



High pressure phase equilibrium of wax: A new thermodynamic model



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HIGHLIGHTS

- New high pressure approach for SL fugacity ratio of wax thermodynamic model.
- New approach is based on using the available thermophysical properties.
- New correlations of pressure versus temperature in SL and OD solid regions.
- Evaluation of three UNIQUAC models for the non-ideality of solid wax phase.
- High pressure model based on new approach of SL fugacity and a modified UNIQUAC.

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This paper is dedicated to the late Professor Jamshid Fathikalajahi.

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ABSTRACT

A problem in the thermodynamic modeling of wax precipitation at high pressure is the extension of liquid to solid fugacity ratio of pure component to high pressure, related to the molar volume integral of pure component in the liquid and solid phases. In this work, overcoming to this is achieved by using the Clapeyron equation to make a relationship between the thermophysical properties and changing of the pure component molar volume during the phase change. These thermophysical properties are enthalpies and pressure–temperature (PT) saturation slope in the solid–liquid (SL) and order–disorder (OD) solid regions. In this work, by the available experimental data, dependency of saturation pressure on temperature is obtained for some pure normal alkanes (n-alkanes). Based on these functions, the average values of 4.5 and 3.5 are calculated for the PT slope in two regions of the SL and OD solid, respectively. By these findings, a new approach is constructed for the liquid to solid fugacity ratio of pure component at high pressure. To demonstrate the priority of the new method, 458 data points of the SL phase change temperature of different n-alkanes mixtures at a wide range of carbon number, composition and pressure are employed. Then, three UNIQUAC models are investigated to combine with the new approach to describe the non-ideal behavior of the solid wax phase. The results justify the reliability of the new model using a recent modified version of UNIQUAC with an average absolute deviation percent (AAD%) of 0.8%.

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1. Introduction

The wax formation phenomenon, an obstacle in the petroleum industries, has been investigated in different scientific fields such as thermodynamic and transport phenomena. Many researchers addressed the wax formation issue from different aspects such as theoretical and experimental investigation of wax formation thermodynamic [1–5], deposition of wax in pipelines [6,7] or the wax formation effect on the rheological properties of oils [8].

In the petroleum industries, the most encountered operation conditions are in pressure higher than atmospheric pressure. On the other hand, the investigations indicate that the wax formation

can occur at high pressure. Owing to this, from the thermodynamic point of view, significant efforts have been devoted by the researchers to investigate the wax precipitation at high pressure condition. The main core of any SL equilibrium model is to relate the fugacity in liquid to solid phase for pure components and apply it to the fugacity of mixture. At high pressure, a term of molar volume integral versus pressure appears in this relationship. The lack of sufficient knowledge of order and disorder solid molar volume functionality versus pressure causes a difficulty in the calculation of this term. Owing to this, one of the aims of this work, mainly focused on it, is the estimation of this term in a predictive manner based on the Clapeyron equation [9] and thermophysical properties. By the Clapeyron equation [9], the differences of molar volumes in SL and OD solid phase transitions are calculated in the relation of the enthalpies and slope of PT diagram in these regions. By this procedure, the new approach is constructed in the condition that the predictive characteristic is preserved. The proposed

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Nomenclature

<i>a</i>	parameter of PR EoS	τ	characteristic energy parameter
<i>b</i>	parameter of PR EoS	θ	area fraction
<i>f</i>	fugacity	Φ	segment fraction
<i>H</i>	molar enthalpy	φ	fugacity coefficient
<i>K</i>	equilibrium constant		
<i>MW</i>	molecular weight	Superscripts	
<i>m</i>	number of data points	ds	disorder solid
<i>n</i>	carbon number	f	fusion
<i>P</i>	pressure	l	liquid
<i>P₀</i>	standard atmospheric pressure	od	order-disorder
<i>q</i>	P-UNIQUAC structural parameter	os	order solid
<i>R</i>	universal gas constant	s	solid
<i>r</i>	P-UNIQUAC structural parameter	sat	saturation
<i>T</i>	temperature	sl	solid–liquid
<i>V</i>	molar volume	sub	sublimation
<i>x</i>	mole fraction	tot	total
<i>Z</i>	coordination number	vap	vaporization
		Subscripts	
Greek letters		<i>i</i>	component <i>i</i> and counter for data points in AAD% calculation
β	coefficient in Pauly et al. model	<i>j</i>	component <i>j</i>
η, η'	constants in equations of saturation pressure versus temperature for pure component in SL (fusion) and OD solid phase transition	<i>k</i>	component <i>k</i>
Δ	difference	0	standard condition
δ	coefficient in Nasrifar and Fani Kheshti model		
γ	activity coefficient		
λ	pair interaction energy		

approach are compared to other high pressure models based on the methods of Pauly et al. [10], Ghanaei et al. [11] and Nasrifar and Fani Kheshti [12].

