

Modelling phase equilibria in systems with organic solid solutions

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1. INTRODUCTION

The formation of alloys of inorganic compounds has been known for centuries, yet it is not only on metallurgy and ceramics that metals and inorganic salts in general form mixed crystals. Reports on the formation of alloys, or solid solutions, of organic compounds, although still rare, have been appearing regularly in the last few years for aromatic compounds, such as substituted benzenes and naphthalenes [1-3], pyrene and anthracene [4-6], for carbohydrates [7], terpenes [8], neopentane derivatives [9-10] and fullerenes, besides solid solutions of C₆₀ with C₇₀ [11-12] solid solutions of C₆₀ in sulphur have been reported [13]. Nevertheless it is among the molecules with long n-alkyl chains such as n-alcohols [14], fats [15], soaps [16] and alkanes [17-20] that solid solutions appear more frequently. Although most of these alloys are still just interesting academic curiosities, these new materials seem quite promising and interesting applications for some of them have been identified. N-alkane blends have been patented for energy storage and preservation of food, medicine and cell tissues [21]; solutions of aromatics based on pyrene have interesting optical properties [4-6]. Surfactants of controlled properties [16] and the manipulation of the behaviour of fats to confer them new organoleptic characteristics [15] have been surfacing showing the exciting possibilities of these new materials.

Although the materials based on n-alkane alloys have been used for long as candles, waterproof coatings, pharmaceutical and cosmetics, and in spite of paraffin waxes being a valuable by-product of petroleum refining, the research on n-alkane solid solutions has been mainly prompted by its dark side: The damages and losses caused by wax precipitation from petroleum fluids. Every year wax deposition costs billions of dollars in preventive maintenance, remediation of pipeline blockages and losses of production [22,23]. Better computer models can help anticipate the problems allowing for preventive actions, optimization of actions and avoid losses by shutting down of production or by accident.

The presentation of this chapter will focus on the prediction of the wax precipitation from petroleum fluids both at high pressures, in reservoir conditions, or at low pressures, as stock tank oil or fuels. In the final section the application of the model proposed to other systems of organic solid solutions will be discussed.

2. STATE OF ART

The modelling of wax formation in petroleum fluids is based on the thermodynamic description of the equilibrium between the solid wax and the hydrocarbon liquid phases. The general Solid-Liquid Equilibrium equation relates, for each compound, the fugacities of both phases in the standard state, f° , with the pure component thermophysical properties [24]:

$$\left(\ln \frac{f^{ol}}{f^{os}} = \frac{\Delta_{fus} H_i}{RT_{fus,i}} \left(\frac{T_{fus,i}}{T} - 1 \right) + \frac{\Delta_{t2} H_i}{RT_{t2,i}} \left(\frac{T_{t2,i}}{T} - 1 \right) - \frac{\Delta_s^l C_{p,m}}{R} \left(\ln \frac{T}{T_{fus,i}} + \frac{T_{fus,i}}{T} - 1 \right) \right)_i \quad (1)$$

All the Solid Liquid Equilibrium models available, independent of the nature of the solid phase, are based on this equation. Their differences derive from the approach to the description of the solid and liquid phases fugacities, f , the definition of the solid phase nature and composition, and consequently on the values adopted for the thermophysical properties.

2.1 Non-ideality of the liquid phase

For the description of the liquid phase two approaches have been adopted. For low pressures the liquid phase is either taken as ideal [25-27] or a free energy model is used [28-32]. At high pressures the fluid phase is described by an Equation of State [33-39].

2.2 Non-ideality of the solid phase

Two opposite approaches have been adopted for the solid phase. The authors either assume that the solid phase is formed by several independent pure (pseudo) components [34-36] or that it is a solid solution, stable or not, of all the material that crystallises. Among the authors that consider the formation of a solid solution some take it as ideal [25,26,33] but most of them adopt some form of free energy model to describe the non-ideality of the solid phase [27-32].

2.3 Solid phase and thermophysical properties

The misty region in most models is the definition of what is the solid phase forming. Early authors assume that all compounds present in the fluid eventually crystallise [28-30]. This concept can still be found in recent authors [33-36] in spite of the growing evidence that only compounds with long n-alkyl chains crystallise to form the wax. Today even the authors that consider the presence of other molecules in the solid phase agree that the main part of the wax fraction is formed by n-alkanes. These molecules have multiple solid habits (rotator, triclinic, monoclinic, orthorhombic...) depending on the temperature and parity of the alkyl chain [40]. The thermophysical properties associated to these transitions are strongly *dependent* on the solid phase adopted in the modelling. Most authors, behind a generic label of 'solid', fail to clearly state the solid phase they are working with. The evidence today is that the alkyl chains in the wax adopt an orthorhombic structure [41-45] even if some isoalkanes or alkyl aromatic compounds are present as inclusions [46]. The correlations for thermophysical properties used are strongly associated to the solid phase adopted. When the solid phase is poorly defined the thermophysical properties used by the model are fitted to a set of wax formation data and the values adopted, typically fairly different from the pure compounds data, actually compensate for weaknesses in the non-ideality description. These correlations are of limited applicability for systems other than those used in the development of the correlation [26, 30, 35-37]. Only few authors clearly state the solid phase adopted, the compounds present in the solid phase and use, in accordance, thermophysical properties for the pure compounds [27, 31-33, 38,39].

Based on these considerations the thermodynamic wax formation models proposed in the literature can be divided into five categories: Won's, Erickson's, Ungerer's, Calange's and

Predictive free energy models. These models, their differences and similarities are described below.

2.4 Won's model class

Won's models such as Won [28, 47], Hansen et al. [29] and Pedersen et al. [30] are characterized by adopting the Regular Solution Theory for the description of the solid phase non-ideality and assuming that all compounds are crystallisable. The solubility parameters are usually correlated to sets of data on wax formation [29, 30] and the correlations for the thermophysical properties adopted, common to other models that often use the Won's correlations for the thermophysical properties [28] do not distinguish between the different hydrocarbon families. They are also characterised by the importance attributed to the heat capacity term on Eq. (1) being the correlation for heat capacities proposed by Pedersen et al. [30] still used by models of Ungerer's type.

