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A New Thermodynamic Model for Paraffin Precipitation in Highly Asymmetric Systems at High Pressure Conditions

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KEYWORDS

Solid-fluid equilibrium, Paraffin wax, High pressure, Asymmetric systems, Clausius-Clapeyron equation, Thermophysical properties

ABSTRACT

The predictions of the crystallization temperature and the amount of precipitates of paraffin waxes at high pressure conditions may be inaccurate using existing thermodynamic models. This is mainly due to the lack of experimental data on the molar volume of solid paraffins at high pressures. This inaccuracy is even more pronounced for mixtures of high asymmetry. The present work provides a new accurate modelling approach for solid-fluid equilibrium (SFE) at high pressure conditions, more specifically, for highly asymmetric systems. In
contrast to the conventional methods for high pressure SFE modelling which define Poynting molar volume correction term, to calculate the paraffin solid phase non-ideality at high pressures, the new method exploits the values of thermophysical properties of importance in SFE modelling (temperatures and enthalpies of fusion and solid-solid transition) evaluated at the high pressure condition using a new insight to the well-known Clausius-Clapeyron equation. These modified parameters are then used for evaluation of the fugacity in the solid phase at higher pressure using the fugacity of pure liquid at the same pressure and applying the well-established formulation of the Gibbs energy change during melting. Therefore, the devised approach does not require a Poynting correction term. The devised approach coupled with the well-tested UNIQAC activity coefficient model is used to describe the non-ideality of the solid phase. For the fluid phases, the fugacities are obtained with the SRK EoS with binary interaction parameters calculated with a group contribution scheme. The model is applied to highly asymmetric systems with SFE experimental data over a wide range of pressures. It is first used to predict crystallization temperature in binary systems at high pressures and then verified by applying it on multicomponent mixtures resembling intermediate oil and natural gas condensates.
1. Introduction

Formation of paraffinic solids is well documented to be able to impose considerable operational costs due to decreasing flow efficiency and, in the worst case, pipeline blockage. Due to high expenses of the remediation approaches for wax deposition problem (such as chemical dissolution and pigging), prevention is always the best option which in turn calls for accurate risk assessment of the wax formation problem, i.e. identifying the temperature/pressure conditions under which the waxes form. Although not as important as temperature, the pressure can have a significant effect on the wax phase boundary (see for example the work of Pan et al.\textsuperscript{1}). In fact, as outlined by Pauly et al.\textsuperscript{2}, in mixtures with significant light end proportions, the pressure change can considerably affect the chance of wax formation through retrograde condensation, depressurization and Joule-Thomson effect. Several thermodynamic models have been proposed in the literature for estimating wax precipitation onset and the amount of wax formed inside the wax phase boundary. The performance of existing models are (as will be shown later) good at low pressure conditions as long as accurate thermodynamic models for the description of fluid and solid phases as well as a precise correlation for calculating thermophysical properties of alkanes are utilised. Paraffinic SFE calculations at high pressures using existing methodologies may show high deviations compared to experimental data, more visibly in systems of high asymmetry with high proportions of the light end which are the main subject of this study. The main motive for studying such systems is their resemblance of volatile oils and gas condensates which might form wax\textsuperscript{1,3}. With similar intention, a handful of experimental studies in the literature, mainly on binaries, have been focused on SFE in highly asymmetric systems. The purpose of the current study is the development of a new thermodynamic model for the extension of one of the accurate existing schemes for SFE modelling to high pressures. The next section provides the background on the modelling wax precipitation at high pressures and the
complete formulation of the developed model. It also presents a modification of an existing method. An extensive comparison of the devised methodology with the existing models is then provided in the Results and Discussions Section.

2. Methodology

2.1. Background

The equilibrium calculations in the paraffin wax forming systems require evaluation of the fugacity of precipitating components in the solid phase(s) which, consequently, calls for the evaluation of fugacity of pure components in the solid state. The fugacity of pure paraffins in the solid state, $f^{*S}_{i}$, are well-established to be related to the pure components’ liquid fugacity, $f^{*L}_{i}$, by:

$$\frac{f^{*L}_{i}}{f^{*S}_{i}} = \exp \left( \frac{\Delta H^e_i}{RT} \left( 1 - \frac{T}{T^l_i} \right) + \frac{\Delta H^r_i}{RT} \left( 1 - \frac{T}{T^r_i} \right) \right) \quad (1)$$

It is assumed here that the Gibbs free energy change due to thermal contributions during phase changes (heat capacity effect) are negligible, as confirmed through sensitivity analysis. In the equilibrium calculations, the pure components fugacities in the solid state are then used to calculate the fugacity of components in the solid solution by:

$$f^{S}_{i} = x^{S}_{i} f^{*S}_{i} \gamma^{S}_{i} \quad (2)$$

Using Eq. 1 and Eq. 2 as well as an accurate thermodynamic model to describe fluid phases and a robust activity coefficient model to calculate activity coefficient of components in the solid solution, $\gamma^{S}_{i}$, one can easily specify the solid-fluid equilibrium state characteristics applying a robust multiphase flash algorithm. The application of Eq. 1 requires accurate values of thermophysical properties which are normally measured at components triple point
pressure. Therefore, precise evaluation of wax phase boundary (or more accurately, wax
disappearance temperatures, WDT) at sufficiently low pressures near to the reference state
pressure (in this work 0.1 MPa) is an easy task, provided that a combination of strong
thermodynamic models are utilized. One such combination, as applied in the current work
consists of:

i. *Thermodynamic model for fluid phases:* Soave-Redlich-Kwong (SRK) EoS\(^6\) is used
to describe fluid phases and binary interaction parameters are calculated by Jaubert
and Mutelet\(^7\) group contribution scheme (JMGC) as presented by Qian et al.\(^8\). This
method was originally developed for the Peng and Robinson\(^9\) (PR) EoS and then
extended to the SRK EoS as presented by Jaubert and Privat\(^10\) is used. In the absence
of associating fluid, which is the case for the mixtures investigated here, the SRK-
JMGC model has a proven capability to accurately describe fluid-fluid equilibria\(^10\).
Jaubert and Mutelet\(^7\) combined their group contribution method with a cubic EoS to
model VLE in highly asymmetric systems. They found that their group contribution
scheme coupled with a cubic EoS gives better results compared to EoS/G\(^E\) approaches
of LCVM\(^11\) (which is widely used for describing fluid in solid-fluid equilibria of
waxy systems in several example works\(^3,12–16\)) and MHV\(^2\)\(^17\). The JMGC method for
binary interaction parameters in modelling wax forming systems has been applied in
some publications\(^18,19\). In order to be consistent, in this work, the fugacity of pure
components in the liquid state are also calculated with the SRK EoS.

