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Prediction of Solvent Effect on Asphaltene Precipitation at Reservoir Conditions

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Abstract

The aim of the current study is to evaluate the effects of inhibitors or solvents on asphaltene precipitation under reservoir conditions. To this end, the interaction between live oil and solvent, and its side effects on precipitated/dissolved asphaltene were predicted via Miller's entropy modified polymer solution theory under reservoir conditions. Then, the adjustable parameters of the model were tuned using experimental the data of asphaltene precipitation within a live oil sample. The obtained adjusted parameters were considered to monitor the effects of solvent injection, miscible gas injection, and natural depletion on asphaltene deposition through an oil sample. Finally, Peng-Robinson equation of state was applied to calculate vapor-liquid equilibrium conditions. The results showed that the output of the model was really in good agreement with all experimental, field, and theoretical data.

Keywords: Asphaltene, Precipitation, Inhibitor, Solvent

Introduction

Due to the importance and necessity of asphaltenic solvent application and considering the cost and supply limitations of commercial solvents, predicting the solvent effects can give us a hand on controlling and removing asphaltene deposits of petroleum fluids. As a matter of fact, asphaltene particles are known as the most polar and heaviest components of petroleum fluids and because of the complex phase behavior of asphaltene components, developing a comprehensive thermodynamic model has been turned into a big challenge.

Generally there are about four distinct types of thermodynamic models for asphaltene precipitation prediction. Common modeling methods include (1) the solubility model, (2) the solid model, the (3) colloidal model, and (4) the micellization model. The solubility models are based on the simplified Flory-Huggins polymer theory [1] and describe asphaltene stability in terms of reversible equilibrium solution. Hirschberg et al. [2] proposed a solubility precipitation model based on the Soave equation of state. Kawanaka et al. [3] and Cimino et al. [4] developed a precipitation model on the basis of polymer-solution thermodynamics. This model is believed to be a good application of the polymer solution theory; so it provides a good representation of asphaltene-phase behavior. However, it needs accurate experimental data to adjust the parameters of this model. Park and Mansoori [5] and later Nor-Azlan and Adewumi [6] proposed another model based on the statistical thermodynamics of polymer solutions. Leontaritis and Mansoori [7] proposed a thermodynamic colloidal model which was able to predict the onset of asphaltene flocculation. According to this model, asphaltenes exist in the oil as solid particles in a colloidal suspension and is stabilized by resins adsorbed on their surface. In this model, according to the theories of surface-chemistry, thermodynamic processing methods are applied to study the precipitation of asphaltenes. This model can reflect the real state of crude oils and is effective for asphaltenes and the molecular weights of asphaltene [8,9]. Another theoretical model for asphaltene precipitation is the solid model. In this model, asphaltene phase is considered as a solid phase (liquid-solid equilibrium). Solid models may require many empirical parameters and excessive tuning to match experimental data [10]. Nghiem et al. [11] proposed their model by considering the precipitated asphaltene as a pure solid dense phase; in their model the heaviest component in the oil can be split into two parts: the non-precipitating and precipitating components.

The precipitating component is taken as asphaltene. Chung [12] developed his precipitation model by treating asphaltene as a lumped pseudo-component (compound) and the other components as solvents. Vafaie et al. [13,14] applied association theory to the prediction of asphaltene deposition. The recent theoretical model of asphaltene precipitation is the asphaltene micellization model. Asphaltene aggregation, micelle core formation, resin adsorption onto asphaltene surface, resin shield deformation, and finally micelle formation play the key role in this model. Victorov and Firoozabadi [15] used the principle of the Gibb›s free energy minimization to determine equilibrium composition and the amount of vapor-liquid and asphaltene phases.

The application of simple polymeric solvents, their trimmed models, and the new proposed model can be considered as a powerful package for asphaltene modeling studies. Solubility parameter is one of the best concepts for describing the phase segregation phenomena, and, to some extent, this is the main advantage of the new proposed model. Comparing the property changes of non-asphaltenic fluids with asphaltenic samples shows the positive effects of the proposed solvent on asphaltene flocculation condition.

The aim of this work is to predict the effects of solvents on asphaltene precipitation and flocculation conditions using the developed thermodynamic models.