2.5 Erickson's model class

Erickson's models assume an ideal solid phase. On this model class can be considered the models of Erickson et al. [25, 48], Pedersen [26] and Rønningsen et al. [37]. The predictive version of Calange's model assuming ideal solid phase [33] can also be characterized as belonging to this class. They assume the presence of non n-alkanes in the solid phase, sometimes even of very light compounds like in the Calange's model [49], and the thermophysical properties correlations used are, although with modifications, those proposed by Won [28].

2.6 Ungerer's model class

The models of this class are based on a seminal idea proposed by Leivobici to use Eq. (1) for the estimation of the solid phase fugacity [34]. This allows the description of the liquid phase by an Equation of State providing an approach that extends the description of wax formation to high pressures. This idea has made its way into all the other model classes being today generally adopted for high pressure VLSE description. What individualizes this kind of models is a solid phase as being formed by multiple pure solid phases. Ungerer et al. [34] proposed this approach for synthetic mixtures of non co-crystallisable compounds but its extension to crudes, first at low pressures by Lira-Galeana et al. [35] and then by Pan et al. [36] for high pressures continues using the assumption that all pseudocomponents used in the fluid characterisation crystallise as pure independent compounds. Non-paraffins are considered to be also present in the solid phase but the thermophysical properties correlation proposed by Won [28] is used only for the n-alkanes. New correlations are proposed for the other hydrocarbon families. Like the models of Won's type these models continue to use the heat capacity term of Eq. (1) shown by some authors to be negligible [33, 50] and abandoned in most of the other model classes. As expected for these models the pseudocomponent definition and characterization plays a dramatic role in the modelling with the oil characterization acting as a tuning parameter [51].

2.7 Calange's model class

These models are characterised by using the solid phase non-ideality as a fitting parameter. Typically a cubic EOS describes the fluid phases and the activity coefficient of the solid phase is treated as a tuning parameter [33, 49,52]. Other parameters can be used to fit the experimental data such as binary interaction parameters, thermophysical properties [52, 53], and the oil characterization. Although successful in correlating experimental data given

their flexibility these models have no predictive character and its use holds some danger because they reproduce the experimental data available whether it is accurate or wrong.

2.8 Predictive free energy model class

On these models a predictive free energy model describes the non-ideality of the orthorhombic solid solution of alkyl chains. This type of models can be traced back to Won [28] and his approach to the estimation of the solid phase solubility parameter based on the heats of sublimation of pure compounds. This suggestion can be found in the Predictive Local Composition concept proposed by Coutinho and Stenby [31] where the interaction energies are estimated from the heats of sublimation of pure compounds. This approach was first applied to the Wilson Model [31, 54] and then extended to NRTL and UNIQUAC [55]. Predictive UNIQUAC [27, 32] proved to be very successful in the description of wax formation for a broad range of fluids [56,57] considering that the wax phase was formed by only n-alkane molecules and adopting correlations for the thermophysical properties based on the orthorhombic solid phase of the pure n-alkanes.

2.9 Modelling high pressure wax formation

Although the initial models proposed for each of these approaches focused in the low pressure fluids [26-33, 35, 47] the need for a model that could describe the wax formation in live oil at reservoir conditions promoted the development of the models for high pressures [34, 36-39, 48-49, 53]. The approach followed in all cases is based on the suggestion by Leivobici [34] for the estimation of the solid fugacities, with the Poyinting correction to take into account the pressure dependence, and to use a cubic Equation of State for the description of the fluid phases. The dependence of the solid phase non ideality with pressure was taken into account, deliberately or not, by underestimating the volume decrease in the phase transition as demonstrated by Pauly et al. [38].

A systematic effort of comparison of these models performance for crudes has not been reported yet. Unfortunately the authors usually do not perform comparisons between the models proposed and other models available in the literature. The limitations of the Won's type models are evident from the results reported by Pedersen [26] and Calange [33]. Erickson's type model if not carefully used can lead to the problems reported for Calange's model [49] where due to the ideal nature of the solid phase even methane can be found on it. Ungerers's type models in their approach to the description of the solid phase lack a sound thermodynamical basis as discussed by Pedersen and Michelsen [51] and physics as the solid phase used does not agree with the reality. Fitting models, if carefully tuned, can describe about any set of experimental data. These models are of limited utility as, lacking predictive capacities, experimental data must be available and they reproduce the experimental data even if this is of poor quality. The soundest thermodynamical approach and that has been most widely applied in the open literature to quite a number of different systems from complex synthetic mixtures to fuels and crudes are the Predictive free volume models. This approach was also found to be the best in a comparison with other wax formation models on a complex synthetic mixture [54] reported by Pauly and Daridon. The multicomponent SLE data for hydrocarbon systems produced at University of Pau became a reference in the field and today all the new models reported are being tested against them.

3. WAX FORMATION MODEL

As discussed above and according to the experimental evidence [41-45] the model hereafter presented considers the wax formed by n-alkanes crystallising from a fluid as orthorhombic solid solutions [31-32]. The condition of equilibrium between the Liquid, Solid and Vapour phases is given by the equality of the fugacities in all phases for each individual component, i:

$$f_i^v(T, P, x_i^v) = f_i^l(T, P, x_i^l) = f_i^s(T, P, x_i^s) \quad (2)$$

Taking the liquid phase as the reference phase, the equilibrium ratios, K_i^v and K_i^s , are defined as:

$$K_i^v = \frac{x_i^v}{x_i^l} = \frac{\phi_i^l(P)}{\phi_i^v(P)} \quad (3)$$

$$K_i^s = \frac{x_i^s}{x_i^l} = \frac{\phi_i^l(P)}{\phi_i^s(P)} \quad (4)$$

where ϕ_i , are the fugacity coefficients and the x_i the mol fractions for the different phases .

