The Scott-Magat Polymer Theory for Determining Onset of Precipitation of Dissolved Asphaltene in the Solvent + Precipitant Solution

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INTRODUCTION

Asphaltene precipitation in oil industry can cause serious operational, safety and economical problems because it causes fouling in the reservoir, in the well, in the pipeline and in the production and processing facilities. Asphaltene phase behavior has therefore been the subject of numerous theoretical studies [1-34]. One of the fundamental difficulties encountered in describing the phase behavior of asphaltene-containing systems is the lack of suitable characterization parameters [1, 7]. In fact, asphaltenes are not well-identified components/ mixtures. They consist of several polar components of aromatic nature with high molecular weights [1, 7]. In the majority of cases, the complexity of the asphaltene fraction leads to the assumption that the asphaltenes can be regarded as one single pseudo-component (monodisperse) [1, 7]. The main drawback of the monodisperse models is that they may not take into account the aggregation phenomena of asphaltenes [1, 7]. In fact, the aggregation process produces a molecular weight distribution of aggregates, which also causes a polydispersity in asphaltene properties [1, 7]. A few models use a polydisperse concept in terms of asphaltene properties, especially molecular weight and size [21-23].

The traditional models reported in the literature normally use polymer solutions theories (Scatchard-Hildebrand [7], Flory-Huggins [7, 35], and Scott-Magat [36]) to model the phase behavior of asphaltene-containing fluids [1, 2, 5, 7, 8, 14, 20-23]. In addition to these models, there are also a few models, which are based on cubic equations of state [17, 24]. New thermodynamic models have recently been developed, which can take into account the aggregation nature of asphaltene [5, 13, 16, 26-31]. On the other hand, most of the models reported in the literature assume that the precipitated phase consists of asphaltene only and the presence of non-asphaltene components in the precipitated phase is normally ignored. Cimino et al. [2, 14] employed the Flory-Huggins polymer theory [35] and assumed that the precipitated phase contains not only asphaltene but also a fraction of non-asphaltene components. They showed that their proposed model [2, 14] can better predict phase behavior of dissolved asphaltene in mixtures of solvents and precipitants and none of the literature models is capable of predicting this behavior satisfactorily. Cimino et al. [2, 14] also reported a need to modify other polymer theory based asphaltene models in order to take into account the presence of non-asphaltene components in the precipitated phase.

In this work, we use a more comprehensive polymer theory than the Flory-Huggins model [35], namely the Scott-Magat polymer theory [36] for modeling asphaltene phase behavior. Different from the Flory-Huggins polymer theory [35] based asphaltene models (which assume that asphaltenes have homogeneous structure and properties), the Scott-Magat polymer theory [36] based asphaltene models assume that asphaltenes have heterogeneous structure and the polydispersity can be taken into account in the molecular weight of asphaltene. Kawanaka et al. [21, 22] and Park [23] used this theory for modeling asphaltene phase behavior. However, they assumed that the precipitated phase consists of asphaltene only. Using this theory [36], and assuming that the precipitated phase consists of both asphaltene and non-asphaltene components, we propose a thermodynamic model. It is shown that the new model is similar to a previously reported model based on the Flory-Huggins polymer theory [35], namely Cimino et al. [2, 14] model, in which the precipitated phase consist of asphaltene and non-asphaltene components.
THERMODYNAMIC MODEL BASED ON FLORY-HUGGINS POLYMER THEORY

Following the Flory-Huggins polymer theory [20], the chemical potential change of the maltene (asphaltene free oil) relative to a reference value, \( \Delta \mu_m \), and the chemical potential change of the asphaltene relative to a reference value, \( \Delta \mu_a \), are given, respectively by [8]:

\[
\Delta \mu_m = RT \ln \Phi_m + (1 - \Phi_m) \left( \frac{V_m}{V_a} \right) + \chi (1 - \Phi_m)^2
\] (1)

\[
\Delta \mu_a = RT \ln (\Phi_a) + (1 - \Phi_a) \left( \frac{V_a}{V_m} \right) + (1 - \Phi_a)^2 \frac{V_a}{V_m} \chi
\] (2)

where \( R \), \( T \), \( \Phi_m \), \( V_m \), \( \Phi_a \) and \( V_a \) are universal gas constant, temperature, volume fraction of maltene, molar volume of maltene, volume fraction of asphaltene and molar volume of asphaltene, respectively. \( \chi \) stands for interaction parameter between asphaltene and maltene and is given by the following equation [2, 8, 14]:

\[
\chi = \frac{V_m [(\delta_m - \delta_a)^2]}{RT}
\] (3)

where \( \delta_m \) and \( \delta_a \) are solubility parameters (the square root of the internal energy of vaporization per molecular volume) for the maltene and the asphaltene, respectively. In the above equation [36, 38]:

\[
\Phi_a = 1 - \Phi_m = \frac{x_a V_a}{x_a V_a + x_m V_m}
\] (4)

or

\[
\Phi_a = \frac{w_a / \rho_a}{w_a / \rho_a + w_m / \rho_m}
\] (5)

where \( x_a \) and \( x_m \) are the mole fractions of asphaltene and maltene, respectively. \( w_a \) and \( w_m \) are the weight fractions of asphaltene and maltene, respectively and \( \rho_a \) and \( \rho_m \) represent the mass densities of asphaltene and maltene, respectively.