ii. *Thermophysical properties estimation correlation:* Experimental evidence has shown
that for pure odd alkanes, the dominant crystalline structures in multicomponent solid
solutions is orthorhombic\(^20–23\). This observation is also valid for cases where solid
solution consists only of even alkanes\(^24\). In this regard, except for cases where the
solid solution is a pure even heavy paraffin, the thermophysical properties of
compounds, i.e., fusion temperature, $T_i^f$, solid-solid transition temperature, $T_i^{tr}$, enthalpy of fusion $\Delta H_i^f$ and enthalpy of solid-solid transition, $\Delta H_i^{tr}$, are evaluated using the correlations of Coutinho and Daridon\textsuperscript{25}. In these set of correlations, the odd paraffins properties are extended by extrapolation to the even alkane properties\textsuperscript{26}. Using these correlations, the values of thermophysical parameters are evaluated at reference pressure, $P_0$ (assuming that the thermophysical properties of pure components at the triple point pressure and the reference pressure are the same\textsuperscript{24}). In the cases of binary asymmetric systems, where the solid phase is a pure even paraffin, the thermophysical properties of the paraffin used are those reported in the comprehensive work of Dirand et al.\textsuperscript{27}.

iii. *Activity coefficient model for the solid solution*: In this work the UNIQUAC activity coefficient model in its original form as developed by Abrams and Prausnitz\textsuperscript{28} (later utilized by Coutinho\textsuperscript{29} for the non-ideality of paraffinic solid phase(s)) is used to evaluate paraffinic solid components activity coefficients in solid solution, $\gamma_i^S$. Details of this model and its formulation and parameterization can be found elsewhere\textsuperscript{26}.

Finally, accurate values for critical properties and acentric factor of components, especially the heavy alkanes, are required. In this work, the critical properties and acentric factor pure components are taken from the DIPPR database [35].

### 2.2. Modeling wax phase boundary at high pressures

For high pressures, generally, two approaches can be utilized to evaluate fugacity of components in the solid solutions in complex multicomponent waxy mixtures:

1- *Poynting term models*: In these models, the fugacities of the solid phase(s) evaluated at the reference pressure (using Eq. 1 and Eq. 2) are translated to higher pressures using a Poynting correction term i.e.:
Here, $\bar{v}_i^S$ is the molar volume of component $i$ in solid solution and $P_0$ is the reference pressure (0.1 MPa). Examples of this type are the works of Pauly et al.\textsuperscript{12}, Morawski et al.\textsuperscript{30}, Ghanaei et al.\textsuperscript{31,32} and Nasrifar et al.\textsuperscript{19}. Correct calculation of the Poynting correction term requires an accurate model to evaluate the molar volume of components in the solid solution. Due to scarcity of experimental data to develop such a model, different authors have presented a variety of methods to estimate the Poynting term. Pauly et al.\textsuperscript{12} have assumed that the molar volume of components in solid solution is equal to the pure component molar volume in the liquid state multiplied by a pressure independent constant variable $\beta$ through:

$$\int_{P_0}^{P} \frac{\bar{v}_i^S}{RT} \, dP = \int_{P_0}^{P} \frac{\beta v_i^L}{RT} \, dP = \beta \frac{\ln(f_i^{*L}(P))}{\ln(f_i^{*L}(P_0))}$$  \hspace{1cm} (4)$$

Where $v_i^L$ and $v_i^L$ are the molar volume of the pure normal alkane $i$ in the solid and liquid states, respectively. The assumption of a constant pressure-independent $\beta$ contradicts the fact that by increasing pressure, reduction in liquid the molar volume of a component is to higher extents than in the solid state. Morawski et al.\textsuperscript{30} used Clausius-Clapeyron equation to modify $\beta$, though again $\beta$ is considered to be pressure independent. They also assumed that enthalpies of fusion and solid-solid transition of normal alkanes are pressure independent. Furthermore, Morawski et al.\textsuperscript{30} model requires evaluation of a composition-dependant adjustable parameter and in this sense is not fully predictive. The works of Nasrifar and Fani-Kheshty\textsuperscript{19} and Ghanaei et al.\textsuperscript{31} are a modification of the
Morawski et al.\textsuperscript{30} model, attempting to remove the adjustable parameter. Accordingly, Nasrifar and Fani-Kheshty\textsuperscript{19} proposed the following formulation for the Poynting term:

\[
\int_{P_0}^{P} \frac{\tilde{v}_i^S}{RT} dP = -\delta \left( \frac{\Delta H_i^f + \Delta H_i^p}{R^2T^2} \right) (P - P_0) \tag{5}
\]

Here, $\delta$ is constant equal to 0.002 m$^3$/kmol obtained by fitting WDT of pure normal paraffins. However, Ghanaei et al.\textsuperscript{31}, by assuming constant slopes for fusion and solid-solid transition temperatures of pure paraffins by increasing pressure, developed the following formulation for the Poynting term:

\[
\int_{P_0}^{P} \frac{\tilde{v}_i^S}{RT} dP = \frac{P - P_0}{RT^2} \left( \frac{\Delta H_i^f}{\frac{dP^*}{dT_f}} + \frac{\Delta H_i^p}{\frac{dP^*}{dT_{tr}}} \right) \tag{6}
\]

