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A further discussion on solid-liquid equilibrium in complex synthetic paraffinic systems with the effects of solid-solid transition

Juheng Yang [a], Wei Wang [a, b, **], Huirong Huang [a], Jiaqi Wang [a], Jimiao Duan [d], Dan Wang [a], Guoyun Shi [a], Jing Gong [a, b, *], Bohui Shi [a, c]

[a] National Engineering Laboratory for Pipeline Safety, China University of Petroleum, Beijing 102249, PR China
[b] MOE Key Laboratory of Petroleum Engineering, China University of Petroleum, Beijing 102249, PR China
[c] Beijing Key Laboratory of Urban Oil and Gas Distribution Technology, China University of Petroleum, Beijing 102249, PR China
[d] Department of Military Petroleum Supply Engineering, Logistical Engineering University, PR China

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ABSTRACT

A predictive thermodynamic model for the prediction of wax precipitation in paraffinic mixtures is developed, on the basis of the wax prediction model (RSFV-IRSW) established by Yang et al. (2016), where the liquid phase is described by the combination of regular solution model and Flory free-volume equation, and the solid phase is modelled by the combination of improved regular solution model and Wilson equation. Advancements are adopted in the present work: 1. The influence of transition enthalpy between disorder and order solid phases on liquid-solid fugacity ratio of pure component is considered; 2. A method for the precise calculation of fusion enthalpy and transition enthalpy is suggested; 3. The boundary condition to decide whether one component would precipitate out to form the solid phase is added. The predictive model, RSFV-IRSW, predictive Wilson and regular solution model are tested against the experimental data of complex synthetic paraffinic systems. Results show that the predictive model behaves the best with high prediction accuracy in terms of the characteristics of wax precipitation curve and the composition of solid phase.

1. Introduction

Wax formation is a difficulty in petroleum industries. The heavy components in petroleum fluids will crystallize and gradually deposit on the pipe wall, with the cooling effect resulted from the cold environment. Wax formation and precipitation cause serious risks including production rate decline, pigging plugging, pipeline blockage, exploitation operation cessation, higher crude viscosity and, consequently, higher pumping costs [1]. Therefore, it is essential to develop a predictive thermodynamic model for the prediction of wax precipitation in petroleum industry.

For thermodynamic models of solid-liquid equilibrium in waxy mixtures, it is necessary to calculate the liquid-solid fugacity ratio of pure component ($f^L_{pure,i}/f^S_{pure,i}$). And the solid-liquid equilibrium constant of component i (K^{SL}) can be calculated by Equation (1):

$$K^{SL} = \frac{\gamma_i^L}{\gamma_i^S}\frac{f^L_{pure,i}}{f^S_{pure,i}} \tag{1}$$

where γ_i^S and are, respectively, the activity coefficients of component i in solid and liquid phases. It is evident that a precise description of $f^L_{pure,i}/f^S_{pure,i}$ is of great significance for the calculation of K^{SL} and, consequently, for the high prediction accuracy for the solid precipitation characteristics in paraffinic systems.

The crystallization behavior of heavy alkanes has been mainly studied at atmospheric pressure and polymorphism was found for n-alkanes with odd carbon number between 9 and 43 and

* Corresponding author. National Engineering Laboratory for Pipeline Safety, China University of Petroleum, Beijing 102249, PR China.
** Corresponding author. MOE Key Laboratory of Petroleum Engineering, China University of Petroleum, Beijing 102249, PR China.
E-mail addresses: w.wang@cup.edu.cn (W. Wang), ydgj@cup.edu.cn (J. Gong).

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with even carbon number between 20 and 44 [2–12]. However, a number of thermodynamic models [13–19] only take the fusion enthalpy into account without the consideration of the influence of solid-solid transition on the solubility of heavy paraffins. This simplification should augment the prediction error. On the other hand, there are also wax prediction models where the polymorphism phenomenon during the solidification is taken into account, such as predictive Wilson equation [20], predictive UNIQUAC [21], Ji's systematic wax model [22] and Chen's model [23]. In fact, Ghanaei et al. [24] conducted an exhaustive sensitivity analysis for the parameters in the liquid-solid fugacity ratio calculation, and proved that the phase change enthalpies have the greatest influence on the calculation of liquid-solid fugacity ratio.

It is proved that all the β'_n and β''_n solid solutions undergo the same variations as the orthorhombic C23 or C25 varies from their δ transition to their fusion point, such as [25–28]:

$$\beta'_n \text{ and } \beta''_n \rightarrow (\text{Fmmm}) - \text{RI}(\text{Fmmm}) \rightarrow \alpha - \text{RII}\left(\text{R}\bar{3}\text{m}\right) \rightarrow \text{liquid}$$

where $\rightarrow$ represents first-order transition, and $\Rightarrow$ denotes higher-order transition; β'_n and β''_n are the orthorhombic intermediate solid phases; β(Fmmm) is the orthorhombic solid phase; β-RI(Fmmm) is the RI rotator state of β(Fmmm); α-RII indicates the rhombohedral rotator solid phase. Thus, it is evident that the transitions between solid and liquid phases are complicated and the neglects of the solid-solid transitions will augment the prediction error for solid-liquid equilibrium.

