



# Prediction of wax precipitation with new modified regular solution model



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## ABSTRACT

In present work, an improved regular solution model is established, based on the concept of regular solution and local composition theory. The local volume fractions  $\varphi_{ij}$  are considered to include the influence of interaction energy between molecules on molecules' local distribution. A new expression for molar excess Gibbs free energy ( $g^E$ ) is developed for the calculation of activity coefficients. Regular solution (RS), Wilson (W) and modified regular solution (MRS) are used for the non-ideality of solid phase and regular solution is adopted for liquid phase. Compared with the experimental data of binary, ternary and quaternary n-alkane systems, the advantage of RS-MRS is illustrated, with the best predictions of wax appearance temperature (WAT) and solid precipitation curve, which proves that the non-random molecules distribution caused by interaction energy between molecules is essential for  $g^E$ . It is the application of  $\varphi_{ij}$  that enhances the prediction accuracy of RS-MRS.

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## 1. Introduction

Wax deposition has been a serious challenge in petroleum production, transportation and storage. When the fluids temperature is lower than the wax appearance temperature (WAT), the heavy components in fluids will precipitate out and eventually deposit on pipe wall. With the growth of wax deposition, the cost on pumping becomes more expensive and the risk for pigging plugging or pipeline blockage rises [1]. Especially, the particular remediation of pipeline blockage in subsea oil pipelines at depths of around 400 m can cost \$1 million/mile [2]. To assure the safety of pipeline transportation and reduce the cost of production, it is essential to establish an accurate thermodynamic method to predict the precipitation of wax in petroleum fluids.

Regular solution theory was firstly employed to describe the solid-liquid equilibrium in crude oil system by Won [3], and the modified correlation for solubility parameter was applied to deal with the non-ideality of solid phase. To improve the established thermodynamic model [3], Won [4] used the combination of regular solution and Flory–Huggins to describe the non-ideality of liquid phase. The new wax prediction model precisely predicts the

cloud point of waxy mixtures and the composition of precipitated wax. Hansen et al. [5] employed polymer solution theory for the non-ideality of liquid phase, neglecting the non-ideality of wax phase. The interaction parameters in Hansen's model [5] were determined by fitting the model to the measured cloud point temperatures of the North Sea crude oils, which may limit the accuracy of Hansen's model for other crude oils. Pedersen et al. [6] further improved Won's model [3] by considering the heat capacity difference between phases and modifying the correlations for solubility parameter and fusion enthalpy. The influence of pressure was included into regular solution model by Thomas [7] with the consideration of the molar volume difference between solid and liquid phases. Lira-Galeana et al. [8] proposed a wax thermodynamic model where wax phase was assumed to be multiple pure solid phases and the non-ideality of vapor and liquid phases were calculated by PR-EOS. However, recent advances showed that Lira-Galeana model [8] is not proper for the systems with large carbon number difference [9]. A predictive version of the Wilson equation was developed by Coutinho et al. [10] according to lattice theory, where local volumetric fractions were substituted by local mole fractions. Afterwards, an evaluation of several activity coefficient models including UNIFAC (UNIQUAC Functional Group Activity Coefficients), Flory–Huggins, Flory free-volume and entropic free-volume was carried out and the results showed that Flory free-volume and entropic free-volume better described the liquid

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phase in alkane systems [11]. Thereafter, Coutinho [12] developed a new model for solid-liquid equilibrium in alkane systems, where UNIQUAC (Universal Quasichemical) was used to calculate solid phase non-ideality, and the combination of UNIFAC and Flory free-volume was introduced to depict liquid phase non-ideality.

Further, Pauly et al [13]. Established an EOS- $G^E$  thermodynamic model where the non-ideality of liquid and vapor phases were described by the SRK-EOS associated with UNIFAC and for solid phase, the predictive Wilson equation was applied. Ji et al. [14] presented a new correlation for the calculation of activity term in EOS. The comparison between SRK and PR for the description of liquid and vapor was conducted, while the Poynting correction term was neglected by using the new correlations for fusion properties. The reference pressure was set to be the operating pressure. Sansot et al [15]. Applied Pauly's solid-liquid-vapor equilibrium prediction model [13] to petroleum fluids and improved it by tuning  $\lambda_{ls}$  with an adjustable parameter  $\xi_{ls}$  to take the end effect into account. Chen et al. [16] presented a thermodynamic model to predict the wax precipitation in crude oil. The modified SRK-EOS was used to describe vapor and liquid phases, and UNIQUAC was chosen to calculate the activity coefficients of solid phase. In Chen's model [16], a new method for volumetric parameter was recommended and an improvement of the correlation for vaporization enthalpy was employed in UNIQUAC. Then, Chen et al. [17] considered the influence of pour point depressant on wax precipitation. EOS- $G^E$  was used for liquid phase non-ideality and solid phase was modeled by UNIQUAC.