Based on Ghanaei et al.\textsuperscript{31}, with an accurate estimate and regardless of the carbon number of the pure alkane the values of 4.5 MPa.K$^{-1}$ and 3.5 MPa.K$^{-1}$ can be assigned to saturation pressure slope changes with temperature for fusion, $\frac{dP^*}{dT_f}$, and solid-solid transition, $\frac{dP^*}{dT_{tr}}$, for all heavy alkanes. To obtain this the authors have assessed a large database of experimental fusion and solid-solid transition temperatures of pure alkanes at high pressure reported in the literature\textsuperscript{27,33–39}. Based on the current study evaluations and some work in the literature\textsuperscript{30} this assumption is indeed precise (it will be shown later on, utilized in a different scheme). This way they removed the need for parameter $\delta$ defined in Nasrifar and Fani-Kheshty\textsuperscript{19} work. However in both methods the same assumptions, as that of Morawski et al.\textsuperscript{31} hold. It should be noted that Ghanaei and co-authors have also presented another high pressure wax model\textsuperscript{32}, again by devising a formulation for the Poynting term, developed a few years prior to their latest approach described here. In our
evaluations, only the performance of their recent model is assessed. Finally, there are other works in the literature estimating the Poynting term by assuming the solid phase to be incompressible and the liquid molar volumes are evaluated at average pressures. Due to these questionable assumptions, especially in the cases studied here, such works are not assessed here.

2- No-Poynting term models: In the second approach, the pure components solid fugacities are calculated at high pressure using Eq. 1 with the thermophysical properties evaluated at the same high pressure \( P \), i.e. no Poynting correction term is required. The method of Ji et al.\(^{40}\) belongs to this group. In this method, a linear correlation is used to evaluate \( T^f_i \) of alkanes at higher pressure, with an accurate estimate that the slope of change of fusion temperature by increasing pressure \( \frac{dP^*}{dT_f} \) is a constant value for heavy alkanes (as discussed earlier). Therefore, one can write:

\[
T^f_i(P) = T^f_i(P_0) + \left( \frac{P - P_0}{\frac{dP^*}{dT_f}} \right) \tag{7}
\]

A constant of 5.0 MPa.K\(^{-1}\) for \( \frac{dP^*}{dT_f} \) is suggested by Ji et al.\(^{40}\). In the original work of Ji et al.\(^{40}\) the parameter \( T^f \) is the only thermophysical property of pure heavy alkane for which updated values are evaluated at higher pressures and the rest are held constant. Based on our experience if \( T^f \) is the only thermophysical properties modified at \( P \), the model deviations from experimental behaviour can be significant at high pressures. The same observation is made in the evaluations made by Nasrifar and Fani-Kheshty\(^{19}\). Therefore, here, apart from the new model developed, first, a modified version of Ji et
model is presented, in which not only the fusion temperatures but also the solid-solid transition temperatures of pure alkanes are updated at high pressure similarly by:

$$T_{tr}'(P) = T_{tr}'(P_0) + \left( \frac{P - P_0}{\Delta P_{tr}} \right)$$ \hspace{1cm} (8)

It will be shown later that, despite the simplicity of the approach, the modified Ji method provides better results compared to that of “Poynting term” methods. In the modified Ji model the value of slopes $\frac{dP_{tr}}{dT_f}$ and $\frac{dP_{tr}}{dT_{tr}}$ are those suggested by Ghanaei et al.\textsuperscript{31} i.e. 4.5 MPa.K\textsuperscript{–1} and 3.5 MPa.K\textsuperscript{–1}, respectively. As a final note to the methods in the second category, it is assumed that the activity coefficient of components in the solution is fairly constant with pressure. This is a reasonable assumption. In fact, differentiation of the logarithm of activity coefficient with respect to pressure yields\textsuperscript{4}:

$$\left( \frac{\partial (\ln (y_i^S))}{\partial P} \right)_{T,X} = \left( \frac{\tilde{V}_i^E}{RT} \right)$$ \hspace{1cm} (9)

To see the effect of pressure on the activity coefficient the example case of binary n-pentane + n-hexadecane is considered. For this highly asymmetric system, the absolute value of excess molar volume is reported\textsuperscript{41} to be as high as \(-1.1581 \text{ cm}^3 \text{ mol}^{-1}\) (for 0.7034:0.2966 molar ratio). Using this value in Eq. 9, at room temperature, a pressure change of 100 MPa is translated into only about 4.5% change in activity coefficient. Furthermore, the volume effect of mixing is decreasing by increasing pressure in paraffinic systems (see for example\textsuperscript{42} and, obviously, the excess molar volume of solid solutions are smaller than that of liquid solutions, therefore one would expect even much smaller changes in activity coefficient in the solid solution at high pressures and hence the assumption of independency of activity coefficient from pressure is plausible.
Based on several investigations, (and as will be shown for modified Ji, Pauly et al., Nasrifar and Fani-Kheshty and Ghanaei et al. models) the performance of the methods in both categories are comparatively acceptable for mixtures of low asymmetry with overall compositions having a low amount of light ends. The efficiency of the aforesaid methods, however, is poor in mixtures of high asymmetry which have high proportions of light ends, as will be presented later on. The deviations become even more as the pressure increases. This issue is addressed in some works and seemingly has prevented the authors accurately modelling the experimental data. In this work, the aim is to tackle the problem of wax phase boundary estimation at higher pressure, especially for highly asymmetric systems, by developing a new model. Therefore, the work presents two new solid-liquid equilibrium high pressure models based on “No-Poynting term” approach i.e. (i) the modified Ji model, described earlier and (ii) a new accurate scheme described in the next section. The reason why two new methods are presented here will be discussed in the results section.