3.1 Low pressure

At low pressure the vapour phase is neglected and the solid phase equilibrium constants are obtained directly from Eq. (1) as:

$$K_i^s = \frac{\gamma_i^l}{\gamma_i^s} \exp\left(\frac{\Delta_{fus} H_i}{RT_{fus,i}} \left(\frac{T_{fus,i}}{T} - 1\right) + \frac{\Delta_{t2} H_i}{RT_{t2,i}} \left(\frac{T_{t2,i}}{T} - 1\right)\right) \quad (5)$$

The heat capacities term of this equation was found negligible [33, 50] and is not used. The correlations used for the thermophysical properties are presented on the Fluid Characterization section below.

3.1.1 The liquid phase activity coefficient

Since the solubility of n-alkanes is similar in different non-polar solvents as shown by Coutinho and Darridon [27] the liquid phase may be assumed ideal and the activity coefficient taken as unit. This approach simplifies considerably the calculation and the Fluid Characterization.

Alternatively a more rigorous approach may be used with liquid phase non-ideality described by a modified UNIFAC model:

$$\ln \gamma_i = \ln \gamma_i^{res} + \ln \gamma_i^{comb-fv} \quad (6)$$

The residual term, $\ln \gamma^{res}$, describing the energetic interactions between unlike molecules, such as aromatics and aliphatics, is given by the modified UNIFAC [59-61], while the size difference effects and free volume contributions, $\ln \gamma^{comb-fv}$, are described by the Flory-free volume equation [27]:

$$\ln \gamma_i^{comb-fv} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \quad \text{with} \quad \phi_i = \frac{x_i (V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j (V_j^{1/3} - V_{wj}^{1/3})^{3.3}} \quad (7)$$

where V_i is the molar volume obtained from the literature or estimated by Elbro group contribution method [62]. The V_{wi} is the van der Waals volume of component i estimated using the Bondi method [63] or alternatively using the UNIFAC volume parameters r [59-61]

$$V_{wi} = 15.17 \times r_i \quad (8)$$

3.1.2 The Solid Phase activity coefficient - Predictive UNIQUAC

For the solid phase non-ideality the Predictive UNIQUAC model is used [32, 55]

$$\ln \gamma_i^s = \ln \left(\frac{\Phi_i}{x_i^s} \right) + 1 - \frac{\Phi_i}{x_i^s} - \frac{Z}{2} q_i \left(\ln \left(\frac{\Phi_i}{\theta_i} \right) + 1 - \frac{\Phi_i}{\theta_i} \right) + q_i - q_i \ln \left(\sum_{j=1}^n \theta_j \tau_{ji} \right) - q_i \sum_{j=1}^n \frac{\theta_j \tau_{ij}}{\sum_{k=1}^m \theta_k \tau_{kj}} \quad (9)$$

Here τ_{ji} is

$$\tau_{ji} = \exp \left(- \frac{\lambda_{ji} - \lambda_{ii}}{q_i RT} \right) \quad (10)$$

and the λ_{ji} are the interaction energies. The area fraction, θ_i , and the segment fraction, Φ_i , are

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (11)$$

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (12)$$

using a new definition for the structural parameters r and q [32]. The correlations for the r and q values with the n-alkane chain length are:

$$r_n = 0.1 C_{ni} + 0.0672 \quad (13)$$

$$q_n = 0.1 C_{ni} + 0.1141 \quad (14)$$

The predictive local composition concept [31] allows for the estimation of the interaction energies. The interaction energies, λ_{ii} , are estimated from the heat of sublimation of a pure orthorhombic crystal,

$$\lambda_{ii} = -\frac{2}{Z}(\Delta_{sub}H_i - RT) \quad (15)$$

with Z being the coordination number. It has a value of 6 for orthorhombic crystals. Correlations for the heat of sublimation are provided at the end of the Chapter. The interaction energy between two non-identical molecules is given by

$$\lambda_{ij} = \lambda_{ji} = \lambda_{jj} \quad (16)$$

where j is the n-alkane with the shorter chain of the pair ij .

This model is purely predictive, requiring for the calculation of the phase behaviour nothing but the pure component thermophysical properties.

3.2 High pressure

At high pressure a gamma-phi approach will be used to describe the VLSE. The fugacity coefficients for the equilibrium ratio of the fluid phases, Eq. (3), will be estimated by a cubic equation of state while the fugacity of the solid phase required for the equilibrium ratio of the solid phase, Eq. (4), will be obtained from Eq. (1) corrected for the pressure by the Poynting correction.

3.2.1 Fluid phase fugacities

The evaluation of liquid and vapour fugacity coefficients is performed with the Soave-Redlich-Kwong Equation of State [64]:

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)} \quad (17)$$

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

$$b = \sum_i x_i b_i \quad (18)$$

whereas for the a parameter the LCVM mixing rule is used:

$$\alpha = \left(\frac{a}{bRT} \right) = \left(\frac{\lambda}{A_v} + \frac{1-\lambda}{A_m} \right) \left(\frac{G^E}{RT} \right) + \frac{1-\lambda}{A_m} \sum_i x_i \ln \left(\frac{b}{b_i} \right) + \sum_i x_i \alpha_i \quad (19)$$

Here A_m , A_v and λ are constant. The excess Gibbs free energy G^E of the liquid mixture is calculated using the modified UNIFAC group contribution method [61] with interaction parameters on the following form:

$$\Psi_{ij} = \exp\left(-\frac{A_{ij} + B_{ij}(T - 298.15)}{T}\right) \quad (20)$$

The parameters were estimated by Boukouvalas et al. [65, 66].

The critical properties for light gases are widely available in the literature (e.g. Poling et al. [67]). For the heavy components the Twu correlations [68], described in the next section, are used.

