A new predictive UNIQUAC for modeling of wax formation in hydrocarbon fluids

João A.P. Coutinho⁎, Fátima Mirantea, Jerome Paulyb

a CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal
b Laboratoire des Fluides Complexes, Centre Universitaire de Recherche Scientifique, Université de Pau, Avenue de l’Université, BP 1235, 64013 Pau, France

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Abstract

A new UNIQUAC based predictive local composition model is here compared against predictive Wilson and predictive modified UNIQUAC on their abilities to predict wax formation. For that purpose a very large database of phase equilibrium data of both synthetic and real hydrocarbon fluids, at both low and high pressures, will be used. It is shown that the new UNIQUAC model does not suffer from the limitations, or is much less affected by them, than the models previously proposed. The global description of the phase equilibrium for all the systems studied is also significantly superior to the two other models.

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1. Introduction

Recently [1] we have been revisiting the predictive local composition models previously proposed for the description of wax formation in hydrocarbon fluids [2–6]. Although the models were globally very successful in the description of both wax formation in synthetic, well-defined, fluids [4–7] as for complex poorly defined real fluids, such as diesels [8–11] and crudes [12–18], we had been able to identify over the years a number of limitations and shortcomings that deserved some reflection and work.

It was difficult to understand and to accept that although Predictive modified UNIQUAC was much superior for complex mixtures [4–11], providing a more physically sound and accurate description of these mixtures, it was not able to provide a representation of simple systems as good as Wilson [1,19]. This problem was clear in the two recent publications on the subject [1,19] for systems with three and five paraffins in a solvent and was also observed on this work for a number of other simple systems.

Another problem was the overestimation of the crystallization of light compounds in mixtures of paraffins with a broad range of chain lengths. Although this situation was expectable for Wilson since this model produces a single solid phase it was found also for modified UNIQUAC for which the light paraffins, that were not present in the solid phase as shown by the experimental data, were still predicted to be part of the wax by the model contributing thus not only to a poor description of the solid phase composition but also for an overestimation of the total wax content.

The new version of the UNIQUAC model proposed in a previous article [1] seems to overcome, or at least strongly reduce, these problems for the two systems studied on that article. It was important to make a broad evaluation of this new solid phase model and an extensive comparison of its performance against the performance of the most successful predictive local composition models such as Wilson and modified UNIQUAC, and also to evaluate its performance at high pressures. This is what will be done in this work.

We will start by presenting the three predictive local composition models under study. The database of solid liquid equilibrium of n-alkanes in hydrocarbon solvents and of wax formation in fuels and crudes compiled is then presented. Then the three models here studied are evaluated by comparing their predic-

⁎ Corresponding author. Tel.: +351 234 401 507; fax: +351 234 370 084.
E-mail address: jcoutinho@dq.ua.pt (J.A.P. Coutinho).

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2. Wax formation modeling

The condition of equilibrium between the vapour, liquid and solid phases can be expressed in terms of equality of the fugacities for each individual component in all phases:

\[ f_v^i(T, P, x^i) = f_l^i(T, P, x^i) = f_s^i(T, P, x^i) \]  

(1)

Taking the liquid phase as the reference phase, the equilibrium ratios, \( K_v^i \) and \( K_s^i \), are defined as:

\[ K_v^i = \frac{x_i^v}{x_i^l} = \frac{\phi_i^v}{\phi_i^l} \]  

\[ K_s^i = \frac{x_i^s}{x_i^l} = \frac{\phi_i^s}{\phi_i^l} \]  

(2)

Where \( \phi_i \) are the fugacity coefficients and \( x_i \) are the mole fractions for the different phases.

2.1. Low pressure

Solid–liquid equilibrium can be described by an equation relating the composition of component \( i \) in the solid and liquid phases with their non-ideality and the thermophysical properties of the pure component [20]:

\[ \ln \frac{x_i^{\text{tot}}}{x_i^l} = \ln \left( K_i^l \right) + \frac{\Delta H_i^{\text{res}}}{RT} \left( \frac{T_{fus}}{T} - 1 \right) + \frac{\Delta H_i^{\text{tot}}}{RT} \left( \frac{T_{fus}}{T} - 1 \right) \]  

(4)