Prediction of the Effect of Aromatic Solvents on Asphaltene Precipitation

Here, Miller-Modified Flory-Huggins model was applied to predict the effect of aromatic solvents on asphaltene precipitation for some Iranian live oils. Further details on this model can be accessed through the work of Mousavi-Dehghani et al. [16,17]. The polymeric nature of asphaltene compounds in petroleum mixtures enhances the usage of polymer solution and lattice theories for asphaltene precipitation modeling. The original and modified Flory-Huggins based models are the common polymer solution models which they have applied for this study. It was found that the modification of modified Flory-Huggins model could improve the ability and accuracy of the model [16]. This modification includes the replacement of the entropy (combinatorial) term of the modified Flory-Huggins (MFH) model via Miller's entropy term [17]. The residual term (enthalpy change of mixing) in Flory-Huggins (FH) theory can also be modified by introducing pair interaction parameter l_{aL} [19,20]. The final equation is expressed as read [16,17]:

$$\frac{\Delta\mu_a^L}{RT} = \frac{v_a(1-\phi_a^L)^2}{RT}\left[(\delta_a-\delta_L)^2 + 2l_{aL}\delta_a\delta_L\right] + \left[\ln\phi_a^L - \frac{z}{2}\ln\left[1-\frac{2}{z}\left(1-\frac{v_a}{v_L}\right)(1-\phi_a^L)\right]\right] = 0 \tag{1}$$

where, Δμ is the change of chemical potential; also, v, ϕ, z, and δ stand for molar volume, volume fraction, coordination number, and solubility parameter respectively. Subscripts (or superscripts) a and L refer to asphaltene and asphaltene-free phases respectively. Referring to Equation 1, asphaltene molar volume and asphaltene solubility parameter are the main adjustable parameters which can be adjusted via experimental data on asphaltene precipitation at different pressures and temperatures. What should be considered is that adjustable parameters must be changed in reasonable ranges. The adjusted parameters are used for the prediction of the effect of solvents on the asphaltene precipitation in the original oil sample. The added solvent enters into the asphaltene-free oil phase and changes the original oil properties. The molar volume and the solubility parameters are the main properties which change via the addition of the solvent.

Composition Analysis of Oil Samples and Solvent Properties

The compositional analysis of selected Iranian live oil samples are given in Table 1. The properties of two common asphaltene solvents, namely toluene and NNP, are given in Table 2. The saturation pressure and onset pressure of the candidate oil samples at reservoir temperatures are given in Table 3. Moreover, Table 4 gives the SARA (saturated, aromatic, asphaltene, and resin) analysis.

The analysis shows heavy fractions in each crude oil. This analysis is the most common standard method used in the petroleum industry for the separation of heavy oils into compound classes.

Table 1: Reservoir fluid composition of the live oil samples

	Reservoir Fluid Composition (mole %)	
Components	Sample 1	Sample 2
H_2S	1.87	0.00
N2	0.31	0.30
CO_2	3.37	0.93
C_1	43.59	18.91
C_2	8.58	7.20
C_3	6.27	5.21
iC_4	1.64	1.11
nC_4	4.89	2.93
iC_5	2.20	1.05
nC_5	2.49	1.14
C_6	1.91	5.44
C_7	0.89	4.11
C_8	3.01	3.43
C_9	2.05	3.07
C_{10}	1.84	2.95
C_{11}	1.39	2.59
C_{12}^+	13.71	39.62
GOR SCF/STB	1317	278
C_{12+} Mw	300	330
C_{12+} ρ 60/60 ˚F	0.9025	0.9636

Table 2: Properties of solvents

Property	Solvent	
	NNP	Toluene
Mw, g/mole	220.35	92.141
Tc, K	757	591.8
Pc, bar	20.7	41.09
Acentric Factor, w	0.9	0.264
δ,Mpa$^{0.5}$	19.455	18.346
Molar Volume, υ cm^3/mole	232	106.556

Table 3: Saturation pressure and onset pressure at reservoir temperature

Sample	SDS* onset pressure	
	No. 1	No. 2
Temperature,°C	121.1	222
Onset pressure, kPa	36604.3	-
Saturation Pressure, kPa	25283.1	1379

Table 4: Heavy fraction analysis

Specification	Samples	
	No. 1 (Weight %)	No. 2 (Weight %)
Saturated	52.49	40.89
Aromatic	41.04	48.79
Resin	5.48	2.61
Asphaltene	0.99	7.71

SARA analysis is done for crude oils including vacuum distillates, atmospheric and vacuum residues, bitumens, and asphalts so that material losses from light ends (volatiles) are minimal [21].

