

A NEW INVESTIGATION ON WAX PRECIPITATION IN PETROLEUM FLUIDS: INFLUENCE OF ACTIVITY COEFFICIENT MODELS

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Abstract

The wax precipitation is a major problem in the production, transportation and processing of Petroleum fluids. In this work, wax deposition in Petroleum fluid flowing has been investigated using solid solution model and multi-solid phase model. In order to predict the wax precipitation, combinations of models (regular solution theory, UNIFAC, UNIQUAC, Wilson and ideal solution model) for the prediction of solid and liquid phases have been investigated. In order to compare the performance of these models, the wax precipitation experimental data were predicted using these models. The results show that the Wilson and UNIQUAC predict the behavior of solid phase better than the other activity coefficient models. Also, ideal solution model for solid phase causes the deviation from experimental data in wax appearance temperature prediction to increase. The Wilson model is not accurate for prediction of the liquid phase. The results show that Lira-Galeana model from multi-solid (MS) phase category with The Wilson model is capable of prediction the wax precipitation experimental data with the AADs of 12.8 to 18.68%, whereas the Ji model from solid solution (SS) category correlates predict the wax precipitation experimental data with the AADs 21.4 to 24.8%.

Keywords: Wax deposition; Thermodynamic models; pipe lines.

1. Introduction

Crude oil is a complex mixture of hydrocarbons, consisting of waxes, asphaltenes, resins, aromatics and naphthenics. Among these, wax precipitation is a major problem in oil productions facilities and transportations pipe lines. Wax precipitation can result many problems such as decrease production rates, increase power requirements and failure of facilities in petroleum industry. Wax is the high molecular weight paraffin fraction of crude oil that can be separated below pour point of crude oil. The solubility of waxes with high molecular weight decreases by decreasing in temperature. In the transportation of waxy crude oil in a cold environment at temperatures below the oil pour point, the temperature gradient in the oil creates a concentration gradient in the dissolved waxes due to their difference in solubility. The driving force, created by the concentration gradient, transfers the wax from the oil toward the pipe line wall where they precipitate and form a solid phase. The solid phase reduces the available area for the oil flow, which in turn causes a drop in the pipe flow capacity. As shown in Figure 1, the types of wax crystals are included: Macrocrystalline, Microcrystalline and Crystal deposit Network of Wax. The steps of wax formation are shown in Figure 1.

Recently the experimental and modeling of precipitation and deposition of heavy cut in Iranian crude oils was investigated by Jafari Behbahani *et al.* [1-8].

In order to predict the wax precipitation conditions a reliable thermodynamic model is necessary. A literature review shows that models of wax precipitation can be classified into two different categories. The first important category in modeling of wax precipitation uses a cubic EOS for vapor-liquid equilibrium and an activity coefficient model for solid-liquid equilibrium.