2.3. New proposed method

In the current study, a new method based on the “No-Poynting term” approach is developed to model the non-ideality of paraffinic solid phases at high pressures. The aim here is to have accurate estimations of thermophysical properties of pure paraffins at high pressure, using their values in the reference state and a proper formulation to modify them to account for high pressure effect. Prior to discussing the development of the model, to have a better understanding the of solid-fluid equilibrium behaviour of highly asymmetric systems, investigations are first carried out for simple binary systems of high asymmetry, for which experimental solid-fluid phase boundary data are available. According to Seiler et al. the combination of Eq. 1 and Eq. 2 can be extended to high pressure range if the pressure dependence of both enthalpies of fusion and the solid-solid transition is taken into
consideration. Here, the Clausius-Clapeyron equation\textsuperscript{44} is used to take the dependency of $\Delta H^f$ to pressure into consideration. Using Clausius-Clapeyron equation, for the fusion:

$$\Delta H^f_i(P) = (v^L_i(P) - v^S_i(P)) T^f_i(P) \left(\frac{dP^*}{dT_f}\right)_i$$  \hspace{1cm} (10)

As mentioned, for n-alkanes, with an accurate estimate, the fusion temperature $T^f$ changes linearly with pressure and the slope is a constant value independent of pressure and the carbon number of the pure paraffin. Therefore, using Eq. 10, one can easily relate the enthalpy of fusion at high pressure $P$ to the same property in reference pressure $P_0$ by:

$$\frac{\Delta H^f_i(P)}{\Delta H^f_i(P_0)} = \left(\frac{v^L_i(P) - v^S_i(P)}{v^L_i(P_0) - v^S_i(P_0)}\right) \frac{T^f_i(P)}{T^f_i(P_0)}$$  \hspace{1cm} (11)

Here, as described, the fusion temperature of pure alkane at reference pressure ($T^f_i(P_0)$) is calculated by the correlations proposed by Coutinho and Daridon\textsuperscript{25} except for the cases of binary asymmetric systems where the solid solution is a pure even normal alkane in which case for the heavy alkane $i$, $T^f_i(P_0)$ is taken from the work of Dirand et al.\textsuperscript{27}. Eq. 7 with $\frac{dP^*}{dT_f}$ of 4.5 MPa.K$^{-1}$ as suggested by Ghanaei et al.\textsuperscript{31} is used to calculate fusion temperature of pure alkane $i$ at high pressure, $T^f_i(P)$.

As mentioned, based on Pauly et al.\textsuperscript{12} one can relate the molar volume of heavy alkanes in the liquid state to the same value in the solid state by multiplying it with constant value, i.e.:

$$v^S_i = \beta v^L_i$$  \hspace{1cm} (12)

Where, according to Pauly et al.\textsuperscript{12}, for pure alkanes $\beta$ is equal to 0.86 and is assumed to be pressure independent. For mixtures, due to excess volume effect they have suggested the value of 0.9 for $\beta$. A constant, pressure independent value, assigned for $\beta$ is questionable as
obviously the effect of compaction due to high pressure is less in the solid state compared to liquid state. Hence, one would expect that by increasing the pressure the value of $\beta$ should increase. Accordingly, in this work, $\beta$ is defined to be pressure dependent, hereafter denoted as $\beta^f$ for fusion, assuming to increase linearly with pressure (in the simplest possible way) i.e.:

$$\beta^f(P) = \beta^f(P_0) + \alpha(P - P_0)$$  \hspace{0.5cm} (13)$$

Here $\alpha$ is a positive constant. Despite the simplicity of Eq. 13, as will be presented later on, the formulation devised proves very accurate. Using the data reported by Schaerer et al.\textsuperscript{45} an average value of 0.895 is assigned to $\beta^f(P_0)$ which is representing the ratio of pure alkane liquid state to solid state molar volume at reference pressure (very similar to Pauly et al.\textsuperscript{12} value of $\beta$). In this way Eq. 11 can be reduced to:

$$\frac{\Delta H^f_i(P)}{\Delta H^f_i(P_0)} = \left(\frac{1 - \beta^f(P)}{1 - \beta^f(P_0)}\right) \frac{T^f_i(P)}{T^f_i(P_0)}$$ \hspace{0.5cm} (14)$$

Using the same approach, however with a different variable named $\beta^{tr}$ to make a distinction, for alkanes showing order-disorder solid-solid transitions, the following formula can be written to update $\Delta H^{tr}$ at high pressures:

$$\frac{\Delta H^{tr}_i(P)}{\Delta H^{tr}_i(P_0)} = \left(\frac{1 - \beta^{tr}(P)}{1 - \beta^{tr}(P_0)}\right) \frac{T^{tr}_i(P)}{T^{tr}_i(P_0)}$$ \hspace{0.5cm} (15)$$

Again by using Schaerer et al.\textsuperscript{45} data the value of 0.958 is assigned to $\beta^{tr}(P_0)$ which represents the ratio of pure alkane disordered to ordered solid state molar volume at reference pressure. Similar to fusion, as mentioned, the same trend in change of $T^{tr}$ of a pure alkane by pressure is observed, i.e. increasing with constant $\frac{dP}{dT^{tr}}$ of 3.5 MPa.K\textsuperscript{-1} as suggested by
Ghanaei et al.\textsuperscript{31}. Therefore, Eq. 8 is used to evaluate $T^{tr_i}(P)$. With the same approach applied for fusion as presented in Eq. 13, for solid-solid transition it is proposed that:

$$
\beta^{tr}(P) = \beta^{tr}(P_0) + \alpha(P - P_0) \quad (16)
$$

In theory, the value of $\alpha$ in Eq. 16 should be different from that of Eq. 13. However, the aim here is to have one adjustable parameter, and as will be shown later on, a single value of $\alpha$ for both of the equations can accurately model highly asymmetric systems. Having adjustable parameters to model solid-fluid equilibrium at high pressures is acceptable (see for example Morawski et al.\textsuperscript{30} and Rodriguez-Reartes et al.\textsuperscript{46} models for paraffinic binary systems).

To sum-up in the current approach the following steps should be taken to calculate non-ideality in the solid phase at high pressure $P$:

1- Using proper correlations/database the thermophysical properties of pure components i.e. $T^f_i, T^{tr}_i, \Delta H^f_i, \Delta H^{tr}_i$ are evaluated at the reference pressure $P_0$.

