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Modification of a thermodynamic model and an equation of state for accurate calculation of asphaltene precipitation phase behavior

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Abstract

In this study, DPTG (Dashtizadeh–Pazuki–Taghikhani–Ghotbi) equation of state has been modified for calculation of phase behavior of fluids and solubility parameter. The accuracy of the modified EOS has been proved by estimation of the properties of some hydrocarbons such as densities of methane and condensate gases, vaporization enthalpy, sublimation pressure, compressibility factor and comparison of the obtained results with the results of the present equations of state such as NJ (Nasrifar–Jalali), ZMJL (Zhi–Meiren–Jun–Lee) and PR (Peng–Robinson). Then, the Flory–Huggins model has been modified and asphaltene precipitation phase behavior at different ratios of solvents in the crude oil has been predicted by the modified EOS and the developed Flory–Huggins model. Comparison of the obtained results with the experimental data of asphaltene precipitation and the calculated ones by the main Flory–Huggins model shows the accuracy of the developed model.

Keywords: Asphaltene precipitation; Phase behavior; Solubility parameter; EOS; Thermodynamic model

1. Introduction

Asphaltene is defined as a component of the crude oil which is precipitated by adding low molecular weight solvents (*n*-alkanes) [1]. Amount and nature of asphaltene precipitation depend on the kind of precipitator, oil–solvent ratio, oil–solvent contact time, pressure and temperature. Asphaltene precipitation affects on oil production, oil processing and transportation. During oil production, asphaltene precipitation is gradually formed and it reduces the reservoir permeability and porosity and finally blocks the wellhead [2]. In oil processing, the implemented thermal changes cause asphaltene precipitation decomposition and coke formation. Then, when coke precipitates on the catalyst, it will be deactivated. Since above subject accompanies extensive economical losses, so theoretical and experimental study of effective parameters on asphaltene precipitation will be necessary in order to understand the main mechanism of asphaltene precipitation formation for prevention of that phenomenon and also obtaining the necessary information for development of available models. However, experimental activities by themselves cannot be enough to achieve a clear picture of the conditions and possible problems because widely doing the experiments besides involving high costs is impossible at some cases. So, models should come through by which the above issues would be predicted with a reasonable accuracy. Molecular thermodynamic models, colloidal model and fractal accumulation model are the most considerable models to predict asphaltene precipitation.

In the molecular model [3–7], asphaltene precipitation is considered as a solute liquid in the oil and thermodynamically reversible. In the colloidal model [8,9], asphaltene particles are considered as solid and flocculated particles

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Nomenclature

a	attraction parameter (MPa m^6 $kmol^{-2}$)
A	parameters in Eq. (10)
b	molar co-volume (m^3 $kmol^{-1}$)
f	parameters in Eq. (10)
H	enthalpy
P	pressure (MPa)
r	molar volume ratio
R	universal gas constant
SR	solvent ratio (m^3 solvent/kg oil)
T	temperature (K)
v	volume (m^3 $kmol^{-1}$)
w	mass fraction
x	liquid phase mole fraction
y	vapor phase mole fraction
Z	compressibility factor

Greek symbols

ϕ	volume fraction
ρ	density (kg/m^3)
ω	Pitzer acentric factor
μ	chemical potential
Δ	difference between the solubility parameters of oil–asphaltene
δ	solubility parameter

Subscripts

c	critical
i, j	dummy index
r	reduced
1	asphaltene
2	oil mixture

Superscripts

cal	calculation
L	liquid
exp	experimental

in the crude oil, which are stabilized by aromatic molecules of resin covering the particles surface. Asphaltene particles are coalesced mechanically or by electrical absorption by resins solvating and then precipitated. The fractal accumulation model [10] is an integration of two theories of molecular and colloidal, which includes kinetic and thermodynamic theories of accumulation.

In this study, the Flory–Huggins model has been modified as a base model for prediction of phase behavior of polymer solution to model asphaltene precipitation phase behavior at different solvent ratios in the crude oil and the obtained results are compared with the experimental data [12] and the main Flory–Huggins model. Meanwhile, considering the important role of solubility parameter in this model and as accurate calculation of the solubility parameter has a considerable effect on the model results, so, DPTG equation of state [11] has been modified for accurate calculation of the solubility parameter. Also, the accuracy of the modified EOS has been studied by estimation of the properties of some hydrocarbons such as densities of methane and condensate gases, vaporization enthalpy, sublimation pressure, compressibility factor and comparison of the obtained results with the results of some known equations of state such as NJ [15], ZMJL [16] and PR [17].

2. Asphaltene precipitation modeling

Asphaltene is a heavy hydrocarbon, so in this study, a modified Flory–Huggins model predicts the phase behavior of asphaltene precipitation. Based on this model, asphaltene is treated as a pure liquid pseudo-component in which asphaltene precipitation has no effect on liquid–vapor equilibrium. So, using two-phase equilibrium calculations (liquid–vapor as well as liquid–liquid calculations) is applied instead of multi-phase equilibrium calculations. In addition, crude oil is considered as a binary homogeneous mixture of asphaltene and solvent. In accordance with the developed Flory–Huggins model [13] and by considering indices 1 and 2 for asphaltene and oil, the activity coefficient for asphaltene is expressed as follows:

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{1}{r_2}\right)\phi_2 + \frac{d\phi_2^2}{(1 - f\phi_2)} \tag{1}$$

where φ is the volume fraction, r is the molar volume ratio, f and d are the adjustable parameters of above model. In the other hand, by considering $\Delta\mu_1 = RT\ln a_1$, the correlation of asphaltene chemical potential is as follows:

$$\mu_1 - \mu_1^{\circ} = RT\left[\ln \phi_1 + \left(1 - \frac{1}{r_2}\right)\phi_2 + \frac{d\phi_2^2}{(1 - f\phi_2)}\right] \tag{2}$$

In order to measure the asphaltene precipitation at different solvent ratios, the equilibration conditions is written as a separate phase:

$$\mu_1^{s} = \mu_1^{L} \tag{3}$$

Applying correlations (2) and (3), below equation will be obtained:

$$\ln \phi_1^{S} + \left(1 - \frac{1}{r_2^{S}}\right)\phi_2^{S} + \frac{d\left(\phi_2^{S}\right)^2}{\left(1 - f\phi_2^{S}\right)} = \ln \phi_1^{L} + \left(1 - \frac{1}{r_2^{L}}\right)\phi_2^{L} + \frac{d(\phi_2^{L})^2}{(1 - f\phi_2^{L})} \tag{4}$$