Since the crystal habit of the solid phase is orthorhombic [2–6,22–27] the properties for the even numbered chain length paraffins are obtained by interpolating the values for the odd numbered alkanes. The heats and temperatures of phase transition are obtained from correlations previously proposed [28] based on the values by Broadhurst [29]:

\[ T_{\text{fus}}(K) = 421.63 - 0.936 \times 421 \exp(-7.8945(C_{\text{at}} - 1)^{0.07744}) \]  

(5)

\[ T_{\text{fus}}(K) = 420.42 - 134.784 \exp(-4.344(C_{\text{at}} + 6.592)^{0.14627}) \]  

(6)

And

\[ \Delta_{\text{fus}}H_i (\text{kJ/mol}) = 3.7791C_{\text{at}} - 12.654 \]  

(7)

\[ \Delta_{\text{fus}}H_i (\text{kJ/mol}) = 0.0355C_{\text{at}}^2 - 0.2376C_{\text{at}}^2 \]  

\[ + 7.400C_{\text{at}} - 34.814 \]  

(8)

With

\[ \Delta_{\text{fus}}H = \Delta_{\text{fus}}H - \Delta_{\text{fus}}H \]  

where \( C_{\text{at}} \) is the number of carbon atoms in n-alkane \( i \). These equations are valid from pentane to n-alkanes larger than n-C\text{\textsubscript{10}}H\textsubscript{22} for the melting temperatures, \( T_{\text{fus}} \), and total heats of melting, \( \Delta_{\text{fus}}H \). The solid phase transitions occur for n-alkanes between n-C\textsubscript{10}H\textsubscript{22} and n-C\textsubscript{14}H\textsubscript{29} inclusive.

From Eq. (4), using a multiphase flash algorithm, the composition and the amount of the phases in the equilibrium can be calculated if a model for the non-ideality of the solid and liquid phases is available.

2.2. 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. (2) 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. (3) will be obtained from Eq. (4) corrected for the pressure by the Poynting correction [30].

2.5. The liquid phase activity coefficient

In liquid hydrocarbon mixtures, the non-ideality arises both from entropic effects, such as size difference and free volume effects, and energetic interactions between unlike molecules as aromatics and aliphatics. At low pressure the non-ideality of the liquid phase can be described by an activity coefficient model:

\[ \ln y = \ln y^\text{pos} + \ln y^\text{comb} - \text{iv} \]  

(10)

Where \( \ln y^\text{pos} \) is given by modified UNIFAC [31] and describes the energetic interactions between the aromatic and aliphatic molecules. The combinational and free volume effects resulting from the size difference between the molecules will be here described by the Flory–free volume model [32]:

\[ \ln y^\text{comb} - \text{iv} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \]  

(11)

With \( \phi_i = \frac{\sum_i V_i (V_i - \phi_i V_i)}{V_m (V_m - \phi_i V_i)} \)

Where \( V_i \) is the molar volume and \( V_m \) is the van der Waals volume of component \( i \).

2.4. The solid phase non-ideality—predictive local composition models

The solid phase non-ideality will be described by Wilson [2,3,33] and the two versions of UNIQUAC [1,5,6,34].
The Wilson equation used in this work can be written as

\[ \frac{RT}{P} = \sum_{i=1}^{n} x_i \left[ \sum_{j=1}^{n} \frac{x_j (\lambda_{ij} - \lambda_{ji})}{RT} \right] \]  

(12)

and the UNIQUAC model as

\[ \frac{RT}{P} = \sum_{i=1}^{n} x_i \ln \left( \frac{\Phi_i}{\theta_i} \right) + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} q_{ij} \ln \left( \frac{\Phi_j}{\theta_j} \right) \]  

(13)

with

\[ \Phi_i = \frac{x_i \lambda_i}{\sum_{i=1}^{n} x_i \lambda_i} \]  

(14)

where \( z \) is the coordination number. A value of the coordination number of 6 will be used for the Wilson \([2,3,28]\) and modified UNIQUAC \([5,6,28]\) and consequently named modified UNIQUAC. \( r \) and \( q \), obtained directly from the UNIFAC parameter table \([34]\), and is subsequently named modified UNIQUAC.

\[ r = \frac{\rho_{\text{org}}}{\rho} = 0.1C_{\text{org}} + 0.0672 \]  

(15)

\[ q = \frac{\rho_{\text{org}}}{\rho} = 0.1C_{\text{org}} + 0.1141 \]  