2- With values of 4.5 MPa.K$^{-1}$ for $\frac{dP^*}{dT^f}$ and 3.5 MPa.K$^{-1}$ for $\frac{dP^*}{dT^{tr}}$, Eq. 7 and Eq. 8 are used to evaluate $T^f_i$ and $T^{tr}_i$, respectively, at high pressure $P$.

3- Adjusting the value of $\alpha$ and using values of 0.895 for $\beta^f(P_0)$ and 0.958 for $\beta^{tr}(P_0)$, Eq. 13 and Eq. 16 are used to evaluate $\beta^f$ and $\beta^{tr}$, respectively, at high pressure $P$.

Guidelines for assigning a correct value for $\alpha$ will be presented in the results section.

4- Using (i) the values of $T^f_i$ and $T^{tr}_i$ at reference pressure $P_0$ and their values at high pressure $P$, calculated in Step 2, (ii) the values of $\beta^f$ and $\beta^{tr}$ at reference pressure $P_0$ (i.e. 0.895 and 0.958) and their values at high pressures $P$ (calculated in Step 3) and (iii) $\Delta H^f_i$ and $\Delta H^{tr}_i$ at reference pressure $P_0$, (calculated in Step 1), Eq. 14 and Eq. 15 are used to evaluate $\Delta H^f_i$ and $\Delta H^{tr}_i$, respectively at high pressure $P$. 
Having calculated the value of all thermophysical properties at high pressure $P$, Eq. 1 and Eq. 2 are directly used to evaluate the fugacity of components in the solid solution at high pressure.

As described earlier, for the modified Ji method, steps 3 and 4, are not required. In fact, the modified Ji method is a special form of the, more general, new model proposed here for which:

$$\frac{\Delta H_{f,i}(P)}{\Delta H_{f,i}(P_0)} = 1$$

(17)

And:

$$\frac{\Delta H_{tr,i}(P)}{\Delta H_{tr,i}(P_0)} = 1$$

(18)

As both modified Ji and the new model are proposed here, to make the distinction, hereafter, the term “this work model” refers to the newly developed method, not the modified Ji.

3. Results and Discussions

In this section, the performance of the developed model is compared with the modified Ji, Pauly et al.\textsuperscript{12}, Nasrifar and Fani-Kheshty\textsuperscript{19} and Ghanaei et al.\textsuperscript{31} models. To have fair evaluations of the models, the SRK+JMGC model and UNIQUAC activity coefficient model are used to describe the non-idealities of fluid and solid phase, respectively, for all high-pressure methods. The SRK+JMGC model used here to describe fluids is fully predictive and no tuning of model parameters to match saturation pressure data is made prior to wax calculations. It will be shown that the performance of all these existing models in systems with lower proportions of the light end in moderate pressure ranges is good, provided the requirement discussed earlier in the Background Section. Therefore, the main focus here is on highly asymmetric systems of high proportions of the light end at high pressures, resembling gas condensates and volatile oils, for which experimental wax phase boundary
data are available. Data on such systems are scarce. The uncertainty in the experimental wax phase boundary data used here to evaluate models is low as they are corresponding to wax disappearance points. It is well established that wax disappearance temperature (WDT) data are better representatives of true thermodynamic melting point compared to wax appearance temperature (WAT)\textsuperscript{37,48}. The evaluations are first carried out for binary asymmetric systems, then synthetic multicomponent asymmetric wax mixtures and are graphically represented for selected systems with low, moderate and high proportions of methane. Furthermore, reporting model errors from low to high pressure range using Average Relative Error (ARE) percent, i.e. by: \[
\frac{1}{N} \sum_{i}^{N} \frac{|T_{i}(\text{Exp}) - T_{i}(\text{Cal})|}{T_{i}(\text{Exp})} \times 100
\] can be misleading as the high temperature ranges would result in small AREs regardless of the model utilized. Therefore, instead, the Average Absolute Error (AAE) is used for the comparisons which is defined by (N: number of points):
\[
AAE\% = \frac{1}{N} \sum_{i}^{N} |T_{i}(\text{Exp}) - T_{i}(\text{Cal})| \times 100
\] (19)

3.1. Binary methane + heavy alkane mixtures

Here, the models results for binary asymmetric systems (with experimental wax phase boundary data available) methane + n-hexadecane\textsuperscript{49}, methane + n-heptadecane\textsuperscript{35}, methane + n-eicosane\textsuperscript{39}, methane + n-docosane\textsuperscript{50}, methane + n-tetracosane\textsuperscript{51} and methane + n-triacontane\textsuperscript{52} are presented. A total of 457 data points of WDT in binary asymmetric mixtures are used for evaluations. In this study the WDT data of asymmetric systems for which the data are not reported at high pressures of at least 50 MPa (e.g.\textsuperscript{53–58} for which the solid-fluid phase boundary data are reported up to 12 MPa), or the systems for which the uncertainty in the critical/physical properties of the heavy end component is high (e.g.\textsuperscript{59}) are not used in evaluations. In all the systems evaluated wax phase boundary data in low to very high proportions of methane with a variety of molar ratios were measured. The graphical
comparisons are shown for selected low, moderate and high proportions of methane in example binary mixtures methane + n-heptadecane, methane + n-eicosane and methane + n-triacontane in Figure 1 to Figure 3. As the deviations of existing models are very high in the case of systems methane + n-triacontane, depicting evaluation results in all proportions in a single graph makes interpretations difficult, therefore it was decided to show them separately in the way presented in Figure 3. As the first major observation in the model evaluations (and as observed in Figure 1 to Figure 3), for the binary systems tested, adjusting a single value of \( \alpha \) can accurately model the wax phase boundary, in a fixed binary system regardless of the proportion of the methane in the mixture. As an example, as shown in Figure 3, the \( \alpha \) equal to \( 1.38 \times 10^{-4} \) MPa\(^{-1}\) gives an accurate match in low to high proportions of methane in binary mixture methane + n-triacontane. The adjusted value of \( \alpha \) for each case is presented in Table 1. As shown in this table, except for the case of methane + n-hexadecane system the value of \( \alpha \) have almost the same order of magnitude in all the binary system. The models deviations are presented in Table 2 in terms of AAE for all the data points. According to this table, the results of “this work model” with a single \( \alpha \) for each case in very low to very high proportions of light end (methane) are accurate. The superiority of the proposed model is clearer in binary systems of higher asymmetry (see results for methane + n-tetracosane and methane + n-triacontane in Table 2 where the deviation of existing models are very high at high pressures. Interestingly, even if the average value of \( \alpha \) over the binary systems i.e. \( 1.23 \times 10^{-4} \) MPa\(^{-1}\) is used for all the cases, still the performance of the proposed method is much better than the alternative methods.
**Figure 1:** Binary methane + n-heptadecane solid-fluid phase boundary. The results for “this work model” are shown by adjusted $\alpha$ of $1.18 \times 10^{-4}$ MPa$^{-1}$.