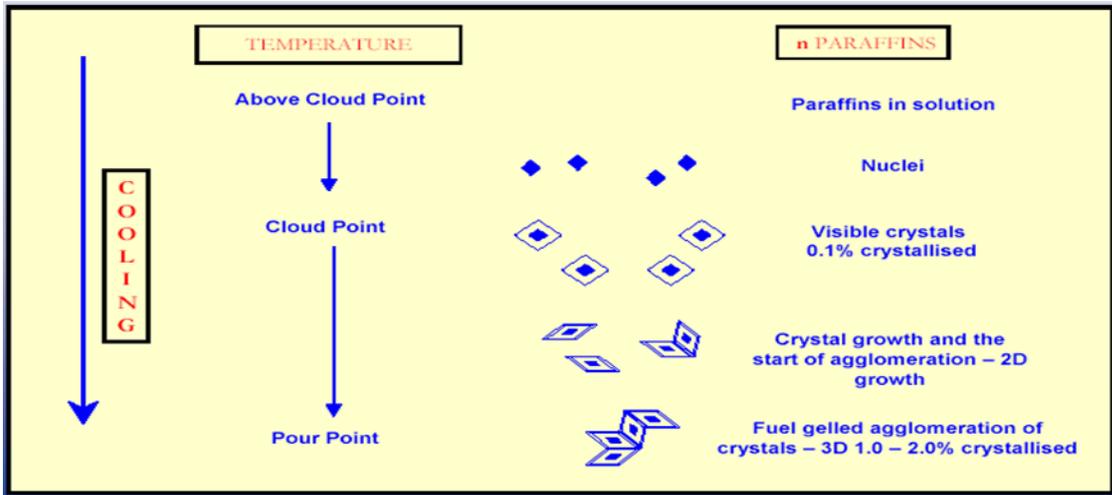


Figure 1 The steps of wax formation

These models are based on solid solution (SS) theory which assumes that all the components in the solid phase are miscible in all proportions [9-14]. Chen et al. proposed the new correlations for the melting points and solid–solid transition temperatures of treated paraffin based on the experimental results by differential scanning calorimeter (DSC) [15]. The required thermodynamic properties of pure n-paraffin are first estimated, and then a new approach based on the UNIQUAC equation is described. Finally, the impact of pressure on wax phase equilibrium is studied. The second approach based on multi-solid (MS) phase model uses only an EOS for all phases in equilibrium; in fact an EOS is used directly for vapor–liquid equilibrium, and solid phase is described indirectly from the EOS by fugacity ratio which assumes that each pure or pseudo component that precipitates constitutes a separate solid phase which is not miscible with other solid phases [16-20]. In this work, thermodynamic modeling of wax phase behavior in crude oil has been investigated using the Ji model from solid solution (SS) category solid solution model and Lira-Galeana model from multi-solid (MS) phase category using regular solution theory, UNIFAC, UNIQUAC, Wilson and ideal solution model for the prediction of solid and liquid phases.

2. Theoretical section

The studied models in this work include:

2.1 Multi-solid phase model

In multi-solid (MS) wax models developed by Lira-Galeana *et al.* [21], each solid phase is considered as a pure component which does not mix with other solid phases and can exist as a pure solid (solid assumption). The number and the identity of precipitating components are obtained from Michelsen's [22] phase–stability analysis which states that component i may exist as a pure solid:

$$f_i(P, T, z) - f_{pure,i}^s(P, T) \geq 0 \quad i = 1, \dots, n \quad (1)$$

where $f_i(P, T, z)$ is the fugacity of component i with feed composition z and $f_{pure,i}^s(P, T)$ is the fugacity of pure component i in solid phase. This model is based on the precipitation of certain heavy components of the crude with average properties and performs calculations for the liquid/multi-solid phase. The criterion of vapor–liquid–solid equilibrium is that the fugacities for every component i , must satisfy the following equations:

$$f_i^V = f_i^L = f_{pure,i}^s(P, T) \quad i = 1, \dots, N \quad (2)$$

$$f_i^V = f_i^L \quad i = 1, 2, \dots, N \quad (3)$$

where f is the fugacity, n is the total number of components, and N_s is the number of solid phases determined. The fugacities of each component in the vapor and liquid phases are

calculated by the equation of state. The solid phase fugacities of the pure components, $f_{pure,i}^s(P, T)$, can be calculated from the fugacity ratio expressed as follow :

$$\ln\left(\frac{f^s}{f^L}\right)_{Pure,i} = \frac{\Delta h_i^t}{RT} \left(\frac{T}{T_i^f} - 1\right) \frac{\Delta C_{pi}}{R} \left[1 - \frac{T}{T_i^f} + \ln\left(\frac{T_i^f}{T}\right)\right] \quad (4)$$

T_i^f is the fusion (melting) temperature

$$\Delta C_{pi} = C_{pi}^L - C_{pi}^S \quad (5)$$

where C_{pi}^L and C_{pi}^S are the heat capacity of pure component i at constant pressure corresponding to liquid and solid phases, respectively.

$$\Delta h_i^t = \Delta h_i^f - \Delta h_i^{tr} \quad (6)$$

where Δh_i^f and Δh_i^{tr} are the enthalpy of fusion and the enthalpy of first solid state transition, respectively.