(16)

The predictive local composition concept \([1–6]\) allows the estimation of the interaction energies, \( \lambda_{ij} \), used by these models without fitting to experimental data. The pair interaction energies between two identical molecules are estimated from the heat of sublimation of an orthorhombic crystal of the pure component:

\[ \lambda_{ii} = \frac{2}{\sqrt{3}} (\Delta_{\text{sub}} H - RT) \]  

(17)

where \( Z \) is the coordination number. A value of the coordination number of 6 will be used for the Wilson \([2,3,28]\) and modified UNIQUAC \([5,6,28]\) and for UNIQUAC \([31,34]\). The heats of sublimation, \( \Delta_{\text{sub}} H = \Delta_{\text{fus}} H + \Delta_{\text{vap}} H + \Delta_{\text{t2}} H \), are calculated at the melting temperature of the pure component. The heat of sublimation, \( \Delta_{\text{sub}} H \), is assessed using a correlation by Morgan and Kobayashi \([35]\) and the heats of phase transition are obtained from the correlations presented above.

The pair interaction energy between two non-identical molecules is given by

\[ \lambda_{ij} = \lambda_{ji} \]  

(18)

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

2.5. Liquid phase fugacity

The evaluation of liquid and vapour fugacity coefficients under high pressure requires the use of an equation of state (EOS). Since the non-ideality of liquid solutions made up of asymmetric components is well described with an excess Gibbs energy model at atmospheric pressure \([1–19]\), a mixing rule which combines an equation of state with a \( G^E \) expression is used to describe the fugacity in the fluid phases.

Among the various EOS/GE mixing rules available the LCVM \([36]\) was chosen because it yields a good prediction of high-pressure vapour-liquid equilibrium of asymmetric light/heavy hydrocarbons systems \([37]\). Due to the superior description of the pure compounds fugacities the equation of state SRK corrected with the volume translation of Peneloux et al. \([38]\) was used:

\[ P = \frac{RT}{V - b} - \frac{a}{V(V + b)} \]  

(19)

For mixtures, the linear mixing rule is kept for the parameter \( b \):

\[ b = \sum x_i b_i \]  

(20)

Whereas for the \( a \) parameter the LCVM mixing rule is used:

\[ a = \left( \frac{a}{RT} \right)_A \left( \frac{a}{RT} \right)_B \left( 1 + \frac{1 - \lambda}{A_m} \right) \left( \frac{G^E}{RT} \right) + \frac{1 - \lambda}{A_m} \frac{x_i x_j}{x_i} + \sum x_i \theta_i \]  

(21)

Here \( A_m, A_i, A_j \), and \( \lambda \) are constant. The excess Gibbs free energy \( G^E \) of the liquid mixture is calculated using the modified UNIFAC group contribution method \([31]\).