Tabatabaei-Nejad et al. [18] introduced a thermodynamic model for petroleum reservoir fluids. The EOS was used to depict vapor and liquid phases, and regular solution theory was employed to describe solid phase. According to Tabatabaei-Nejad's research, fusion temperature has the greatest influence on the prediction of WAT and wax precipitation curve, compared with other factors such as fusion enthalpy, solid solubility parameter and binary interaction parameter BIP [18]. Farayola et al [19]. suggested a wax prediction model with the application of PT-EOS for liquid phase and UNIQUAC model for solid phase. The predicted results showed that PT-EOS surpassed PR-EOS in terms of WAT and wax precipitation curve. Nasrifar et al. [20] investigated the solid-liquid equilibrium of paraffin mixtures in a large temperature range, where Clapeyron equation was used to reflect the pressure influence on solid phase. Nasrifar et al. [21] further established a multiphase thermodynamic model for waxy systems, which can predict the equilibrium of vapor-liquid, solid-liquid, solid-vapor and solid-liquid-vapor. Ehsan et al. [22] developed a simplified wax model with the use of new generalized heat capacity correlations for liquid, disorder and order solid phases. Results showed that new correlations reduced the deviation of prediction from experimental data. Based on the former solid-liquid prediction model, Ehsan et al. [23] presented a new thermodynamic model for high pressure phase equilibrium of wax. In this model, the Clapeyron equation was used to build a relationship between the thermophysical properties and the molar volume variation of pure component during phase change. Behbahani et al. [24] compared the prediction capability of four different methods: artificial neural network method, ANN architecture and algorithm, multi-solid phase model and solid solution (SS) theory. Results showed that the developed model based on Artificial Neural Network gave the best prediction. Aftab et al. [25] studied the wax disappearance temperature (WDT) of ternary systems and evaluated the capability of  $\gamma$ - $\gamma$  approaches and  $\gamma$ - $\phi$  approaches for the prediction of WDT. Results showed that the combination of regular solution theory for the liquid phase with predictive Wilson applied for the solid phase led to the best accuracy for studied ternary systems.

In the research of phase equilibrium, regular solution has its

wide application due to its simplicity and high efficiency to describe the non-ideality of liquid and solid phases. Regular solution assumes that molecules in solution have a random distribution, leading to the probability of collision between two molecules being proportional to the volume fractions of those molecules. However, the assumption deviates from the fact that the interaction between molecules (local composition theory) is essential for the molecules distribution. Present work aims to improve regular solution model by introducing local composition consideration. And simple n-alkane systems are used to test the developed modified regular solution.

## 2. Thermodynamic model

The liquid-solid fugacity ratio at standard state from Pederson's research is used [6]:

$$\ln \frac{f_i^{oL}}{f_i^{oS}} = \frac{\Delta H_{f,i}}{RT} \left( 1 - \frac{T}{T_{f,i}} \right) - \frac{1}{RT} \int_T^{T_{f,i}} (\Delta C_p)_i dT + \frac{1}{R} \int_T^{T_{f,i}} \frac{(\Delta C_p)_i}{T} dT \quad (1)$$

where  $f_i^{oL}$  and  $f_i^{oS}$  are the fugacity of liquid and solid phases in standard state respectively.  $\Delta H_{f,i}$  is the fusion enthalpy.  $\Delta C_p$  represents the difference of specific heat capacity between liquid and solid phases.  $T_{f,i}$  is the fusion temperature of component i.  $R$  is the gas universal constant.

When the  $\gamma$ - $\gamma$  approach is employed to describe the non-ideality of liquid and solid phases, the solid-liquid equilibrium constant of component i,  $K_i^{SL}$ , can be written as:

$$\begin{aligned} \frac{x_i^S}{x_i^L} &= K_i^{SL} \\ &= \frac{\gamma_i^L}{\gamma_i^S} \exp \left( \frac{\Delta H_{f,i}}{RT} \left( 1 - \frac{T}{T_{f,i}} \right) - \frac{1}{RT} \int_T^{T_{f,i}} (\Delta C_p)_i dT \right. \\ &\quad \left. + \frac{1}{R} \int_T^{T_{f,i}} \frac{(\Delta C_p)_i}{T} dT \right) \end{aligned} \quad (2)$$

In the following work, the activity coefficients of liquid phase are calculated by regular solution (RS). The non-ideality of solid phase is depicted by three solid solution models including regular solution (RS), modified regular solution (MRS) and Wilson (W). The basic theory of MRS is the combination of regular solution theory and local composition theory. Therefore, regular solution and Wilson model are illustrated priorly before the demonstration of modified regular solution.

### 2.1. Theoretical background

#### 2.1.1. Regular solution theory

There are two assumptions in regular solution theory: 1. The solution composition has no effect on the interaction energy between molecules; 2. The molecules alignment in solution is in a state of complete disorder [26]. Therefore, the interaction probability between molecules should be proportional to the volume fractions of those molecules. According to regular solution theory, the molar excess Gibbs free energy,  $g^E$ , of binary solution can be expressed as [26]:

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