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A modified Flory-Huggins model for prediction of asphaltenes precipitation in crude oil

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Abstract

The Flory-Huggins model has been modified to predict the phase behavior of asphaltene precipitation process by adding solvents such as *n*-C5, *n*-C6 and *n*-C7 to an oil sample. The adjustable parameters of this model are calculated by optimization of an objective function and experimental data of asphaltene precipitation. The amount of asphaltene precipitation has been calculated based on the modified Flory-Huggins model compared with the Flory-Huggins model and the experimental data of references. It is shown that the modified Flory-Huggins model can accurate predict the asphaltene precipitation. Also, the differential solubility parameters of asphaltene and oil at different proportions of solvent have been calculated. The results show that the values of this parameter increases when solvent ratio enhancement.

Keywords: Asphaltene; Precipitation; Flory-Huggins model; Solubility parameter; Crude oil

1. Introduction

Deposition of complex and heavy organic compounds, which exist in petroleum crude particularly in crude oil, can cause a number of serious problems [1,2]. The significance of this problem was discussed in lengths in an earlier paper by the authors [3]. Asphaltene precipitation around the well bore, well tubings, flow lines, separators, pumps, tanks and other equipment has in many occasions, threatened the economic recovery of the oil or increased considerably the cost of producing it. Trbovich and King [4] listed 11 different causes of asphaltenes deposition (CO_2, rich gas), ph shift, mixing of crude streams, incompatible organic chemicals, stimulation, shear, pressure drop, streaming potential, temperature drop, charged and bare metal surface.

Experimental activities by themselves can not be enough to achieve a clear picture of the condition and possible problems as widely doing the experiments, besides involving high costs, is impossible in some cases. So, models should be come through by which the above issues would be predicted with a reasonable accuracy.

Several approaches for modeling asphaltene precipitation have been reported in the petroleum literature. The first important approach in modeling asphaltene precipitation in petroleum engineering is due to Hirschberg et al. [5]. The simplest model for the precipitated asphaltene is the single-component solid model that was tried by Gupta [6] and Thomas et al [7]. The previous approaches are based on molecular thermodynamics and are suitable for modeling situations where the asphaltene/resin micelles precipitate essentially unaltered. Leontaritis and Mansoori [8] proposed a different approach for asphaltene flocculation based on a thermodynamic–colloidal model.

In this study, the Flory-Huggines model is modified by the interaction parameter. This parameter is defined based on molecular weight of asphaltene to molecular weight of crude oil ratio in form of polynomial function. Then, the amount of asphaltene precipitation was predicted using SRK EOS and the modified Flory-Huggins models. The results are compared whit the Flory-Huggins model and experimental data of literature [9]. Predictions show a good match with experimental data, demonstrating the reliability of the developed model.

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Nomenclatures

N	number of experimental data
P	pressure (MPa)
R	universal gas constant
T	temperature (K)
v	molar Volume (m^3 $kmol^{-1}$)
w	mass fraction
x	liquid phase mole fraction
y	vapor phase mole fraction
U	internal energy

Greek letters

ϕ	volume fraction
Ω	objective function
μ	chemical potential
Δ	difference between asphaltene and oil solubility parameter
δ	solubility parameter
λ_{PS}	interaction parameter
α_1, α_2, α_3,	parameters in Eq. (7)

Subscripts and superscripts

P	asphaltene
S	solvent
cal	calculation
exp	experimental
l	liquid
o	standard state

2. Modeling the precipitated asphaltene

A Vapor–Liquid–Liquid equilibria (VLLE) model is employed, using separate VLE and LLE calculations to predict the phase splits (vapor, asphaltene and crude oil tractions). The model uses the concept of material balance by coupling with a thermodynamic model. The SRK equation of state is employed for the estimation of the component properties for the lighter fraction and equilibria calculation. The properties of the heavy fractions in the crude oil system are determined using empirical correlations [10]. As asphaltene is a polymeric substance, the theory of polymeric solution is used for prediction of asphaltene precipitation in crude oil. Flory-Huggins model is the simplest model, which has been suggested for study of the phase behavior of polymeric solutions. According to Flory-Huggins theory, the chemical potential of polymeric component is calculated as follow:

$$\frac{\mu_P-\mu_P^O}{RT}=\ln\phi_P+\left(1-\frac{V_P}{V_S}\right)\phi_S+\frac{V_P}{RT}(\delta_P-\delta_S)^2\phi_S^2 \tag{1}$$

where μ, ϕ and V, δ are chemical potential, volume fraction, molar volume and solubility parameter, respectively. Subscriptions P and S are for polymer and solvent phases, respectively. The solubility parameter in Eq. (1) is written as below:

$$\delta_i=\left(\frac{\Delta U}{v}\right)_i^{0.5} \tag{2}$$

where ΔU is the internal energy of vaporization at constant temperature. The values of ΔU and v are calculated by the SRK EOS. The thermodynamic model of F-H does not have a reasonable accuracy for not having an adjustable parameter. In this study, the F-H model is modified as follow:

$$\frac{\mu_P-\mu_P^O}{RT}=\ln\phi_P+\left(1-\frac{V_P}{V_S}\right)\phi_S+\frac{V_P}{RT}(\delta_P-\delta_S)^2\phi_S^2+2\lambda_{PS}\delta_P\delta_S \tag{3}$$

where λ_{PS} is the interaction parameter between polymer and solvent.

The modified Flory-Huggins model (Eq. (3)) is used for estimation of asphahene precipitation in crude oil. In this work, it is also assumed that the asphaltene phase is as a pure liquid pseudo-component in which asphaltene precipitation has not effect on liquid–vapor equilibrium. Also, crude oil is considered as a binary homogeneous mixture of asphaltene and solvent. Based on above assumptions and considering indices P and S for asphaltene and solvent respectively, Eq. (3) will be simplified as below:

$$\frac{\mu_P^L-\mu_P^O}{RT}=\ln\phi_P+\left(1-\frac{V_P^L}{V^L}\right)+\frac{V_P}{RT}((\delta_P-\delta^L)^2+2\lambda_{PS}\delta_P\delta_S) \tag{4}$$

When the differential chemical potentials of asphaltene component are equalized in the two phases of asphaltene and liquid, then:

$$\phi_P^L=\exp\left[\left(\frac{V_P^L}{V^L}-1\right)-\frac{V_P^L}{RT}((\delta_P-\delta^L)^2+2\lambda_{PS}\delta_P\delta_S)\right] \tag{5}$$

where, superscription L is for liquid phase. In respect to Eq. (5), the weight fraction of asphaltene precipitation is calculated as below:

$$w_P=\frac{(1-\phi_P^L)(M_w^L/V^L)}{(1-\phi_P^L)(M_w^L/V^L)+\phi_P^L(M_{wp}/V_P)} \tag{6}$$

where, λ_{PS} in Eq. (5) is the interaction parameter and depends on molecular weight of asphaltene and molecular weight of solvent (crude oil and *n*-alkend solvent) ratio, according to bellow equation:

$$\lambda_{PS}=\alpha_1+\alpha_2\left(\frac{M_{wp}}{M_{ws}}\right)+\alpha_3\left(\frac{M_{wp}}{M_{WS}}\right)^2 \tag{7}$$

The adjustable parameters α_1, α_2 and α_3 Will be obtained by the experimental values of asphaltene precipitation and