



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

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Received 14 March 2006; received in revised form 5 June 2006; accepted 6 June 2006

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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Keywords: Wax; UNIQUAC; Solid–liquid equilibria; High pressure; Diesel; Crude

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-

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tions against the experimental data at atmospheric pressure. The results obtained will be discussed and conclusions will be drawn concerning the advantages of the new UNIQUAC based model for the prediction of wax formation in low-pressure synthetic and real systems.

Finally we will show that the model can be successfully extended to the description of wax formation under high pressures.

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:

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

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

$$K_i^v = \frac{x_i^v}{x_i^l} = \frac{\phi_i^l(P)}{\phi_i^v(P)} \quad (2)$$

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

where ϕ_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]:

$$\ln \frac{x_i^s \gamma_i^s}{x_i^l \gamma_i^l} = \ln \left(K_i^s \frac{\gamma_i^s}{\gamma_i^l} \right) = \frac{\Delta_{\text{fus}} H_i}{RT_{\text{fus},i}} \left(\frac{T_{\text{fus},i}}{T} - 1 \right) + \frac{\Delta_{\text{l2}} H_i}{RT_{\text{l2},i}} \left(\frac{T_{\text{l2},i}}{T} - 1 \right) \quad (4)$$

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]:

$$T_{\text{fus},i} \text{ (K)} = 421.63 - 1,936,412 \exp(-7.8945(C_{ni} - 1)^{0.07194}) \quad (5)$$

$$T_{\text{l2},i} \text{ (K)} = 420.42 - 134,784 \exp(-4.344(C_{ni} + 6.592)^{0.14627}) \quad (6)$$

and

$$\Delta_{\text{tot}} H_i \text{ (kJ/mol)} = 3.7791 C_{ni} - 12.654 \quad (7)$$

$$\Delta_{\text{tot}} H_i \text{ (kJ/mol)} = 0.00355 C_{ni}^3 - 0.2376 C_{ni}^2 + 7.400 C_{ni} - 34.814 \quad (8)$$

with

$$\Delta_{\text{l2}} H = \Delta_{\text{tot}} H - \Delta_{\text{fus}} H \quad (9)$$

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, $T_{\text{fus},i}$, and total heats of melting, $\Delta_{\text{tot}} H$. The solid phase transitions occur for n -alkanes between n -C₉H₂₀ and n -C₄₁H₈₄ inclusive.

From Eq. (4), using a multiphase flash algorithm, the composition and the amount of the phases in 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].

2.3. 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:

$$\ln \gamma = \ln \gamma^{\text{res}} + \ln \gamma^{\text{comb-fv}} \quad (10)$$

where $\ln \gamma^{\text{res}}$ 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]:

$$\ln \gamma_i^{\text{comb-fv}} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i}, \quad (11)$$

$$\text{with } \phi_i = \frac{x_i (V_i^{1/3} - V_{wi}^{1/3})^{3.3}}{\sum_j x_j (V_j^{1/3} - V_{wj}^{1/3})^{3.3}}$$

where V_i is the molar volume and V_{wi} 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

$$\frac{g^E}{RT} = -\sum_{i=1}^m x_i \ln \left[\sum_{j=1}^m x_j \exp \left(\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \right] \quad (12)$$

and the UNIQUAC model as

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[\sum_{j=1}^n \theta_j \exp \left(-\frac{\lambda_{ij} - \lambda_{ii}}{q_i RT} \right) \right] \quad (13)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (14)$$

Two versions of the UNIQUAC model will be compared in this work. The first version has structural parameters, $r_{i\text{org}}$ and $q_{i\text{org}}$, obtained directly from the UNIFAC parameter table [34], and is hereafter named UNIQUAC, the second version uses the definition of the structural parameters r and q previously proposed [5,6,28], and is subsequently named modified UNIQUAC:

$$r_i = \frac{r_{i\text{org}}}{6.744} = 0.1 C_{ni} + 0.0672 \quad (15)$$

$$q_i = \frac{q_{i\text{org}}}{5.40} = 0.1 C_{ni} + 0.1141 \quad (16)$$

The predictive local composition concept [1–6] allows the estimation of the interaction energies, λ_{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:

$$\lambda_{ii} = -\frac{2}{Z} (\Delta_{\text{sub}} H_i - RT) \quad (17)$$

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 10 for UNIQUAC [31,34]. The heats of sublimation, $\Delta_{\text{sub}} H = \Delta_{\text{vap}} H + \Delta_{\text{fus}} H + \Delta_{\text{t}2} H$, are calculated at the melting temperature of the pure component. The heat of vaporisation, $\Delta_{\text{vap}} H$, 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

$$\lambda_{ij} = \lambda_{ji} = \lambda_{jj} \quad (18)$$

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

The solid–liquid equilibrium model is thus a purely predictive model that uses in the calculation of the phase behavior only pure component properties. The three models here evaluated will be used to predict phase equilibrium for a number of systems previously presented in the literature. Both data for synthetic, well-defined, fluids as well as data for real fluids such as diesels and crudes will be used to compare the performances of these three models.

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:

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)} \quad (19)$$

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

$$b = \sum_i x_i b_i \quad (20)$$

Whereas for the a parameter the LCVm mixing rule is used:

$$\alpha = \left(\frac{a}{bRT} \right) = \left(\frac{\lambda}{A_v} + \frac{1-\lambda}{A_m} \right) \left(\frac{G^E}{RT} \right) + \frac{1-\lambda}{A_m} \sum_i x_i \ln \left(\frac{b}{b_i} \right) + \sum_i x_i \alpha_i \quad (21)$$

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 [31].