Tuning of the Model Using Experimental Precipitation Data

Table 5 gives the adjusted parameters of the model for the original samples. The adjusted parameters are 1) asphaltene average molecular weight, 2) asphaltene molar volume, 3) asphaltene solubility parameters, and 4) the asphaltene/asphaltene-free oil interaction parameter. As it can be seen, the values of the adjusted parameters are in reasonable ranges.

The variation of the molar volume of samples 1 and 2 with respect to toluene addition is depicted in Figures 1 and 2 respectively. At pressures above bubble point, a partly change is sensed during the toluene injection; however, below the bubble point pressure, due to releasing of dissolved gases, the effects of toluene on oil is appeared and the molar volume of oil is deduced subsequently.

The effect of NNP injection on the molar volume of oil sample 1 is also depicted in Figure 3. The high amount of NNP molar volume causes a considerable increase in oil molar volume.

Table 5: Adjusted parameters of the model for the used samples

Adjusted parameter	Sample 1	Sample 2
Asphaltene Molecular Weight (g/mole)	950	950
Asphaltene Molar Volume (cc/mole)	200.44	404.8
Asphaltene Solubility Parameter (MPa)$^{0.5}$	21.242	20.77
Coordination Number (Z)	3.5	3.5
Asphaltene- Deasphalted Oil Interaction Parameter	0.1194	0.0027