**Figure 2:** Binary methane + n-eicosane solid-fluid phase boundary. The results for “this work” model are shown by adjusted $\alpha$ of $1.34 \times 10^{-4}$ MPa$^{-1}$. 


Figure 3: Binary methane + n-triacontane solid-fluid phase boundary. The results for “this work model” are shown by adjusted $\alpha$ of $1.35 \times 10^{-4}$ MPa$^{-1}$. The evaluation are made for systems with (a) 89.7 (b) 50 and (c) 15 mol% methane in the binary mixture. $\triangle$: Experimental SLVE WDT data $\bigcirc$: Experimental SLE WDT data; -- This work model; \ldots Modified Ji model; \ldots Pauly et al. model; \ldots Nasrifar and Fani-Kheshty model; \ldots Ghanaei et al. model

It is important to note that the value of AAEs reported in Table 2 may seem to be at odds with those reported for similar systems in Pauly et al.$^{12}$ work for C1-nC24 and C1-nC22 systems. However, in their evaluations for these mixtures Pauly et al.$^{12}$ ignored the data points of more than 90% methane in these mixtures which correspond to region of high deviation with existing models, whereas, here the models are evaluated with systems (binary and multicomponent) having as high as 97 mol% light end. That is why for these two mixtures they have obtained smaller values of AAEs. If the same data points are used here similar AAEs will be obtained. This choice may be due to higher deviations in modelling VLE of asymmetric systems of the higher light end as pointed out by Jaubert and Mutelet.$^{7}$
Table 1: The adjusted values of parameter α (MPa⁻¹) for the binary asymmetric systems investigated

<table>
<thead>
<tr>
<th>Binary system</th>
<th>C1-nC16</th>
<th>C1-nC17</th>
<th>C1-nC20</th>
<th>C1-nC22</th>
<th>C1-nC24</th>
<th>C1-nC30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adjusted α</td>
<td>0.74×10⁻⁴</td>
<td>1.18×10⁻⁴</td>
<td>1.34×10⁻⁴</td>
<td>1.34×10⁻⁴</td>
<td>1.43×10⁻⁴</td>
<td>1.35×10⁻⁴</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.23×10⁻⁴</td>
</tr>
</tbody>
</table>

Table 2: Average Absolute Error (AAE) of wax phase boundary calculated by different models compared to experimental values for binary asymmetric systems

<table>
<thead>
<tr>
<th>Binary Mixture</th>
<th>Number of data points</th>
<th>Pressure range (MPa)</th>
<th>This work model (α adjusted)</th>
<th>This work model (α = 1.23×10⁻⁴ MPa⁻¹)</th>
<th>Modified Ji (Proposed here)</th>
<th>Pauly et al. 12</th>
<th>Ghanaei et al. 31</th>
<th>Nasrifar and Fani-Kheshty 19</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-nC30</td>
<td>115</td>
<td>3.189-86.80</td>
<td>1.07</td>
<td>1.17</td>
<td>2.76</td>
<td>3.95</td>
<td>3.02</td>
<td>3.00</td>
</tr>
<tr>
<td>C1-nC24</td>
<td>136</td>
<td>1.820-95.62</td>
<td>0.67</td>
<td>1.18</td>
<td>4.34</td>
<td>3.97</td>
<td>4.38</td>
<td>4.06</td>
</tr>
<tr>
<td>C1-nC22</td>
<td>13</td>
<td>4.520-97.68</td>
<td>0.19</td>
<td>0.72</td>
<td>5.75</td>
<td>5.32</td>
<td>6.79</td>
<td>6.24</td>
</tr>
<tr>
<td>C1-nC20</td>
<td>81</td>
<td>95.66-160.19</td>
<td>0.44</td>
<td>0.47</td>
<td>1.12</td>
<td>1.57</td>
<td>1.64</td>
<td>2.26</td>
</tr>
<tr>
<td>C1-nC17</td>
<td>49</td>
<td>10.11-257.50</td>
<td>0.53</td>
<td>0.54</td>
<td>1.16</td>
<td>1.65</td>
<td>1.74</td>
<td>1.87</td>
</tr>
<tr>
<td>C1-nC16</td>
<td>63</td>
<td>6.540-193.10</td>
<td>0.25</td>
<td>0.43</td>
<td>0.34</td>
<td>0.51</td>
<td>0.84</td>
<td>1.43</td>
</tr>
<tr>
<td>Total</td>
<td>457</td>
<td>Average</td>
<td>0.53</td>
<td>0.75</td>
<td>2.58</td>
<td>2.83</td>
<td>3.07</td>
<td>3.14</td>
</tr>
</tbody>
</table>

