained from the proposed model and the experimental data in different ratio of *n*-C6, oil sample (2) (%AAD=4.06).

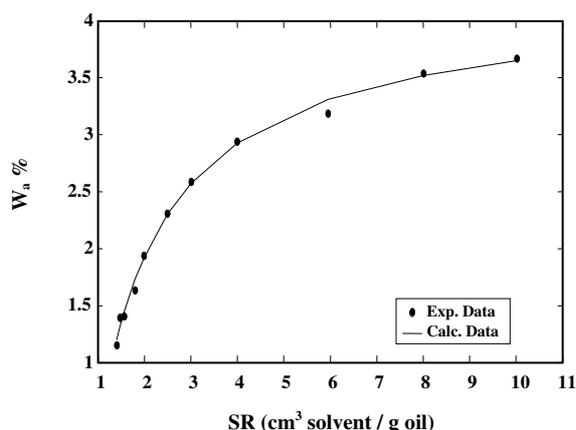


Fig. 6: Comparison between the weight percent of asphaltene precipitation obtained from the proposed model and the experimental data in different ratio of *n*-C7, oil sample (2) (%AAD=2.33).

SR	Solvent Ratio
MW	Molecular Weight
T	Temperature, K
l	Interaction Parameter
F	Ratio Factor
W_a	Mass Fraction of Asphaltene Precipitation
T_B	Average Boiling Point
SG	Specific Gravity at 20°C

Greek letters

μ	Chemical Potential
φ	Volume Fraction
χ	Parameter of Extended (F-H) Model
δ	Solubility Parameter

Subscript

a	Asphaltene
s	Solvent

Superscripts

asph	Rich phase of asphaltene
oil	Maltene phase
exp	Experimental
cal	calculated

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