Table 1: Low pressure data used in model evaluation

<table>
<thead>
<tr>
<th>System</th>
<th>Solvent</th>
<th>Solutes</th>
<th>Temperature range (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol VI</td>
<td>Ethylbenzene</td>
<td>C14–C16</td>
<td>–8 to 10</td>
<td>[4]</td>
</tr>
<tr>
<td>Sol VII</td>
<td>Ethylbenzene</td>
<td>C14–C30</td>
<td>–5 to 9</td>
<td>[4]</td>
</tr>
<tr>
<td>Mix A</td>
<td>Decane</td>
<td>C14–C30</td>
<td>–5 to 18</td>
<td>[40]</td>
</tr>
<tr>
<td>Mix B</td>
<td>Decane</td>
<td>C14–C30</td>
<td>–5 to 20</td>
<td>[40]</td>
</tr>
<tr>
<td>Mix C</td>
<td>Decane</td>
<td>C14–C30</td>
<td>–5 to 20</td>
<td>[40]</td>
</tr>
<tr>
<td>Bin 0</td>
<td>Decane</td>
<td>C14–C30</td>
<td>–10 to 30</td>
<td>[7]</td>
</tr>
<tr>
<td>Bin 1</td>
<td>Decane</td>
<td>C14–C30, C32–C36</td>
<td>–10 to 32</td>
<td>[7]</td>
</tr>
<tr>
<td>Bin 2</td>
<td>Decane</td>
<td>C14–C30, C32–C36</td>
<td>–10 to 33</td>
<td>[7]</td>
</tr>
<tr>
<td>Bin 9</td>
<td>Decane</td>
<td>C14–C30, C32–C36</td>
<td>–10 to 34</td>
<td>[7]</td>
</tr>
<tr>
<td>Bin 13</td>
<td>Decane</td>
<td>C14–C30, C32–C36</td>
<td>–10 to 35</td>
<td>[7]</td>
</tr>
<tr>
<td>CD6–36</td>
<td>C14–C30</td>
<td>C14–C30</td>
<td>–17 to 17</td>
<td>[13]</td>
</tr>
<tr>
<td>Mix 1</td>
<td>Decane</td>
<td>C14–C30</td>
<td>5–28</td>
<td>[19]</td>
</tr>
<tr>
<td>Mix 2</td>
<td>Decane</td>
<td>C14–C30</td>
<td>5–28</td>
<td>[19]</td>
</tr>
<tr>
<td>Mix 3</td>
<td>Decane</td>
<td>C14–C30</td>
<td>5–28</td>
<td>[19]</td>
</tr>
<tr>
<td>Mix 4</td>
<td>Decane</td>
<td>C14–C30</td>
<td>5–28</td>
<td>[19]</td>
</tr>
<tr>
<td>Mix 5</td>
<td>Decane</td>
<td>C14–C30</td>
<td>5–39</td>
<td>[19]</td>
</tr>
<tr>
<td>Mix 6</td>
<td>Ethylbenzene</td>
<td>C14–C13</td>
<td>–9 to 1</td>
<td>[1]</td>
</tr>
<tr>
<td>Mix 7</td>
<td>Ethylbenzene</td>
<td>C14–C13</td>
<td>2 to 20</td>
<td>[1]</td>
</tr>
<tr>
<td>Dextol S</td>
<td>Decane</td>
<td>C14–C30</td>
<td>–23 to –5</td>
<td>[8]</td>
</tr>
<tr>
<td>Dextol NS</td>
<td>Decane</td>
<td>C14–C30</td>
<td>–23 to –5</td>
<td>[8]</td>
</tr>
<tr>
<td>Oils 1–17</td>
<td>Decane</td>
<td>C14–C30</td>
<td>0–50</td>
<td>[39]</td>
</tr>
</tbody>
</table>
2.6. Solid phase fugacity

The equilibrium constant for the solid phase is given by [30]

\[
\ln K_s = \frac{\phi(P)}{\phi(P_0)} \left( \frac{P}{P_0} \right)^{-\beta} = \frac{RT}{\Delta l} \ln \left( \frac{T}{T_0} \right) - \frac{\Delta l}{RT} + \frac{\Delta H_i}{RT} \frac{B_{m,i}}{B_{m,0}} - 1
\]

where \( \beta = 0.9 \) is the ratio between the solid and liquid molar volumes of \( n \)-alkanes [30], and the Peneloux volume corrections, \( C_i \), are introduced to improve the description of the liquid densities [30]. The fugacities of the liquid phase are obtained by the UNIQUAC

The solid content deviations (AAD) are calculated for each system and are shown in Table 5.