3.2. Multicomponent Mixtures

Similar to binary systems, here the evaluations are made only for systems of high asymmetry, where the light end is methane, as all of the existing models perform fairly well for low asymmetric systems. For multicomponent systems again it is observed that a constant value of α is capable of accurately representing the wax phase boundary in a system with fixed
light and heavy ends, regardless of their proportions. This is shown for selected systems of different low to high proportion of methane combined with (i) a ternary mixture of nC16 to nC18 (experimental data from\textsuperscript{60}) in Figure 4 and (ii) multicomponent wax of nC13 to nC22 (wax2 with experimental data taken from\textsuperscript{2}) presented in Figure 5. For all the systems tested, the complete results are presented in Table 3. A set of 403 data points for 5 highly asymmetric mixtures are used for evaluations. As it is shown in this table, by assigning a special $\alpha$ for each system, compared to other models, very small values of AAE would be achieved. For all the data points for multicomponent systems, a common value of $0.95 \times 10^{-4}$ is assigned to $\alpha$. Using this value, again very small values of overall AAE are achieved as shown in Table 3. Furthermore, according to the results, similar to what was observed for binary systems, the modified Ji model performs much better than the other models. This signifies the superiority of the “No-Poynting term” models over “Poynting term” models, when thermophysical properties of heavy alkanes (most significantly, fusion and solid-solid transition temperatures) are correctly evaluated at high pressures. Among the two “No-Poynting-term” methods proposed, the new approach in which the parameter $\alpha$ is introduced is outperforming the modified Ji method as all parameters $T^f_1, T^f_1, \Delta H^f_1, \Delta H^f_1$ are calculated at higher pressure while in the “modified Ji” method only $T^f_1, T^f_1$ are calculated at higher pressure.
Figure 4: Multicomponent methane + (nC16–nC18) solid phase boundary. The results for "this work model" are shown by adjusted $\alpha$ of $1.71 \times 10^{-4}$ MPa$^{-1}$ for (a) 89.48 (b) 59.97 and (c) 19.9 mol% methane in the mixture. ○: Experimental WDT data; ——— This work model; ——— Modified Ji model; ——— Pauly et al. model; ······· Nasrifar and Fani-Kheshty model; --- Ghanaei et al. model
Figure 5: Multicomponent methane + (nC13–nC22) solid phase boundary (“wax2” from the work of Pauly et al.\textsuperscript{2}. The results for “this work model” are shown by adjusted $\alpha$ of $0.55 \times 10^{-4}$ MPa\textsuperscript{-1} (a) 89.76 (b) 79.73 (c) 69. 95 mol% methane in the mixture. ○: Experimental WDT data; —— This work model; –– Modified Ji model; ——— Pauly et al. model; ······· Nasrifar and Fani-Kheshty model; - - - Ghanaei et al. model
Table 3: Average Absolute Error (AAE) of wax phase boundary calculated different models compared to experimental values for multicomponent asymmetric systems

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Number of data points</th>
<th>Pressure range (MPa)</th>
<th>Adjusted $\alpha$ (MPa$^{-1}$)</th>
<th>AAE (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1+(nC16-nC18)</td>
<td>41</td>
<td>4.22–95.94</td>
<td>$1.71\times10^{-4}$</td>
<td>0.34</td>
</tr>
<tr>
<td>C1+(nC22+nC24)</td>
<td>119</td>
<td>96.96–171.4</td>
<td>$1.36\times10^{-4}$</td>
<td>1.32</td>
</tr>
<tr>
<td>C1+(nC24+nC30)</td>
<td>105</td>
<td>103.1–193.1</td>
<td>$1.17\times10^{-4}$</td>
<td>1.16</td>
</tr>
<tr>
<td>C1+(nC13-nC22)</td>
<td>99</td>
<td>0.1–98.59</td>
<td>$0.55\times10^{-4}$</td>
<td>1.10</td>
</tr>
<tr>
<td>C1+(Multi-paraffin)</td>
<td>39</td>
<td>0.1–45</td>
<td>$0.32\times10^{-4}$</td>
<td>0.38</td>
</tr>
<tr>
<td>Total</td>
<td>403</td>
<td>0.1–193.1</td>
<td>Average</td>
<td>0.86</td>
</tr>
</tbody>
</table>

*Adjusted $\alpha$ for each case

**Common $\alpha$ equal to $0.95\times10^{-4}$ MPa$^{-1}$

### 3.3. Notes on the adjustable parameter $\alpha$

Comparing the results presented in Table 2 and Table 3, it is observed that a smaller common value can be assigned for parameter $\alpha$ in binary systems compared to multicomponent systems. This difference can be attributed to the excess volume effects in solid solutions in comparison to pure solids, which results in having non-unity values for activity coefficients. Yet the common values of $\alpha$ are in the same order. Furthermore there is insufficient published experimental data at very high pressures (in orders of 100 MPa) and for a diverse range of asymmetry in the systems. Also, the experimental data used here for model evaluations and adjusting $\alpha$ for each system are measured by different methods (for the data
presented here, visual and calorimetric techniques), coupled with the general uncertainty with wax phase boundary data. Accordingly, it was not possible to check if more intricate functions can model the behaviour of parameters $\beta^f$ and $\beta^{tr}$ at high pressure or if $\alpha$ can be defined as a normal alkane dependant parameter or as a function of the heaviness and/or degree of asymmetry of the system. In absence of wax phase boundary data for systems of low to moderate asymmetry, the modified Ji model, is suggested. Overall as a general guideline, based on the characteristics of a mixture it is advised to assign a value for $\alpha$ within the lower and upper boundaries of $0.3 \times 10^{-4}$ MPa$^{-1}$ to $1.4 \times 10^{-4}$ MPa$^{-1}$ with a common value of $0.95 \times 10^{-4}$ MPa$^{-1}$ as discussed earlier. The performance of this value is shown for an example system of high asymmetry with about 95.96 mol% methane (mixture “wax3” in the work of Pauly et al.) in Figure 6. The grey region in this figure corresponds to the upper and lower wax boundary change using the minimum and maximum values of $\alpha$. Using these values, at pressures as high as 100 MPa an absolute error of $\pm 2.5$ K can be observed, depending on the value of $\alpha$ specified. For this system the best value for $\alpha$ is $0.64 \times 10^{-4}$ MPa$^{-1}$. However, using both “this work model” with common value of $0.95 \times 10^{-4}$ MPa$^{-1}$ and modified Ji method, very similar AAE compared to experimental data is achieved, though “this work model” performs better than modified Ji at higher pressures as presented in Figure 6 compared to “Poynting term” methods which have almost similar performances. This figure, again confirms that between methods without adjustable parameters the method of modified Ji is the one offering the highest accuracy.
Figure 6: Wax phase boundary modelled with different methods for the “wax3” system of Pauly et al.\textsuperscript{2} with 95.96 mol\% methane. The grey region corresponds to the upper and lower wax boundary change using the minimum and maximum values of $\alpha$, i.e. $0.3 \times 10^{-4}$ MPa\textsuperscript{-1} and $1.4 \times 10^{-4}$ MPa\textsuperscript{-1}, respectively. For this system the best value of $\alpha$ is $0.64 \times 10^{-4}$ MPa\textsuperscript{-1}.