Cimino et al. [2, 14] performed some tests to estimate onset of precipitation of dissolved asphaltene in different ratios of solvent and precipitant. The results showed that the precipitated asphaltene does dissolve in appropriate solvent and the ratio of “solvent mass per asphaltene mass” and “precipitant mass per asphaltene mass” is linear and independent of the asphaltene concentration at onset of asphaltene precipitation conditions [2, 14]. Their experiments showed poor capability of colloidal model [25] and traditional Flory-Huggins polymer theory [35] based models [21, 22] in reproducing the observed behavior, where the latter models assume pure asphaltene for the precipitated phase. Cimino et al. [2, 14] employed a more correct application of the Flory-Huggins polymer theory [35] to better represent asphaltene phase behavior. They assumed that not a pure asphaltene phase but a phase containing concentrated asphaltene and a fraction of solvent nucleates on phase separation.

Some simplifications are made by considering the physics of phase splitting. Considering the typically low volume fraction of asphaltene in the oil phase (\( \Phi_a \), which is about 10⁻² to 10⁻³ when the asphaltene weight percent ranges from 1 to 10) the oil can safely be assumed to be pure maltene, that is \( \Phi_a = 0 \) [2, 14]. Such an assumption leads to the following final equation [2, 14]:

\[
\ln [1 - \Phi_a] + \left( \frac{V_m}{V_a} \right) \Phi_a + \chi \Phi_a^2 = 0
\] (6)

where the prime represents the asphaltene-rich phase, and \( \Phi_a \) is the volume fraction of asphaltene in asphaltene-rich phase.

According to this model [2, 14], \( \delta_a \) is assumed to be independent of pressure, and \( \Phi_a \) is assumed to be constant. The parameters \( \delta_a \) and \( \delta_m \) are regressed from experimental data on onset of asphaltene precipitation. \( V_a \) is calculated from density and molecular weight of asphaltene. For given \( \delta_m \), \( \Phi_a \) and temperature, equation (6) only varies with \( V_a \) and \( \delta_a \). Cimino et al. [1, 2] successfully examined the capability of this model [2, 14] against their own experimental data.

THERMODYNAMIC MODEL BASED ON SCOTT-MAGAT POLYMER THEORY

A more comprehensive approach for predicting asphaltene precipitation conditions can be developed by using the Scott-Magat polymer theory [36], in which a distribution of asphaltene molecular weight is taken into account, as mentioned earlier. Based on the Scott-Magat polymer theory [36], the chemical potential change of the maltene relative to a reference value, and the chemical potential change of the asphaltene fraction relative to a reference value (\( \Delta \mu_i \)) are calculated using the following equations [36]:

\[
\Delta \mu_m = RT \ln \Phi_m + (1 - \Phi_m) \left( \frac{1}{M} \right) + \chi (1 - \Phi_m)^2
\] (7)

\[
\Delta \mu_i = RT \ln \Phi_i + (1 - \Phi_i) \left( \frac{M_i}{M} \right) - M_i \Phi_m + \chi M_i \Phi_m^2
\] (8)

where \( \Phi_i \) is volume fraction of the \( i \)th asphaltene fraction. \( M \) and \( M_i \) represent the average molecular weight of asphaltene and the molecular weight of the \( i \)th asphaltene fraction, respectively. \( \chi \) is given by equation (3).

To determine the solubility/precipitation conditions based on the assumption made by Cimino et al. [2, 14], one must utilize the equilibrium conditions between the two-phases:

\[
\Delta \mu_m = \Delta \mu_m
\] (9)

where \( \Delta \mu_m \) is the chemical potential change of the maltene relative to a reference value, as mentioned earlier. The prime represents the asphaltene-rich phase, as pointed out earlier. Therefore:

\[
\ln \Phi_m + (1 - \Phi_m) \left( \frac{1}{M} \right) + \chi (1 - \Phi_m)^2 = 0
\]

or

\[
\ln \Phi_m + (1 - \Phi_m) \left( \frac{1}{M} \right) + \chi (1 - \Phi_m)^2 = 0
\] (10)
According to Scott-Magat polymer theory [36], for values of $\chi$ sufficiently high ($>>0.5$), one may take $\Phi_d=1$ and $\chi=\infty$, so that $\Phi_d$ is a function of $\chi$ alone:

$$\ln[1-\Phi_d]+\Phi_d+\chi\Phi_d^2=0$$  \hspace{1cm} (11)

Equation (11) is similar to equation (6) considering the ratio $V_m/V_a$ in equation (6) is negligibly small compared to unity. The result indicates that taking into account the polydispersity in asphaltene molecular weight is insignificant for the phase behavior modeling of dissolved asphaltene in solvent + precipitant solutions.

CONCLUSIONS

A phase equilibrium model (equation 11) was developed from the Scott-Magat polymer theory [36], which assumes that the precipitated phase consists of an asphaltene fraction and a non-asphaltene fraction, and the oil phase is free of asphaltene (due to low concentrations of asphaltene in the oil phase). It was shown that the new model is similar to a previously reported model (equation 6) based on the Flory-Huggins polymer theory [35], which assumes that the precipitated phase consists of asphaltene and non-asphaltene components. The study showed that taking into account the polydispersity in asphaltene molecular weight does not have important effect on phase behavior modeling of dissolved asphaltene in different ratios of solvent and precipitant.

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