Table 5

<table>
<thead>
<tr>
<th>System</th>
<th>Wilson</th>
<th>Modified UNIQUAC</th>
<th>UNIQUAC</th>
<th>Data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol VI</td>
<td>2.844</td>
<td>0.645</td>
<td>1.453</td>
<td>9</td>
</tr>
<tr>
<td>Sol VII</td>
<td>0.914</td>
<td>1.537</td>
<td>0.634</td>
<td>8</td>
</tr>
<tr>
<td>Mix A</td>
<td>2.089</td>
<td>2.463</td>
<td>1.949</td>
<td>6</td>
</tr>
<tr>
<td>Mix B</td>
<td>2.591</td>
<td>1.032</td>
<td>0.811</td>
<td>6</td>
</tr>
<tr>
<td>Mix C</td>
<td>2.392</td>
<td>1.546</td>
<td>1.215</td>
<td>6</td>
</tr>
<tr>
<td>Bim 0</td>
<td>3.687</td>
<td>0.631</td>
<td>0.333</td>
<td>7</td>
</tr>
<tr>
<td>Bim 3</td>
<td>2.595</td>
<td>0.986</td>
<td>0.724</td>
<td>6</td>
</tr>
<tr>
<td>Bim 5</td>
<td>2.907</td>
<td>0.921</td>
<td>0.684</td>
<td>7</td>
</tr>
<tr>
<td>Bim 9</td>
<td>1.844</td>
<td>0.827</td>
<td>0.697</td>
<td>9</td>
</tr>
<tr>
<td>Bim 13</td>
<td>0.9968</td>
<td>0.7748</td>
<td>0.238</td>
<td>6</td>
</tr>
<tr>
<td>CD6–36</td>
<td>2.061</td>
<td>0.346</td>
<td>0.501</td>
<td>5</td>
</tr>
<tr>
<td>Mix 1</td>
<td>1.6793</td>
<td>2.387</td>
<td>1.105</td>
<td>6</td>
</tr>
<tr>
<td>Mix 2</td>
<td>1.538</td>
<td>5.019</td>
<td>2.535</td>
<td>6</td>
</tr>
<tr>
<td>Mix 3</td>
<td>0.862</td>
<td>1.661</td>
<td>0.706</td>
<td>6</td>
</tr>
<tr>
<td>Mix 4</td>
<td>1.234</td>
<td>1.480</td>
<td>1.148</td>
<td>6</td>
</tr>
<tr>
<td>Mix 5</td>
<td>0.666</td>
<td>1.491</td>
<td>0.377</td>
<td>6</td>
</tr>
<tr>
<td>Mix A*</td>
<td>0.668</td>
<td>0.906</td>
<td>0.655</td>
<td>8</td>
</tr>
<tr>
<td>Mix B*</td>
<td>0.481</td>
<td>1.063</td>
<td>0.289</td>
<td>9</td>
</tr>
<tr>
<td>Diesel S</td>
<td>6.772</td>
<td>2.341</td>
<td>2.691</td>
<td>4</td>
</tr>
<tr>
<td>Diesel NS</td>
<td>7.104</td>
<td>1.729</td>
<td>1.847</td>
<td>6</td>
</tr>
</tbody>
</table>

Average deviation 2.432 1.490 1.050

3. Database of equilibrium data

3.1. Low pressure

An evaluation of model can only be performed on reliable data for well-defined systems. Wax formation data are scarce in the literature and most data available concerns real systems such as fuels and crude that have compositions poorly characterized and the equilibrium data usually reduces to the crystallization temperature and the molar volume of the liquid phase.
point, usually named cloud point or WAT (wax appearance temperature). For crudes the only data set with some equilibrium data below the WAT, in spite of the limited compositional characterization, is the study for a number of crudes presented by Rønningsen et al. [39]. It has been used as benchmark by most wax formation models. Here predictions by the studied models will be compared against these data. All the other data available has been measured by the authors in previous stages of their studies in wax formation during the last 10 years. Most data concerns synthetic mixtures with well-defined composition and of variable complexity. Data sets range from binaries and ternaries in a solvent up to mixtures of 10–30 n-alkanes. Besides these well-defined systems, data for two diesels previously studied by the authors were also used. The low pressure data used in this model evaluation is reported in Table 1. For the high pressures the data used is summarized in Table 2.

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**Fig. 1.** Model results for the solid phase composition of a mixture of n-alkanes between C6 and C36 [13] at four different temperatures. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

**Fig. 2.** Model results for the solid phase composition of n-alkanes for Diesel NS [8]. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.
4. Discussion of results

4.1. Low pressure results

Predictions by the three models studied were compared against the experimental data for the defined systems presented in Table 1. Average absolute deviations, defined as

\[ AAD = \frac{1}{N} \sum_{i=1}^{N} |X_{\text{exp}} - X_{\text{clc}}| \]  

where \( N \) are the number of experimental data points and \( X \) is the property under evaluation, are presented in Tables 3–5.

Fig. 3. Model results for some of the Rønningsen oils [39]. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.
Table 3 reports the deviations for the liquid phase composition, Table 4 for the solid phase composition, and Table 5 for the solid content.