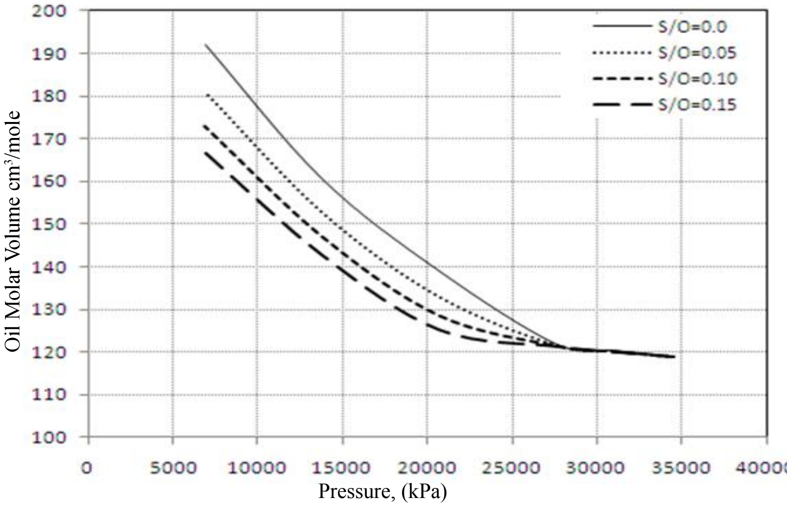

Figure 1: Oil molar volume for different toluene-oil volume ratios, Sample 1

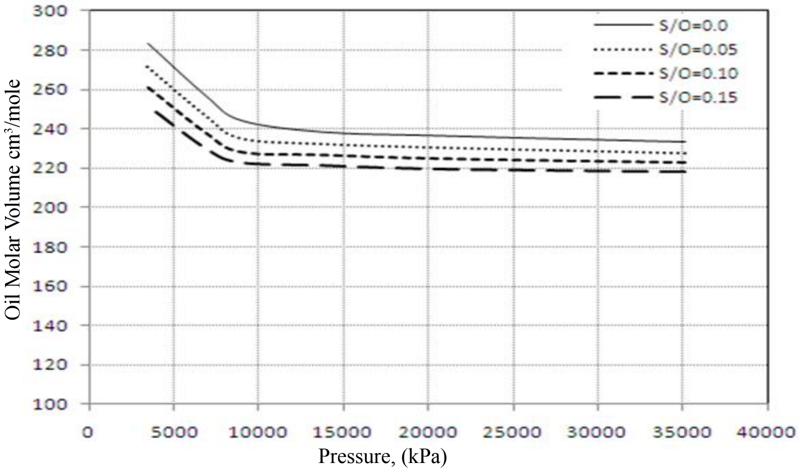

Figure 2: Oil molar volume for different toluene-oil volume ratios, Sample 2

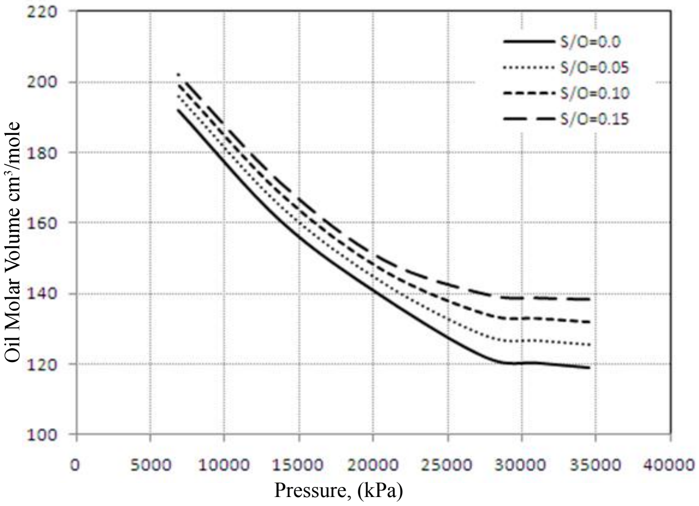

Figure 3: Oil molar volume for different NNP-oil volume ratios, Sample 1

Results and Discussion

The experimental data on asphaltene precipitation are used to tune the adjustable parameters of the model. The adjusted parameters should be in a reasonable and acceptable range. Then, the tuned model can be used for predicting the effects of temperature, pressure, miscible gas injection, and solvent injection on the amount of asphaltene precipitation.

Asphaltene precipitation from oil samples in the presence of inhibitors are examined using a modeling approach. The output results of toluene injection as an asphaltene solvent in oil samples 1 and 2 are shown in Figures 4 and 5 respectively. These figures show changes in the solubility parameter of oil for the different ratios of solvent volume to oil volume (S/O). It can be observed that at pressures above the bubble point, this parameter is increased with the addition of toluene. However, a more reduction in pressure under bubble point has a reverse behavior, and then the solubility parameter is decreased. Adding toluene in oil causes some expected variations in the basic properties of oil. Also, changing oil molar volume and solubility parameter are so important. Due to an increase in oil solubility parameter in the presence of the aromatic solvents, the difference between the solubility parameters of the asphaltene and asphaltene free oils is reduced and the amount of asphaltene precipitation will be decreased.

As shown in Figures 6 and 7, this process was examined for different ratios of toluene volume to oil volume for samples 1 and 2. The precipitation amount of asphaltene for each sample decreases while this ratio increases.

Moreover, NNP was used as an asphaltene precipitation solvent, and the results are depicted in Figures 8 and 9. The results show the same trend in asphaltene precipitation control as seen when toluene was added.
The comparison of the results (see Figures 6 and 9 for example) shows the effective rule of NNP in asphaltene precipitation control. Under the same condition of solvent injection into oil, NNP causes more asphaltene to dissolve.

According to the obtained results, one can conclude that the current model is able to predict the phase behavior of asphaltene-oil in the presence of different solvents.

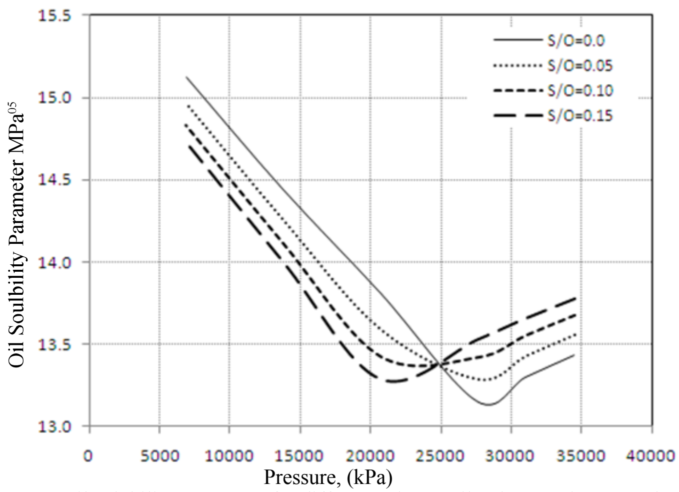

Figure 4: Oil solubility parameter for different toluene-oil volume ratios, Sample 1