By using above equation and an EOS, fugacity in solid and liquid phases, and the numbers of the precipitated solid phases can be calculated. Solid-liquid equilibrium calculations have been performed by using equilibrium and material balance equations. The fugacity coefficient of component i is calculated by an EOS model. Among the EOS models available, the modified PR equation of state is used.

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (7)$$

The parameters a and b of pure component are described by the conventional critical parameters approach. The critical properties and acentric factor required in the evaluation of equation of state parameters are obtained from the Gasem's correlations [23].

For mixtures, the conventional linear mixing rule is kept for the parameter b :

$$b = \sum_i x_i b_i \quad (8)$$

Whereas for the parameter a , the LCV Mmixing rule is used:

$$\frac{a}{bRT} = \left(\frac{\lambda}{A_v} + \frac{1-\lambda}{A_m}\right) \left(\frac{G^E}{RT}\right) + \frac{1-\lambda}{A_m} \sum_i \ln\left(\frac{b}{b_i}\right) + \sum_i x_i \frac{a_i}{b_i RT} \quad (9)$$

where A_m , A_v are constant, then the fugacity coefficient of component i in a mixture, for the PR EOS is given by the following equation:

$$\ln \phi_i^L = \frac{b_i}{b} \left(\frac{PV}{RT} - 1\right) - \ln \frac{P(V-b)}{RT} - \frac{\alpha_i}{2\sqrt{2}} \ln \left[\frac{V+(1+\sqrt{2})b}{V+(1-\sqrt{2})b} \right] \quad (10)$$

$$\alpha_i = \left(\frac{\lambda}{A_v} + \frac{1-\lambda}{A_m}\right) \ln \gamma_i + \frac{1-\lambda}{A_m} \left(\ln\left(\frac{b}{b_i}\right) + \frac{b}{b_i} - 1\right) + \frac{a_i}{b_i RT} \quad (11)$$

2.2. Solid solution (SS) Theory

The modeling of wax formation in petroleum fluids is based on the thermodynamic description of the equilibrium between the solid wax and the hydrocarbon liquid phases. Produced reservoir hydrocarbon fluids at pipeline conditions commonly consist of liquid and vapor phases.

The criterion of vapor-liquid-solid equilibrium is that the fugacities for every component i , must satisfy the following equations:

$$f_i^V = f_i^L = f_{pure,i}^s(P, T) \quad i = 1, \dots, N \quad (12)$$

$$f_i^V = f_i^L \quad i = 1, 2, \dots, N \quad (13)$$

where f is the fugacity, n is the total number of components, and N_s is the number of solid phases determined. The fugacity of each component in the vapor and liquid phases are calculated by the equation of state. The fugacity coefficient of component i in the liquid phase is calculated by an EOS/ G^E model. The modified PR equation of state is used.

2.3 Studied activity coefficient models

The studied activity coefficient models include the regular solution theory, UNIQUAC, Wilson and UNIFAC.

2.3.1. Regular solution theory

In the regular solution theory, the activity coefficient is described as follow [9, 24]:

$$\ln \gamma_i = \frac{V_i(\delta - \delta_i)^2}{RT} \quad (14)$$

where V_i and δ_i are the molar volume, solubility parameter, respectively. The values of δ , φ_i^L and φ_i^S are calculated as follow:

$$\delta = \sum \varphi_i \delta_i \quad (15)$$

$$\varphi_i^L = \frac{x_i^L V_i^L}{\sum x_i^L V_i^L} \quad (16)$$

$$\varphi_i^S = \frac{x_i^S V_i^S}{\sum x_i^S V_i^S} \quad (17)$$

As φ_i^L and φ_i^S are the volume fractions of liquid and solid phases, respectively. By assumption that the liquid and solid molar volumes are equal:

$$V_i^L = V_i^S = V_i = \frac{MW_i}{d_{i,25}^L} \quad (18)$$

The liquid density of each component at 25 °C is calculated as follow:

$$d_{i,25}^L = 0.8155 + 0.6272 \times 10^{-4} MW_i - 13.06/MW_i \quad (19)$$

Solubility parameters in the liquid and solid phases are calculated as follow:

$$\delta_i^L = 7.41 + 0.519(\ln C_{ni} - \ln 7) \quad (20)$$

$$\delta_i^S = 8.5 + 5.763(\ln C_{ni} - \ln 7) \quad (21)$$

2.3.2 UNIQUAC model

The UNIQUAC model is calculated as follows [25, 26]:

$$\ln \gamma_i^S = \ln(\varphi_i / x_i^S) + 1 - \frac{\varphi_i}{x_i^S} - \frac{Z}{2} qi \left(\ln\left(\frac{\varphi_i}{\theta_i}\right) + 1 - \frac{\varphi_i}{\theta_i} \right) + qi - qi \ln(\sum \theta \tau) - qi \sum \theta i \tau i / \sum \theta \tau \quad (22)$$

$$\theta_i = \frac{x_i q_i}{\sum x_j q_j} \quad (23)$$

$$\varphi_i = \frac{x_i r_i}{\sum x_j r_j} \quad (24)$$

$$\tau = \exp \frac{\lambda_{ji} - \lambda_{ii}}{qiRT} \quad (25)$$

$$r_i = 0.001148 C_{ni} + 0.00996 \quad (26)$$

$$q_i = 0.0185 C_{ni} + 0.0211 \quad (27)$$

$$\lambda_{ii} = -\frac{2}{Z} (\Delta H - RT) \quad (28)$$

Z is the coordination number. The value of Z is 6 for the orthorhombic crystals.

2.3.3. Wilson model

The activity coefficients may be calculated by Wilson model as follows [27]:

$$\ln \gamma_i = 1 - \ln(\sum x_j \Lambda_{ij}) - \sum x_k \Lambda_{ik} / \sum x_j \Lambda_{kj} \quad (29)$$

$$\Lambda = \exp \frac{\lambda_{ji} - \lambda_{ii}}{qiRT} \quad (30)$$

2.3.4. UNIFAC model

The activity coefficient of component i is calculated using the UNIFAC method as follows. It is assumed that for mixtures containing alkanes only, the residual term in the UNIFAC model is zero. Thus, mixtures containing different alkanes are described by the combinatorial term. The Staverman–Guggenheim combinatorial term, which is used in UNIFAC, is:

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{Z}{2} q_i \left(\ln \left(\frac{\phi_i}{\theta_i} \right) + 1 - \frac{\phi_i}{\theta_i} \right) \quad (31)$$

where Z is the coordination number. In this work, r_i and q_i have been obtained from the following relations by data fitting presented in the literature:

$$r_i = 0.6744C_{ni} + 0.4534 \quad (32)$$

$$q_i = 0.54C_{ni} + 0.616 \quad (33)$$

3. Results and discussion

The main objective of this section is to compare the performance of activity coefficient models based on solid solution model (SS) and multi-solid (MS) phase model for the experimental data given in the literature [15,28-30] for calculating WAT and the weight percent of wax deposition. The absolute average deviation of the correlated asphaltene precipitation weight percent values obtained for the studied models from their experimental values was calculated by following relation

$$AAD\% = \frac{\sum_{i=1}^N |w_{exp} - w_{model}|}{N} / w_{model} \quad (34)$$

Table 1 shows the average absolute deviation (AADs) of the wax appearance temperature from the experimental data for studied crude oil using multi-solid phase models.