The results suggest that Wilson provides a better description of the experimental data than modified UNIQUAC for the systems with a number of \( n \)-alkanes lower than 6 such as Mix 1–5, Mix A*, Mix B* and Bim 13. Sol I–V from Ref. [4] although not presented here also display a similar behavior. For the other more complex systems, with a larger number of \( n \)-alkanes, the description of modified UNIQUAC is consistently better than Wilson. This was one of the limitations of the models previously proposed. The UNIQUAC model seems to overcome this problem providing a consistent description of both simple and complex systems. It provides a lower deviation than Wilson for simple systems and also a better description of complex systems than modified UNIQUAC.

Another problem with the Wilson and modified UNIQUAC models was the overestimation of the precipitation of the light paraffins in the solid phase predicting their precipitation at higher temperatures above the experimental and in higher quantities than experimentally observed. The UNIQUAC model severely reduces this problem as shown in Fig. 1 for the mixture ‘CD6–36’ [13] where the solid phase composition is presented at four temperatures using the three models. Both Wilson and modified UNIQUAC overestimate the solid phase composition of the light \( n \)-alkanes leading to important deviations to the experimental data. This is particularly important at temperatures removed from the cloud point. The UNIQUAC model, although still displaying some overestimation of the light \( n \)-alkanes precipitation for the lower temperatures, produces a much superior description of the experimental solid phase composition that for most cases is within the experimental uncertainty.

The UNIQUAC model seems to be superior to both Wilson and modified UNIQUAC. These models present global average deviations 50% larger for the liquid phase and at least twice as larger for the solid composition and solid content than UNIQUAC for the well-defined systems studied.
Fig. 6. Model results for the solid phase composition of a mixture of \( n \)-alkanes between C6 and C36 [13] at different conditions of \( T \) and \( P \). Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

The models had their behavior also compared for real systems. For this purpose two diesels [8] and the crudes by Rønningsen et al. [39] were used. For the diesels the \( n \)-alkane composition was well-known but not the non-\( n \)-alkane fraction that acts as solvent. For the crudes no detailed compositional information was available and the generation of a \( n \)-alkane distribution following an approach previously suggested [14] was done. For the diesels the deviations are presented in Tables 3–5. The deviations of UNIQUAC are roughly half of those presented by Wilson and two thirds of those from modified UNIQUAC.

The results presented for the solid phase composition of four \( n \)-alkanes of diesel NS in Fig. 2 clearly display the advantages of the UNIQUAC model over the two other models providing a superior description of the composition of the four \( n \)-alkanes in the entire temperature range studied.

Concerning the crudes no deviations are presented since both the uncertainties related to the composition of the fluid and the

Fig. 7. Model results for the amount of solid deposit (wt.%) vs. the pressure for a Diesel NS [8] at \(-10^\circ\) C. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.
experimental data itself are too important. Results are presented for eight of the crudes in Fig. 3. The two UNIQUAC models present similar results for the amount of precipitated wax and are essentially equivalent. Both provide a description of the experimental data much superior to the Wilson model that overestimates the total wax precipitating from the crudes.

4.2. High pressure results

Predictions by the three models under investigation were compared against the experimental high pressure data for a selection of systems reported in Table 2. Results for these systems are presented in Figs. 4–9.

The conclusions reached for the modeling at atmospheric pressure also apply at high pressure. Concerning the composition of the solid phase versus the pressure we can notice that both Wilson and modified UNIQUAC approaches overestimate systematically the quantity of the lightest alkanes on the solid phase. This problem leads to very important deviations in the representation of the solid phase composition in all the range of pressure as shown in Figs. 4, 6 and 8. On the other hand the UNIQUAC model seems to be more efficient in the simulation of the lightest paraffin leading to a good description of the solid phase composition for all the studied systems.

The Wilson and modified UNIQUAC models also predict a higher amount of solid deposit versus the pressure than the experimentally observed as shown in Figs. 5 and 7. This situation, which was one of major problems of the initial model developed by Pauly et al. [30], seems to be solved by using the predictive UNIQUAC model here proposed. Moreover the slope of the deposition curve versus pressure which was already perfectly described is not affected by changing the $G^e$ model used for description of the non-ideality of the solid phase.

5. Conclusions

The predictive UNIQUAC model here proposed is shown to be superior than the other predictive local composition models...
previously proposed, with a prediction of the SLE data for well-defined synthetic mixtures within the experimental uncertainty. It is shown that this model can also be applied at high pressures using the approach previously proposed by us with similar good results. The model is also here applied to real systems of diesels and crudes producing an excellent prediction of the experimental data.

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References