The performance of modified Ji model is not only comparably good at wax phase boundary modelling but also in measuring the wax content and composition. Due to scarcity of such data at high pressure, the comparisons are only made for a single system of nC10+(nC18-nC30), though with much lower degree of asymmetry compared to the rest of the systems investigated here, for which the experimental wax content and composition are measured by Daridon and Dauphin\textsuperscript{63} at 293.15 K and at different pressures as high as 50 MPa (see Figure 7). For this system, the best value of $\alpha$ to match wax composition data is $0.35 \times 10^{-4}$ MPa\textsuperscript{-1}. This small value (compared to the common value of $0.95 \times 10^{-4}$ MPa\textsuperscript{-1}) for this system of lower asymmetry points to the possible correlation of $\alpha$ with the heaviness of the light-end or, generally speaking, degree of asymmetry of system. Devising such a correlation requires sufficient experimental solid-liquid equilibrium data to be obtained for a vast range of systems with different asymmetry and proportions of light end.
Figure 7: Composition of solid wax evaluated with different models for nC10+(nC18–nC30) mixture of Daridon and Dauphin\textsuperscript{63}. The results for “this work model” are shown by adjusted

\[ \alpha \text{ of } 0.35 \times 10^{-4} \text{ MPa}^{-1} \]
Now, it is justified why here two models were proposed. The new model, by comparison with the modified Ji and other models evaluated here, is capable of accurately modelling the behaviour of solid-liquid equilibria in highly asymmetric systems at high pressure, though it does have an adjustable parameter. Using a common value for this parameter the new model is still superior in a variety of cases. However, in the absence of high pressure WDT data and when the uncertainty in choosing value of adjustable parameter is high or when it is not desirable to use a model with an adjustable parameter the modified Ji model is suggested. As presented earlier, the modified Ji prediction of wax phase boundary as well as wax composition was more accurate than all of the “Poynting term” methods evaluated here.

4. Conclusions and Suggestions

A new model for the most problematic systems in the area of solid-liquid equilibrium modelling of the paraffinic waxy mixture, i.e. highly asymmetric mixtures at high pressure conditions, is developed. The model is based on the “No Poynting term” approach and is shown to be capable of accurately capturing the wax phase boundary behaviour of such systems with a single adjustable parameter which can be fixed regardless of the proportion of light and heavy ends in a mixture of variable ratios of fixed light end and heavy end. The value of the adjustable parameter can vary from one mixture to another. Therefore, using a total of 860 data points for evaluation, common values for the adjustable parameter are assigned. Due to lack of experimental data, it is not possible at present to correlate the value of the adjustable parameter with the degree of asymmetry of the mixture or even assign a more complex form of function to the ratio of molar volume of n-alkanes in the solid state to the same value in the liquid state (here a linear function was used, in the simplest form, with the slope to be the adjustable parameter). Therefore it is suggested to measure more experimental solid-fluid experimental data in systems with a wide range of asymmetry.
Using common values for the adjustable parameter, the model works very well at high pressures. Meanwhile, if it is not desirable to use a model with an adjustable parameter (when uncertainty in its value is high) the modified Ji model, in the way revised in the current study, is suggested as it was clearly shown that the “No Poynting term” methods performance are superior to that of “Poynting term” methods for such problematic systems.

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ABBREVIATIONS

SFE, Solid-fluid equilibrium; WDT, Wax disappearance temperature; SRK, Soave-Redlich-Kwong equation of state; PR, Peng-Robinson equation of state; JMGC, Jaubert-Mutelet group contribution method; VLE, Vapour-liquid equilibrium; LCVM, Linear combination of Vidal and Michelsen mixing rules; MHV2, Second-order modified Huron-Vidal mixing rule;
UNIQUAC, Universal quasi-chemical activity coefficient model; WAT, Wax appearance temperature; AAE, Average absolute error; ARE, Average relative error; SLE, Solid-liquid equilibrium; SLVE, Solid-liquid-vapour equilibrium.

REFERENCES


(7)  Jaubert, J. N.; Mutelet, F. VLE Predictions with the Peng-Robinson Equation of State and Temperature Dependent Kij Calculated through a Group Contribution Method.


(22) Chevallier, V.; Provost, E.; Bourdet, J. B.; Bouroukba, M.; Petitjean, D.; Dirand, M.


(37) Machado, J. J. B.; de Loos, T. W.; Ihmels, E. C.; Fischer, K.; Gmehling, J. Erratum to


(39) van der Kooi, H. J.; Flöter, E.; Loos, T. W. d. High-Pressure Phase Equilibria of {((1−x)CH4+xCH3(CH2)18CH3)}. J. Chem. Thermodyn. 1995, 27 (8), 847–861.


(52) Machado, J. J. B.; de Loos, T. W. Liquid-Vapour and Solid-Fluid Equilibria for the System Methane + Triacontane at High Temperature and High Pressure. Fluid Phase