Alternatively to the LCVm mixing rule the quadratic mixing rule for the a parameter can also be applied

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (21)$$

however due to a mismatch of the fugacities of the fluid and solid phases in the gamma-phi approach the predictive character of the model is lost. With the quadratic mixing rule the interaction energy mismatch for the solid phase, ξ , must be fitted to the WAT of the fluid as described below [69]. The loss in predictive character is compensated by a gain in flexibility.

3.2.2 Solid phase fugacity

As discussed above the fugacity of the solid phase is estimated from Eq. (1). The equilibrium constant for the solid phase is given by [38]

$$K_i^s = \frac{\phi_i^l[P](\phi_i^{lo}[P_0])^{\beta-1}(\phi_i^{lo}[P])^{-\beta} \left(\frac{P}{P_0}\right)^{1-\beta}}{\gamma_i^s[P_0]} \cdot \exp\left\{\frac{(1-\beta)C_i(P-P_0)}{RT} + \frac{\Delta_{fus}H_i}{RT_{fus,i}}\left(\frac{T_{fus,i}}{T} - 1\right) + \frac{\Delta_{t2}H_i}{RT_{t2,i}}\left(\frac{T_{t2,i}}{T} - 1\right)\right\} \quad (22)$$

where $\beta=0.9$ is the ratio between the solid and liquid molar volumes of n-alkanes [38], and the Peneloux volume corrections, C_i , are introduced to improve the description of the liquid densities [38]. The fugacities of the liquid phase are obtained by the SRK-EOS. P_0 is the reference pressure taken as atmospheric pressure.

The activity coefficients can be modelled by the Predictive UNIQUAC model described above. Often this model will entail the presence of multiple solid phases requiring multiple solid equilibrium constants to be used and making the problem more complex from a numerical point of view. The use of the Predictive Wilson for the solid phase activity coefficients allows for a good description of the WAT's with a better numerical stability since a single solid phase will be involved.

3.2.3 The Solid Phase activity coefficient - Predictive Wilson

For multicomponent mixtures the activity coefficients may be alternatively evaluated by Predictive Wilson [31]:

$$\ln \gamma_i = 1 - \ln \sum_j x_j \Lambda_{ij} - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \quad (23)$$

with:

$$\Lambda_{ij} = \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \quad (24)$$

The interaction energies are estimated as discussed above.

Although this solid phase model allows for a good description of the WAT's it underestimates the non-ideality of the solid phase [32] and consequently overestimates the solid fraction formed below the WAT.

The use of the van de Waals one fluid mixing rule for the Equation of State instead of LCVM is possible and simplifies the calculations. Due to the mismatch of the fugacities between the solid and fluid phases caused by the gamma-phi approach used a correction to the interaction energies in the solid phase must be used

$$\lambda_{ij} = \lambda_{ji} = \lambda_{jj}(1 + \xi) \quad (25)$$

the interaction energy mismatch for the solid phase, ξ , is fitted to the WAT at atmospheric pressure or other experimental data available. The model loses some predictive character since at least one data point must be available for the fitting. However this loss is compensated by a greater flexibility of the model and an improved description of the phase equilibrium. Moreover some guidelines for the estimation of the interaction energy mismatch can provide an approximation to the phase equilibrium even in absence of experimental data [69].

3.3 Multiphase flash calculations

The presence of at least three phases (gas, liquid and solid) with multiple solid phases being possible requires the use of a multiphase flash in the calculation of wax formation in hydrocarbon fluids. The algorithm of resolution of the Rachford-Rice equations applied to multiphase systems proposed by Leibovici and Neoschil [70] can be used in the phase equilibrium calculations. It is a very stable algorithm because of its continuity across phase boundaries leading to non-physical phase amounts for the unstable phases. The number of solid phases is a product of the multiphase flash calculation resulting from the instability caused by the non-ideality of the solid solutions. With this approach if p phases are present and the liquid phase is used as reference phase the phase fractions, ψ_i , are obtained from the solution of a systems of $(p-1)$ equations [70, 71]. Given a fluid with a composition z_i , for a generic phase k

$$E_k = \sum_{i=1}^n \frac{(K_i^k - 1) z_i}{1 + \sum_{j=2}^p (K_i^j - 1) \psi_j} = 0 \quad (26)$$

The K_i^k are the equilibrium constants for compound i in phase k . Using this algorithm it is possible to easily estimate the phase fractions and the compositions of each phase present at the equilibrium. Other algorithms more or less time consuming and with various degrees of complexity are also possible [71, 72].

4. FLUID CHARACTERIZATION

For crude oils and other real fluids a detailed composition is generally not available and a fluid characterisation is essential. The characterization used with this model considers that the fluid consists of two types of compounds: the solute, comprising the n-alkanes that crystallise to form a solid phase, and the solvent, formed by all the non-crystallisable compounds. A different approach is used for the characterization of the two types of compounds.

4.1 Characterization of n-alkanes

The work developed by our team indicates that an accurate description of n-alkanes Solid-Liquid Equilibrium cannot be achieved unless each n-alkane is considered individually [43, 54, 56, 73]. The n-alkanes characterization aims at develop a description of the n-alkanes distribution as close as possible to the actual fluid. This distribution is described by two parameters: the total n-alkane content and their decay. These can be obtained in a number of different ways:

4.1.1 Total n-alkane content

- 1- Chromatographic measurements. Gas Chromatography (GC) or High Temperature Gas Chromatography (HTGC) allows for the direct detection and quantification of n-alkanes up to very high molecular weights. It can provide both the total n-alkane content and its decay.
- 2- Solvent precipitation. The UOP 46-85 essay [74], or any of its variants [75-77], are standard procedures that provide a good estimate of the total wax content in a crude oil.
- 3- In the absence of further analytical information the wax content can be obtained from a correlation involving some known property of the oil. A correlation for paraffinic waxy crudes of the total wax content with the oil average molecular weight, Mw, was proposed by Coutinho and Daridon [27]

$$\text{Wax content (C}_{20+}\text{)[wt\%]} = 0.070 * \text{Mw} - 8.3 \quad (27)$$