Therefore, present work is devoted to give a further discussion on paraffinic systems with the effects of solid-solid transition, based on the study of Yang et al.(RSFV-IRSW) [19]. In the improved model, the effects of solid-solid transition enthalpy are included into the calculation of liquid-solid fugacity ratio and a method for the precise calculation of fusion enthalpy and transition enthalpy is suggested. To evaluate the predictive thermodynamic model, three other models, including RSFV-IRSW [19], predictive Wilson equation [20] (P-Wilson) and regular solution model (RS) [13], are tested in terms of wax precipitation curve and the composition of solid phase.

2. Predictive thermodynamic model

In RSFV-IRSW, the solid-solid transition enthalpy is not considered and the solid-liquid equilibrium constant, K_i^{SL}, is expressed as Equation (2) [19].

$$\frac{x_i^S}{x_i^L} = K_i^{SL} = \frac{\gamma_i^L}{\gamma_i^S}\exp\left(\frac{\Delta H_{f,i}}{RT}\left(1-\frac{T}{T_{f,i}}\right) - \frac{1}{RT}\int_T^{T_{f,i}}\Delta C_{p,i}dT + \frac{1}{R}\int_T^{T_{f,i}}\frac{\Delta C_{p,i}}{T}dT\right) \tag{2}$$

However, in the improved thermodynamic model, the general solid-liquid equilibrium equation is used to include the influences of solid-solid transition enthalpy [30]. For each component in the mixture, K_i^{SL} is related to the composition in solid and liquid phases, the nonideality of the phases and the thermo-physical properties of pure component:

$$\frac{x_i^S}{x_i^L} = K_i^{SL} = \frac{\gamma_i^L}{\gamma_i^S}\exp\left(\frac{\Delta H_{f,i}}{RT}\left(1-\frac{T}{T_{f,i}}\right) + \frac{\Delta H_{tr,i}}{RT}\left(1-\frac{T}{T_{tr,i}}\right) - \frac{1}{RT}\int_T^{T_{f,i}}\Delta C_{p,i}dT + \frac{1}{R}\int_T^{T_{f,i}}\frac{\Delta C_{p,i}}{T}dT\right) \tag{3}$$

where $\Delta H_{f,i}$ is the fusion enthalpy of component i; $\Delta H_{tr,i}$ is the solid-solid transition enthalpy of component i; $T_{f,i}$ is the fusion temperature of component i; $T_{tr,i}$ is the solid-solid transition temperature of component i; T represents the operating temperature; $\Delta C_{p,i}$ represents the heat capacity difference between liquid and solid phases; R is the universal gas constant; x_i^S and x_i^L are the mole fractions of component i in solid and liquid phases. The specific correlations for parameters in Equation (3) are demonstrated in Appendix A.

2.1. Liquid phase nonideality

The activity coefficient in liquid hydrocarbon mixtures can be expressed as the product of two contributions: the enthalpy contribution, the energetic interactions between the components, and the entropy contribution, the differences in size and shape between the molecules [31]. Hence, the liquid nonideality can be exactly described by the following equation [20,21]:

$$\ln\gamma = \ln\gamma^{res} + \ln\gamma^{comb-fv} \tag{4}$$

In present work, $\ln\gamma^{res}$ is calculated by RS [15]. The entropy effects given by $\ln\gamma_i^{comb-fv}$ can be described by the Flory free volume equation [20,21]:

$$\ln\gamma^{comb-fv} = \ln\frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i} \tag{5}$$

$$\psi_i = \frac{x_i\left(v_i^{1/3} - v_{wi}^{1/3}\right)^{3.3}}{\sum_j x_j\left(v_i^{1/3} - v_{wi}^{1/3}\right)^{3.3}} \tag{6}$$

where v_i is the molar volume of component i and v_{wi} is the van der Waals volume of component i [32].

2.2. Solid phase nonideality

On the basis of Yang's studies [18,19], the complete expression of g^E for solid phase is adopted to take the combinatorial part (s^E) and the residual part (h^E) into consideration.

$$g^E = h^E - Ts^E = \left(\sum_{i=1}^m x_i^S v_i^S\right)\left(\sum_{i=1}^m\sum_{j=1}^m\left[\delta_i^S\left(\delta_i^S - \delta_j^S\right)\phi_i^S\varphi_{ij}^S\right]\right) + \sum_{i=1}^m\left(x_i^S\ln\frac{\varphi_{ii}^S}{x_i^S}\right) \tag{7}$$

where δ_i^S is solubility parameter of component i; ϕ_i^S is the volume fraction of component i; φ_{ii}^S is the local volume fraction of the molecules identical to the central molecule; φ_{ij}^S is the local volume