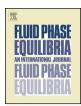
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A modified scaling equation based on properties of bottom hole live oil for asphaltene precipitation estimation under pressure depletion and gas injection conditions



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ABSTRACT

The process of asphaltene precipitation has a substantial effect on oil flow during primary oil production and enhanced oil recovery processes in the petroleum industry. In this work, a modified scaling model based on the PVT properties of bottom hole live oil including resin to asphaltene ratio, onset pressure, bubble point pressure, reservoir temperature, asphaltene content of bottom hole live oil and gas to oil ratio has been proposed to account for asphaltene precipitation under pressure depletion/gas injection conditions and the proposed model was verified using experimental data obtained in this work and also with those reported in the literature. In the proposed scaling model the resin to asphaltene ratio in bottom hole live oil was included as an additional parameter. In order to compare the performance of the proposed scaling model, the asphaltene precipitation experimental data at different pressure were correlated using PC-SAFT, Solid, Flory-Huggins and the proposed models. The results show that the proposed model correlates more accurately the asphaltene precipitation experimental data of bottom hole live oil in comparison to other above mentioned models. Sensitivity analysis shows that the modified scaling model is highly sensitive to the new term of resin to asphaltene ratio and also the gas-oil ratio of bottom hole live oil. Also, a series of experiments was carried to determine the asphaltene precipitation of bottom hole live oil during pressure depletion with Iranian bottom hole live oil samples which is close to reservoir conditions using high pressure-high temperature equilibrium cell.

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1. Introduction

Asphaltenes and resins are the polar fractions of crude oil that can be separated by addition of low molecular weight *n*-alkanes [1]. By definition, asphaltenes are the fraction of a crude oil that is soluble in toluene and insoluble in an *n*-alkane, typically pentane or heptane. These fractions are formed by molecules with a poly aromatic structure containing paraffinic and naphthenic chains, as well as oxygen, nitrogen and sulfur as functional groups or heteroatom. In the other hand, asphaltenes are heavy hydrocarbon molecules that are in colloidal suspension in the oil, stabilized by resins adsorbed on their surface [2]. During asphaltene precipitation, asphaltene particles come out of solution, are solidified and a new solid phases generated in the solution. Asphaltene precipitation may alter the formation wettability and, hence, reduce the

permeability, porosity and sweeping efficiency during enhanced oil recovery processes of the reservoir. Therefore, the prediction of asphaltene precipitation will be essential in the oil reservoir during production as a mean to prevent plugging pore throats thus reducing the rock permeability.

Due to the complexity of asphaltene precipitation phenomena during production, very little experimental results currently exists on asphaltene precipitation under high pressure conditions using bottom hole live oil. The majority of existing works study the asphaltene precipitation using recombined oil (mixture of dead oil and associated gas) which is far from reservoir conditions or using alkane solvents during titration of dead oil. Therefore, such results are not applicable to the real scale, where the complex interactions between the hydrocarbon groups of bottom hole live oil as resin and asphaltene are always present. The asphaltene precipitation is governed by various parameters such as resin to asphaltene ratio, onset pressure, reservoir pressure, bubble point pressure, gas—oil ratio, reservoir temperature and asphaltene content of bottom hole live oil.

The existing models of asphaltene precipitation models are either thermodynamic or scaling models. Thermodynamic

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Nomenclature

GOR gas-oil ratio *P* pressure

 P_b bubble point pressure $P_{
m onset}$ onset pressure

 R_{RA} resin to asphaltene ratio

T temperature

 W_{AP} the amount of asphaltene precipitation W_A asphaltene content of bottom hole live oil

Z adjusted parameter
 X function defined by Eq. (1)
 Y function defined by Eq. (2)

Superscripts

Asph asphaltene Ref reference state

Greek letters

 δ solubility parameter (MPa^{0.5})