4.1.2 The n-alkane decay

The exponential decay of the n-alkanes in oils is well documented in the literature [78-79]. It is defined as the ratio between the mass fractions of two successive n-alkanes

$$\alpha = \frac{wC_n}{wC_{n-1}} \quad (28)$$

Its value can be estimated by:

- 1- Chromatography: Again GC or HTGC can provide information about the paraffin distribution with even better accuracy than for the wax content.
- 2- Simulated distillation: The n-alkane decay can be related to the decay of True Boiling Point or Simulated Distillation fractions [27] by

$$\alpha_{n-alkanes} = \alpha_{sim.dist} - 0.03 \quad (29)$$

- 3- Average value: If no information at all is available the average decay value of $\alpha=0.88$ ($\sigma=0.03$) can be used, with due care, to generate the n-alkane distribution [27].

All the individual paraffins with concentrations higher than 0.05 wt% are considered.

4.2 Characterization of Solvent

One of the major advantages of the model presented here is that it is independent of the characterisation procedure used for the non-crystallisable compounds. Any solvent characterisation can in principle be used since, as shown by Coutinho and Daridon [27], the solubility of the n-alkanes is independent of the nature of the solvent. It is then irrelevant which and how many pseudo-compounds are chosen to describe the solvent as long as the total molar fractions of the n-alkanes and solvent are coherent with the actual oil composition. To fill this requirement the only constraint to the solvent characterization is that the average molecular weight of the oil is conserved through the characterization procedure.

For a matter of simplicity it is recommended that for a fluid not containing light gases a single pseudo-compound be used while for the other fluids at least two pseudocomponents, one for the gases and the other for the heavier compounds, be used.

4.3 Thermophysical properties for the n-alkanes

Once the distribution of n-alkanes established and the solvent pseudocomponents defined it is necessary to estimate the thermophysical properties of the n-alkanes used by the model. The correlations presented for the paraffins heat and temperature of phase transitions are based on the data by Broadhurst [80] and derived following the Marano and Holder [81] approach:

$$T_{fus,i} [K] = 421.63 - 1936412 \exp(-7.8945 (C_{ni} - 1)^{0.07194}) \quad (30)$$

$$T_{i2,i} [K] = 420.42 - 134784 \exp(-4.344 (C_{ni} + 6.592)^{0.14627}) \quad (31)$$

And

$$\Delta_{tot}H_i [kJ/mol] = 3.7791C_{ni} - 12.654 \quad (32)$$

$$\Delta_{fus}H_i [kJ/mol] = 0.00355C_{ni}^3 - 0.2376C_{ni}^2 + 7.400C_{ni} - 34.814 \quad (33)$$

with

$$\Delta_{t2}H = \Delta_{tot}H - \Delta_{fus}H \quad (34)$$

where C_{ni} is the number of carbon atoms in n-alkane i. These equations are valid from pentane to n-alkanes larger than n-C₁₀₀H₂₀₂ for the melting temperatures, $T_{fus,i}$, and total heats of melting, $\Delta_{tot}H$. The solid phase transitions occur for n-alkanes between n-C₉H₂₀ and n-C₄₁H₈₄ inclusive.

The heat of sublimation,

$$\Delta_{sub}H = \Delta_{vap}H + \Delta_{fus}H + \Delta_{t2}H \quad (35)$$

is calculated at the melting temperature of the pure component, and the heat of vaporisation, $\Delta_{vap}H$, is assessed using the PERT2 correlation by Morgan and Kobayashi [82]

$$\Delta_{vap}H/RT_c = \Delta H_v^{(0)} + \omega \Delta H_v^{(1)} + \omega^2 \Delta H_v^{(2)} \quad (36)$$

with

$$\Delta H_v^{(0)} = 5.2804 x^{0.3333} + 12.865 x^{0.8333} + 1.171 x^{1.2083} - 13.116 x + 0.4858 x^2 - 1.088 x^3 \quad (37)$$

$$\Delta H_v^{(1)} = 0.80022 x^{0.3333} + 273.23 x^{0.8333} + 465.08 x^{1.2083} - 638.51 x - 145.12 x^2 + 74.049 x^3 \quad (38)$$

$$\Delta H_v^{(2)} = 7.2543 x^{0.3333} - 346.45 x^{0.8333} - 610.48 x^{1.2083} + 839.89 x + 160.05 x^2 - 50.711 x^3 \quad (39)$$

where $x = (1 - T/T_c)$.

The acentric factor is a quadratic function of the carbon number, C_{ni} ,

$$\omega = -0.000185397 C_{ni}^2 + 0.0448946 C_{ni} + 0.0520750 \quad (40)$$

and the critical properties are obtained from the correlations of Twu [68]

$$\theta = \ln(Mw) \quad (41)$$

$$T_b[K] = [\exp(5.71419 + 2.71579\theta - 0.28659\theta^2 - 39.8544/\theta - 0.122488/\theta^2) - 24.7522\theta + 35.3155\theta^2]/1.8 \quad (42)$$

$$T_c[K] = T_b(0.533272 + 0.343831 \times 10^{-3} T_b + 2.52617 \times 10^{-7} T_b^2 - 1.65848 \times 10^{-10} T_b^3 + 4.60774 \times 10^{-24} / T_b^{13})^{-1} \quad (43)$$

$$P_c[atm] = (1.0 + 0.312(1 - T_b/T_c)^{1/2} + 9.1(1 - T_b/T_c) + 9.4417(1 - T_b/T_c)^2 + 27.1793(1 - T_b/T_c)^3)^2 \quad (44)$$

5. RESULTS

A comparison of the performance of the model described above with predictions by models of the Won, Erickson and Ungerer classes is presented in Figure 1 for a mixture of n-alkanes in the C20-C30 range in decane [54, 83]. The superiority of the Predictive UNIQUAC model is clear. The correlations for the thermophysical properties used are those of Eqs. (30-

34) without which the results would be much worse. It is interesting to notice that although the models generally overpredict the solid fraction but are qualitatively correct the multiple solids model (Ungerer) shows an odd behaviour.