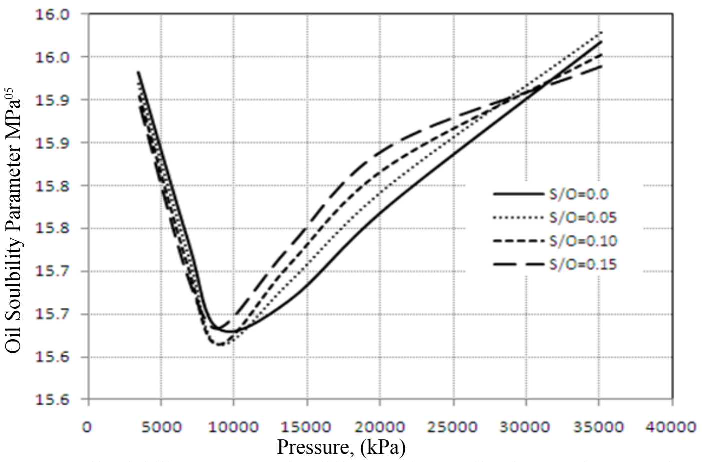

Figure 5: Oil solubility parameter for different toluene-oil volume ratios, Sample 2

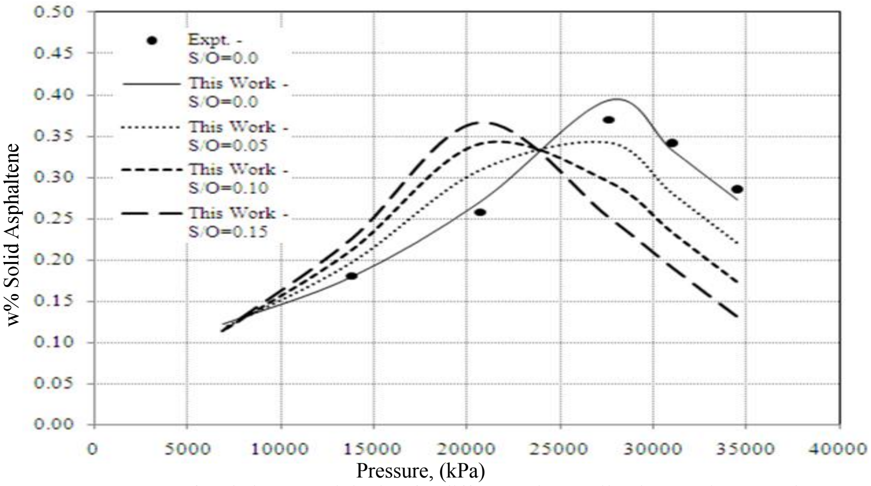

Figure 6: Amount of asphaltene precipitation for different toluene-oil volume ratios, Sample 1

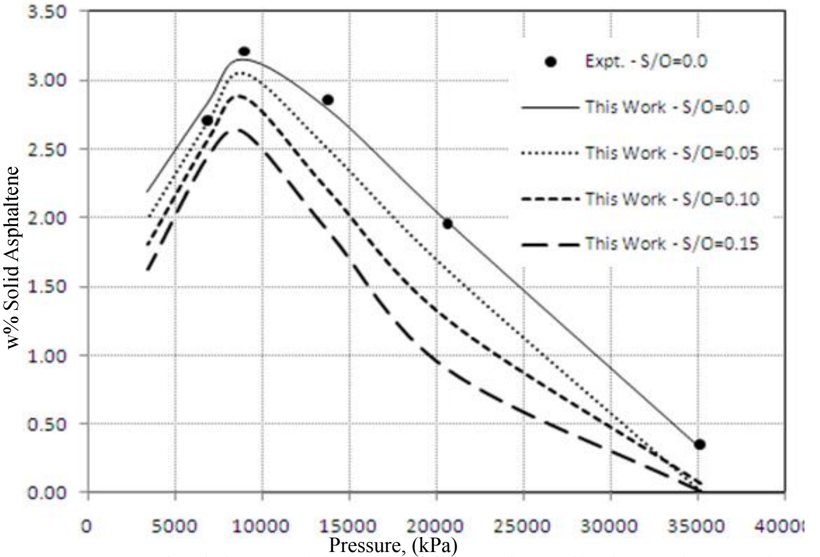

Figure 7: Amount of asphaltene precipitation for different toluene-oil volume ratios, Sample 2