models are based on the complex properties of asphaltene such as interaction coefficient, critical properties, acentric factor, solubility parameter and molecular weight which are not specified, while scaling models are based on the aggregation/gelation phenomena which are not involving the critical properties of asphaltene [3]. The first thermodynamic model treating asphaltenes as solvated in a liquid medium was the Flory theory [4] for polymer solutions. This method decouples the vapor-liquid equilibrium from the liquid-solid equilibrium. The vapor-liquid equilibrium calculations are first done and then a correction is applied to the liquid phase accounting that the vapour phase remains unchanged. Hirschberg and co-workers [5] treated asphaltenes as monodispersed solvated macromolecules without considering resins. Cubic equations of state were not so much investigated. Gupta [6] coupled a solid phase fugacity with a Peng-Robinson model. Victorov and Firoozabadi [7] developed a micellization model. Three major contributions to the process of micelle formation are taken into account: The lyophobic contributions represent the free energy gain upon transferring asphaltene and resin molecules from indefinitely diluted crude to a micelle. The interfacial contribution is a definite positive interfacial tension. Another contribution is the electrostatic contribution. Associating EOS like SAFT are the most advanced EOS [8,9]. As expected, the SAFT EOS, even with fitted parameters, cannot describe the data properly since fugacity of asphaltenes depends on its molar fraction. CPA (Cubic Plus Association) was also used to model asphaltene precipitation [10]. Fahim and Andersen found that the error in constructing asphaltene precipitation by SRK EOS has been dropped from 19% to 10% using the CPA EOS. In our previous publication [11] asphaltene precipitation in a specified Iranian live oil reservoir was studied using PC-SAFT EOS and Solid model [12] and the results showed that PC-SAFT EOS correlates more accurately the onset pressure and asphaltene precipitation amount in comparison with another studied models.

The scaling model is another method for modeling of asphaltene precipitation. Scaling models were proposed in 1996, similarly to the ones used in aggregation and gelation phenomena [3]. Such a method successfully described the amount of precipitated asphaltenes as a function of the solvent-to-crude oil ratio and the molar weight of the solvent. Leontaritis and Mansoori [13] assumed that asphaltenes are insoluble, solid particles peptized by resins adsorbed onto their surfaces. This model has been further developed but it has only been employed for data regression. Rassamdana et al. [3] proposed a scaling equation for the onset of

asphaltene precipitation. Rassamdana and Sahimi [14] extended the scaling model to non-isothermal asphaltene precipitation process by including the temperature in the scaling variables. They have shown that all titration curves of asphaltenic dead oil with normal alkane solvents will collapse into a single curve. Hu et al. [15,16] performed extensive titration experiments on dead oil at several temperatures and concluded that the scaling models are adequate for correlating and predicting the asphaltene precipitation data at different temperatures for normal alkane precipitants but with different exponent. Moradi [17] presented a new scaling model to account the asphaltene precipitation due to gas injection at reservoir conditions. Soltani [18] developed a simple new scaling model for modeling the asphaltene precipitation at different pressure and temperature conditions. Kord [19] developed a new scaling model for live oil and applied to predict a new real data set.

In this work, a modified scaling equation for asphaltene precipitation calculation under reservoir conditions based on PVT properties of bottom hole live oil including resin to asphaltene ratio, onset pressure, bubble point pressure, reservoir temperature, asphaltene content of bottom hole live oil and gas to oil ratio during high pressure and gas injection conditions has been proposed and the model was verified using experimental data obtained in this work and also those found in the literature. Also the performance of the proposed scaling model in comparison to PC-SAFT model, Solid model and Flory-Huggins model using the asphaltene precipitation experimental data obtained in this work and also with those reported in the literature was studied. In the experimental section using bottom hole live oil sample which is close to the reservoir conditions, the asphaltene precipitation during pressure depletion using high pressure high temperature equilibrium cell was investigated.

2. Experimental

2.1. Material

In the majority of previous works, the recombined oil (mixture dead oil and associated gas) or dead oil was used in asphaltene precipitation experiments which its physical properties were far from reservoir oil properties. In this work bottom hole live oil sample from Iranian reservoirs on the Southeast region of Iran which is close to the reservoir conditions was used. The compositional analysis of studied bottom hole live oil using the gas chromatography method is given in Table 1. The asphaltene content of the bottom hole live oils was measured using the SARA analyses. The constituents of crude oils are typically classified by saturates,

Table 1Studied bottom hole live oil composition.

Components	Bottom hole live oil (mol%)
H ₂ S	0.0
N_2	0.3
CO_2	1.83
C_1	22.7
C_2	8.24
C ₃	6.14
i-C ₄	1.19
n-C ₄	3.61
i-C ₅	1.38
n-C ₅	1.59
C ₆	6.95
C ₇	4.1
C ₈	3.88
C ₉	2.49
C ₁₀	4.03
C ₁₁	2.85
C ₁₂ +	28.74

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