To illustrate the performance of the model at low pressures results for a crude oil and diesel are presented. Figure 2 shows the fraction of wax formed in crude 16 [76] below the WAT [83] and Figure 3 the change in liquid phase composition with the crystallisation of n-alkanes for a diesel below the cloud point [56, 83]. In both cases the solvent has been described by a single pseudo-component chosen to match the average molecular weight of the fluid. The n-alkanes for the diesel were obtained from a GC analysis and for the crude the wax content was measured by ketone precipitation [74, 76] and the distribution obtained from the simulated distillation data using Eq. (29).

The description of the phase envelope of a North Sea gas condensate obtained using the LCVm mixing rule is reported in Figure 4 [39, 83]. For the characterization of the fluid no lumping was attempted for the C7- fraction. For the C7+ the n-alkanes were obtained by a GC analysis and a single pseudo-component for the non-crystallisable was used. The critical properties for this pseudo-component were fitted to one data point on the VLE boundary line.

A comparison between the performance of the high pressure modelling using the LCVm and the quadratic mixing rules is reported on Figure 5 for a diesel [69]. The characterization was done as previously [56]. The interaction energy mismatch, ξ , was fitted to the atmospheric cloud point. It can be seen that the use of the quadratic mixing rule not only simplifies the calculation procedure allowing for the use of a well established mixing rule but also provides a better description of the wax formation below the cloud point. The values for the parameter ξ correlate well with the number of n-alkanes present in the distribution as shown in Figure 6. For distributions with a number of alkanes above 15 the value of the interaction energy mismatch becomes approximately constant with $\xi=0.06$. This is a consequence of the maximum number of n-alkanes that can be present in a single solid phase.

6. OTHER SYSTEMS

The applicability of the model described above is not limited to petroleum fluids. The thermodynamic approach used is very general and can be applied to any organic alloy as long as the estimation of interaction energies described by Eq. (16) is relaxed. This *relationship* was derived for n-alkanes and it is not applicable to other compounds. For solutions of n-alkyl chains the Eq. (25) can still be used since the interaction energy mismatch will take into account the deviations to the n-alkane behaviour presented by other systems. This approach, while never attempted before, should work for iso-alkanes, n-alcohols, fats, α -olefins and other sort of waxes. Of particular interest would be the description of the behaviour of Fischer-Tropsch waxes, that involve several of these compounds with long n-alkyl chains, and the dewaxing of base-oils by solvent. For a generic system the interactions between two unlike molecules cannot be associated to the interactions between identical molecules, as suggested by Eqs. (16) and (26). For these systems the interaction energies, λ_{ij} , have to be fitted to experimental data.

Approaches to the description of solid solutions using other excess Gibbs energy models are also possible. Oonk and co-workers have studied multiple solid solutions [2-3, 8-9, 14] successfully using Redlich-Kister polynomials to correlate the excess properties of the

solid phases. For waxes in the high temperature rotator phase Coutinho et al. [83] proposed CDLP, a model based on a Margules equation for the description of the excess properties of the solid phase.

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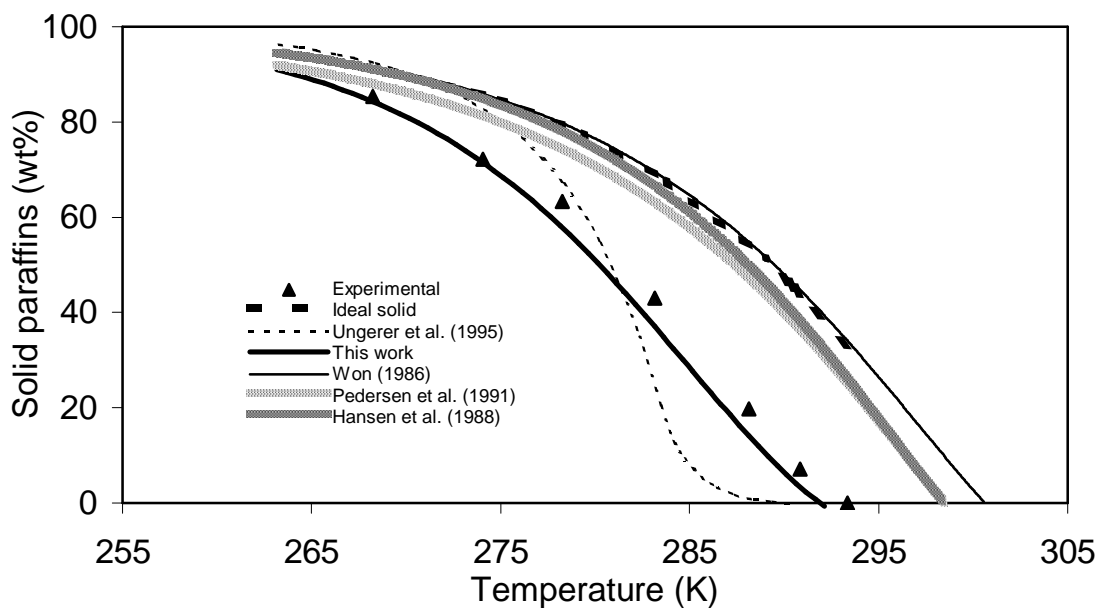


FIGURE 1. Comparison of the performance of Predictive UNIQUAC model [32, 55] with other literature models for the solid phase non-ideality. Reprinted from [83].