Another issue in the thermodynamic modeling of wax formation is the description of the non-ideal behavior of the solid phase. The studies show that the UNIQUAC model can describe the solid wax phase behavior [2,13–15]. Therefore, in this research, in order to obtain a suitable activity coefficient model for this phase, in a solid solution model using the proposed approach of liquid to solid fugacity ratio at high pressure, three predictive UNIQUAC models involving Coutinho [13], Coutinho et al. [14] and Ghanaei et al. [15] will be compared with each other. To allow the critical evaluation of the proposed model accuracy, a sufficient large set of experimental data of the SL phase transition temperature of different n-alkanes mixtures at a wide range of carbon number, composition and pressure is utilized.

2. High pressure thermodynamic model, new approach

Based on the solid solution approach, the following equation is satisfied at the equilibrium.

$$f_i^s(P, T, x_i^s) = f_i^l(P, T, x_i^l) \quad (1)$$

In this equation, $f_i^s(P, T, x_i^s)$ and $f_i^l(P, T, x_i^l)$ are the fugacity of component *i* in the solid and liquid phases in pressure *P*, temperature *T* and mole fraction x_i^s and x_i^l , respectively. The fugacity in the liquid and solid phases is calculated by the following equations:

$$f_i^l(P, T, x_i^l) = x_i^l f_{\text{pure } i}^l \gamma_i^l \quad (2)$$

$$f_i^s(P, T, x_i^s) = x_i^s f_{\text{pure } i}^s \gamma_i^s \quad (3)$$

That, $f_{\text{pure } i}$ and γ_i are the fugacity of pure component *i* and its activity coefficient in the mixture while superscripts of l and s are related

to the liquid and solid phases, respectively. By the definition of equilibrium constant, K_i^{sl} , it can be written:

$$K_i^{sl} = \frac{x_i^s}{x_i^l} = \frac{\gamma_i^l}{\gamma_i^s} \times \frac{f_{\text{pure } i}^l}{f_{\text{pure } i}^s} \quad (4)$$

Based on this equation, the new thermodynamic model is presented in three parts including liquid to solid fugacity ratio of pure component at high pressure, obtaining the PT slope for two curves of SL and OD solid and the last one, the description of solid and liquid phase behavior.

2.1. Liquid to solid fugacity ratio of pure component at high pressure

Ghanaei et al. [15] performed an exhaustive investigation about the terms more contributing in the liquid to solid fugacity ratio of pure component ($f_{\text{pure } i}^l / f_{\text{pure } i}^s$). According to that study, the contribution of heat capacity terms is negligible in comparison with phase changes' enthalpies. Thus, $f_{\text{pure } i}^l / f_{\text{pure } i}^s$ at P_0 can be calculated by the following equations for the components with and without OD solid phase transition, respectively.

$$\frac{f_{\text{pure } i}^l}{f_{\text{pure } i}^s} = \exp \left(\frac{\Delta H_i^f}{RT} \left(1 - \frac{T}{T_i^f} \right) + \frac{\Delta H_i^{\text{od}}}{RT} \left(1 - \frac{T}{T_i^{\text{od}}} \right) \right) \quad (5)$$

and

$$\frac{f_{\text{pure } i}^l}{f_{\text{pure } i}^s} = \exp \left(\frac{\Delta H_i^f}{RT} \left(1 - \frac{T}{T_i^f} \right) \right) \quad (6)$$

That, ΔH_i^f and T_i^f are the molar enthalpy and temperature of SL phase transition (fusion), respectively. Also, the molar enthalpy and temperature of OD solid phase transition are denoted as ΔH_i^{od} and T_i^{od} , respectively. In these equations, *R* is the universal gas constant. Similar to the method previously shown [15], the following equations can be obtained for $f_{\text{pure } i}^l / f_{\text{pure } i}^s$ at pressure *P*.

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