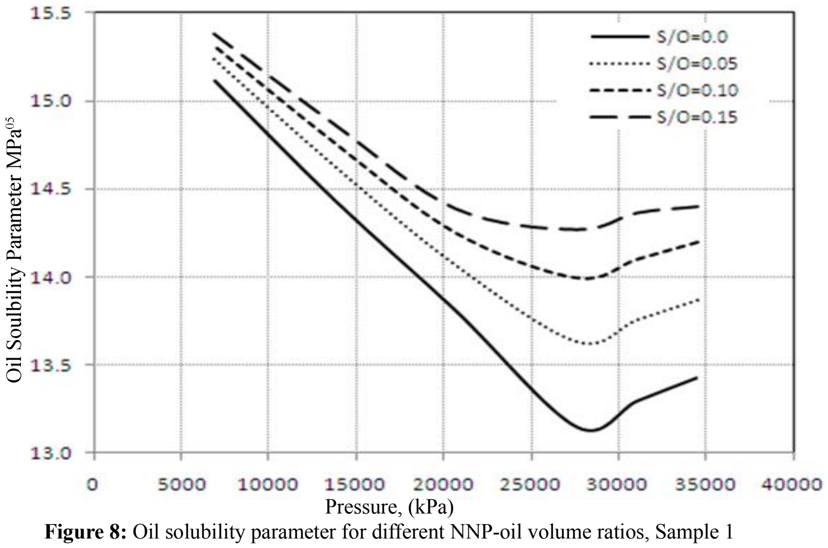

Figure 8: Oil solubility parameter for different NNP-oil volume ratios, Sample 1

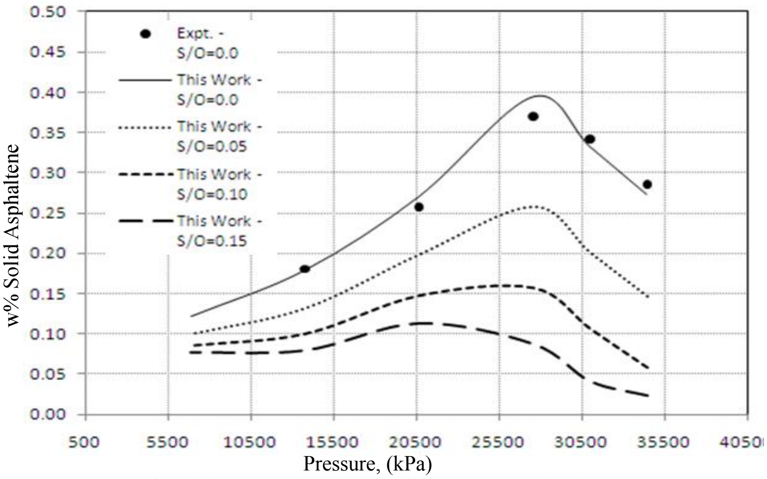

Figure 9: Amount of asphaltene precipitation for different NNP-oil volume ratios, Sample1

Conclusion

The polymer solution model based on Miller-Modified-Flory-Hugging model, which was applied to predict pressure, temperature, paraffinic precipitant, and miscible gas injection processes in the previous study, can be used to predict solvent injection into reservoir fluid under high temperature and high pressure conditions. The model parameters were adjusted via precipitation data on live oil, and then the adjusted parameters were used to predict the effects of different processes such as depletion, precipitant, solvent injection, and gas injection on precipitated asphaltene. The results of the model are in good agreement with all theoretical, field, and experimental data.

Nomenclatures

l_{aL}: pair interaction parameter
v: molar volume
ϕ : volume fraction
δ: solubility parameter
R: universal gas constant
z: coordination number
$\Delta\mu$: change of chemical potential

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