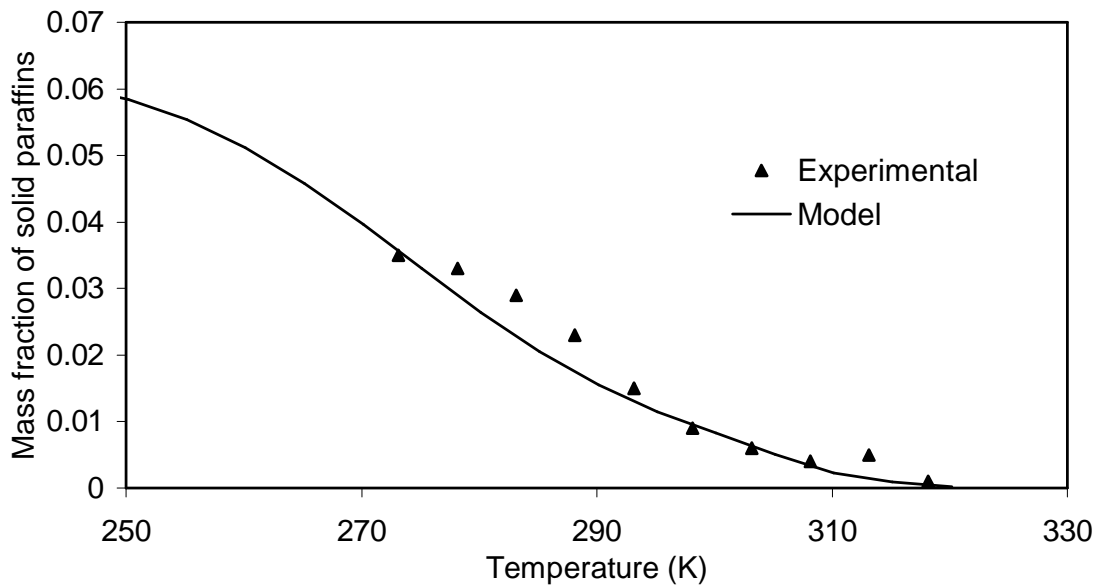


FIGURE 2. Comparison between experimental data and model predictions for the fraction of wax forming in Oil 16 [76]. Reprinted from [83].

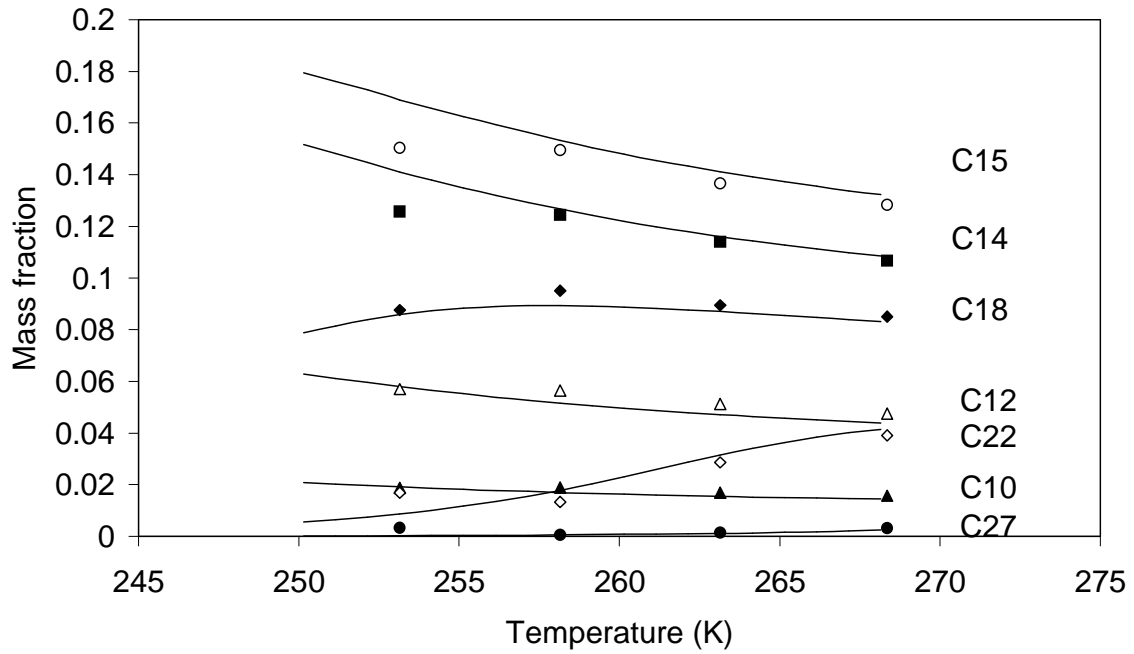


FIGURE 3. Experimental data and model predictions for the temperature dependence of the paraffins composition in the liquid phase for Diesel S [56]. Reprinted from [83].

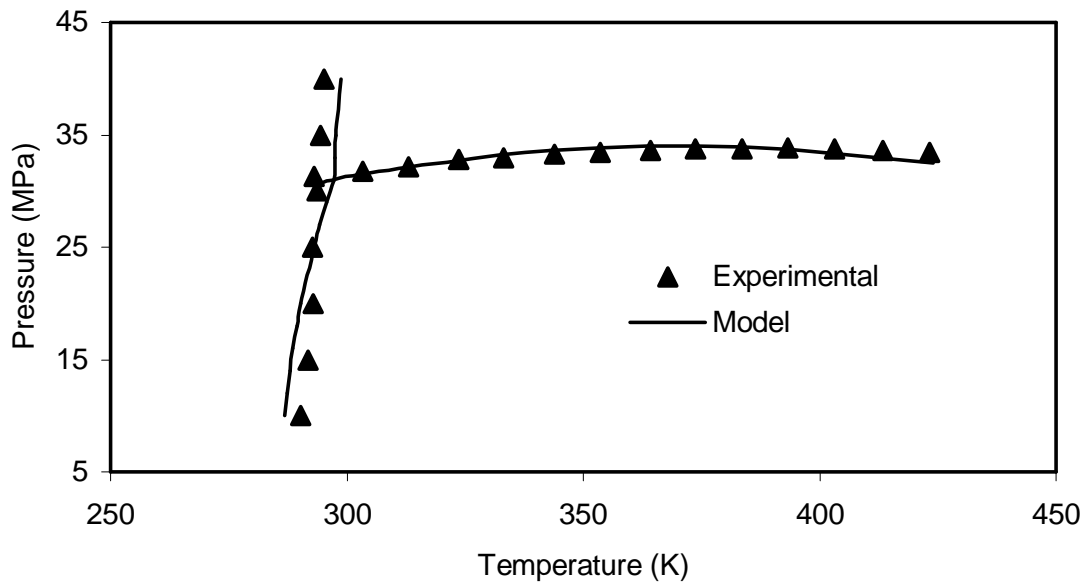


FIGURE 4. Measured and calculated phase envelope for a live oil from North Sea [37]. Reprinted from [83].