Table 1 The AAD% for Wax Appearance Temperature using combinations of activity coefficient models based on multi-solid phase model

The ac investigated activity coefficient model for solid phase	The investigated activity coefficient model for liquid phase	AAD%
Ideal	Ideal	0.7604
Regular solution	Ideal	0.4139
UNIFAC	Ideal	0.7189
UNIQUAC	Ideal	0.1852
Wilson	Ideal	0.6982
Ideal	Regular solution	0.7214
Regular solution	Regular solution	0.5106
UNIFAC	Regular solution	0.8236
UNIQUAC	Regular solution	0.1425
Wilson	Regular solution	0.7541
Ideal	UNIFAC	0.4247
Regular solution	UNIFAC	0.6895
UNIFAC	UNIFAC	0.3852
UNIQUAC	UNIFAC	1.2147
Wilson	UNIFAC	2.1214
Ideal	UNIQUAC	0.4259
Regular solution	UNIQUAC	0.9236
UNIFAC	UNIQUAC	1.2369
UNIQUAC	UNIQUAC	0.4365
Wilson	UNIQUAC	0.3562
Ideal	Wilson	7.2369
Regular solution	Wilson	6.3258
UNIFAC	Wilson	8.6931
UNIQUAC	Wilson	7.2126
Wilson	Wilson	5.2321

Figure 2 shows the performance of activity coefficient models using multi-solid models in prediction the amount of wax precipitation.

Table 2 shows the average absolute deviation (AADs) of the wax appearance temperature from the experimental data for studied crude oil using solid solution models.

Table 2 The AAD% for Wax Appearance Temperature using combinations of activity coefficient models based on solid solution model

The investigated activity coefficient model for Solid phase	The investigated activity coefficient model for Liquid phase	AAD%
Ideal	Ideal	0.7854
Regular solution	Ideal	0.4821
UNIFAC	Ideal	0.7548
UNIQUAC	Ideal	0.2031
Wilson	Ideal	0.7142
Ideal	Regular solution	0.7458
Regular solution	Regular solution	0.5421
UNIFAC	Regular solution	0.8578
UNIQUAC	Regular solution	0.1854
Wilson	Regular solution	0.7541
Ideal	UNIFAC	0.4502
Regular solution	UNIFAC	0.7263
UNIFAC	UNIFAC	0.4125
UNIQUAC	UNIFAC	1.5214
Wilson	UNIFAC	2.6235
Ideal	UNIQUAC	0.4521
Regular solution	UNIQUAC	0.9569
UNIFAC	UNIQUAC	1.5896
UNIQUAC	UNIQUAC	0.4857
Wilson	UNIQUAC	0.4178
Ideal	Wilson	7.9521
Regular solution	Wilson	6.2514
UNIFAC	Wilson	8.8796
UNIQUAC	Wilson	7.8425
Wilson	Wilson	5.6932

Figure 2 shows the performance of activity coefficient models using solid solution models in prediction the amount of wax precipitation.

The results show that the Wilson and the UNIQUAC predict the behavior of solid phase better than the other activity coefficient models. Also, the Wilson model causes the deviation from experimental data and is not accurate for prediction of behavior of the liquid phase. The results indicates that the combination of UNIQUAC for solid phase and Regular solution for liquid phase predict more accurate than other combination of activity coefficient models the wax precipitation behavior in crude oil.

The results show that multi-solid (MS) phase model is capable of prediction the wax precipitation experimental data with the AADs of 12.8 to 8.6%, whereas the solid solution (SS) model predicts the wax precipitation experimental data with the AADs 21.4 to 24.3%. It should be noted that the solid solution (SS) model used two types of thermodynamic models to describe the non-ideality of liquid phase; which makes this model thermodynamically inconsistent. It is observed from the curves that the solid solution (SS) model and multi-solid (MS) phase model overestimate the amount of precipitated wax. The thermodynamic models are based on the complex properties such as interaction coefficient,

critical properties, acentric factor, solubility parameter and molecular weight which are not specified for long chain of wax in crude oil.