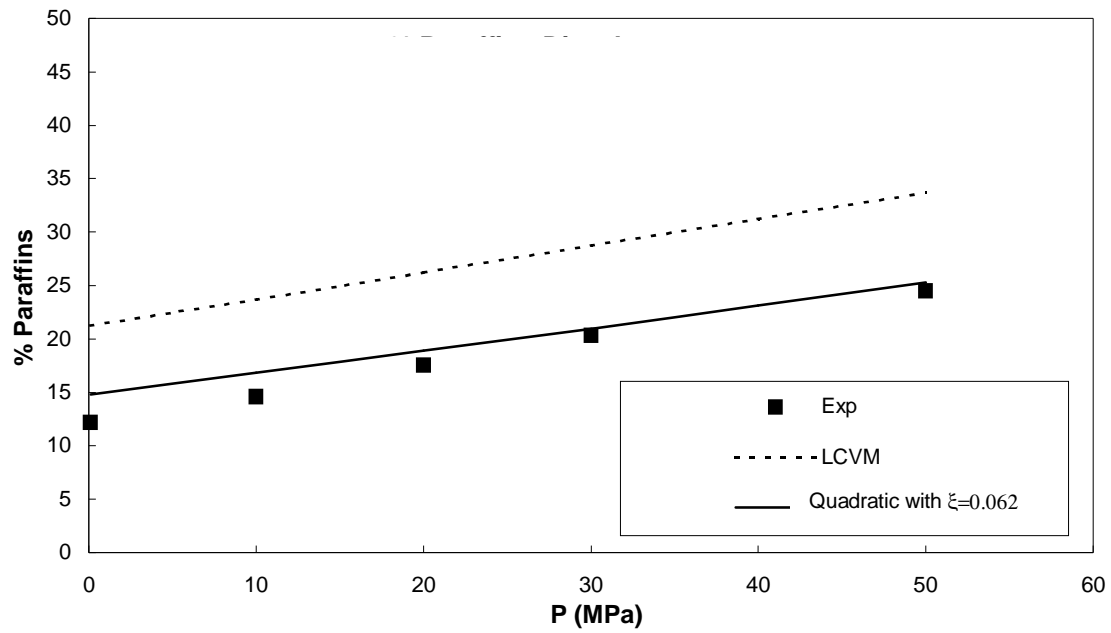


Figure 5- Comparison between the performances of the LCVM and quadratic mixing rules for the high pressure behaviour of a diesel [69].

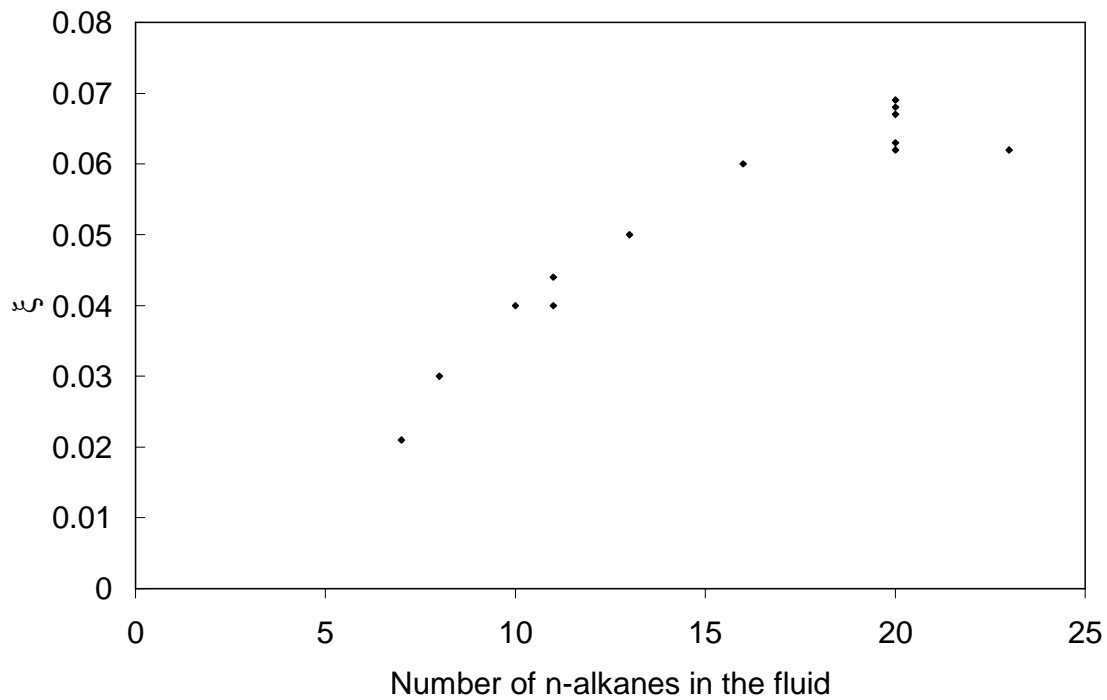


Figure 6- Interaction energy mismatch for various fluids as function of the number of n-alkanes present [69].