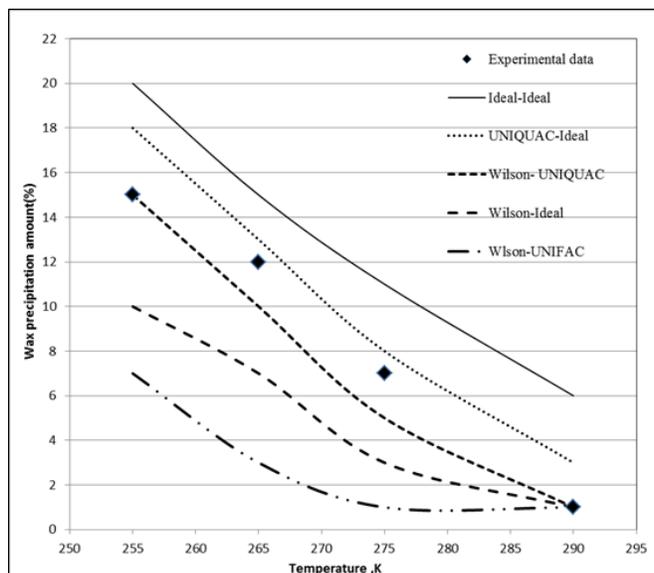


Figure 2 The performance of activity coefficient models using multi-solid models in prediction the amount of wax precipitation.

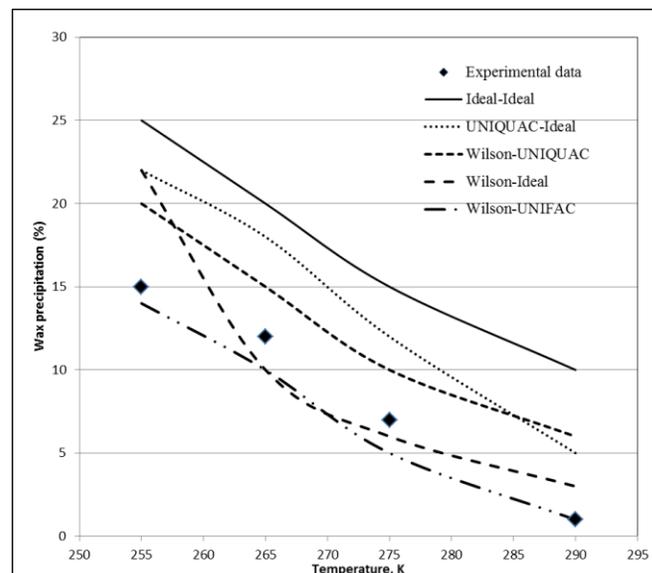


Figure 3 The performance of activity coefficient models using solid solution models in prediction the amount of wax precipitation

Conclusions

In this work, wax precipitation in crude oil has been investigated using solid solution model and multi-solid phase model. In order to predict the wax precipitation, combinations of activity coefficient models include regular solution theory, UNIFAC, UNIQUAC, Wilson model for the prediction of solid and liquid phases have been studied. Also, the studied models were verified using the experimental data given in literature as follows:

1. The results show that the Wilson and the UNIQUAC predict the behavior of solid phase better than the other activity coefficient models.
2. Also, the Wilson model causes the deviation from experimental data and is not accurate for p results indicates that the combination of UNIQUAC for solid phase and Regular solution for liquid phase predict more accurate than other combination of activity coefficient models the wax precipitation behavior in crude oil.
4. The results show that multi-solid (MS) phase model is capable of prediction the wax precipitation experimental data with the AADs of 12.8 to 18.6%, whereas the solid solution (SS) model predicts the wax precipitation experimental data with the AADs 21.4 to 24.3%. It is observed from the curves that the solid solution (SS) model and multi-solid (MS) phase model overestimate the amount of precipitated wax. The thermodynamic models are based on the complex properties such as interaction coefficient, critical properties, acentric factor, solubility parameter and molecular weight which are not specified for long chain of wax in crude oil.

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