Table 1
Low pressure data used in model evaluation

System	Solvent	Solutes	Temperature range (°C)	Reference
Sol VI	Ethylbenzene	C ₁₉ –C ₂₈	–8 to 10	[4]
Sol VII	Ethylbenzene	C ₁₉ –C ₂₈ , fluorene	–5 to 9	[4]
Mix A	Decane	C ₂₀ –C ₃₀	–5 to 18	[40]
Mix B	Decane	C ₁₈ –C ₃₀	–5 to 20	[40]
Mix C	Decane	C ₁₈ –C ₂₇	–5 to 20	[40]
Bim 0	Decane	C ₁₈ –C ₃₆	–10 to 30	[7]
Bim 3	Decane	C ₁₈ –C ₂₅ , C ₂₉ –C ₃₆	–10 to 32	[7]
Bim 5	Decane	C ₁₈ –C ₂₄ , C ₃₀ –C ₃₆	–10 to 33	[7]
Bim 9	Decane	C ₁₈ –C ₂₂ , C ₃₂ –C ₃₆	–10 to 34	[7]
Bim 13	Decane	C ₁₈ –C ₂₀ , C ₃₄ –C ₃₆	–10 to 35	[7]
CD6–36	C ₆ –C ₃₆	C ₆ –C ₃₆	–17 to 17	[13]
Mix 1	Decane	C ₂₅ –C ₂₆	5–28	[19]
Mix 2	Decane	C ₂₅ –C ₂₆	19–29	[19]
Mix 3	Decane	C ₂₅ –C ₂₆	8–28	[19]
Mix 4	Decane	C ₂₅ –C ₂₆	5–28	[19]
Mix 5	Decane	C ₂₅ –C ₂₆	0–30	[19]
Mix A*	Ethylbenzene	C ₁₈ –C ₂₂	–9 to 1	[1]
Mix B*	Ethylbenzene	C ₁₈ , C ₂₄ –C ₂₇	2 to 20	[1]
Diesel S		C ₁₀ –C ₃₂	–23 to –5	[8]
Diesel NS		C ₁₈ –C ₃₂	–23 to –5	[8]
Oils 1–17			0–50	[39]

Table 2
High pressure data used in model evaluation

System	Solvent	Solutes	Pressure range (MPa)	Reference
Mix B	C ₁₀	C ₁₈ –C ₃₀	0.1–50	[41]
CD6–36	C ₆ –C ₃₆	C ₆ –C ₃₆	0.1–50	[13]
Diesel NS		C ₁₀ –C ₃₂	0.1–50	[17]
MPW	C ₁₄	C ₂₀ –C ₄₂	0.1–50	[42]

Table 4
Solid phase composition deviations (AAD)

System	Wilson	Modified UNIQUAC	UNIQUAC	Data points
Sol VI	2.156	0.761	0.816	9
Sol VII	2.109	0.912	0.595	8
Mix A	0.901	2.091	0.569	6
Mix B	2.141	1.163	0.565	6
Mix C	3.807	1.836	1.098	6
Bim 0	1.630	0.990	0.425	7
Bim 3	1.544	0.903	0.442	6
Bim 5	2.469	1.369	0.516	7
Bim 9	3.310	1.588	0.551	7
Bim 13	4.056	1.802	0.390	6
CD6–36	2.265	1.007	0.467	5
Mix 1	0.683	1.286	1.006	6
Mix 2	1.204	2.218	0.952	6
Mix 3	0.683	1.283	0.614	6
Mix 4	0.825	1.416	0.568	6
Mix 5	1.205	1.625	0.965	6
Mix A*	1.950	3.000	1.256	8
Mix B*	1.416	1.988	0.984	9
Diesel S	1.843	1.357	0.848	4
Diesel NS	1.582	1.019	0.614	6
Average deviation	1.889	1.480	0.712	

2.6. Solid phase fugacity

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

$$K_i^s = \frac{\phi_i^l[P](\phi_i^{lo}[P_0])^{\beta-1}(\phi_i^{lo}[P])^{-\beta}}{\gamma_i^s[P_0]} \left(\frac{P}{P_0}\right)^{1-\beta} \times \exp \left\{ \frac{(1-\beta)C_i(P-P_0)}{RT} + \frac{\Delta_{fus}H_i}{RT_{fus,i}} \left(\frac{T_{fus,i}}{T} - 1\right) + \frac{\Delta_{12}H_i}{RT_{12,i}} \left(\frac{T_{12,i}}{T} - 1\right) \right\} \quad (22)$$

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 SRK-EOS. P_0 is the reference pressure taken as atmospheric pressure.

For the activity coefficients the three models under investigation will be used to compare their performances.

Table 3
Liquid phase composition deviations (AAD)

System	Wilson	Modified UNIQUAC	UNIQUAC	Data points
Sol VI	0.310	0.123	0.175	9
Sol VII	0.174	0.074	0.075	8
Mix A	0.228	0.198	0.152	6
Mix B	0.347	0.243	0.209	6
Mix C	0.275	0.159	0.183	6
Bim 0	0.163	0.106	0.065	7
Bim 3	0.206	0.151	0.094	6
Bim 5	0.186	0.133	0.126	7
Bim 9	0.175	0.130	0.119	7
Bim 13	0.152	0.214	0.156	6
CD6–36	0.139	0.044	0.039	5
Mix 1	0.517	0.770	0.398	6
Mix 2	0.534	0.755	0.509	6
Mix 3	0.694	1.020	0.508	6
Mix 4	1.684	1.998	1.542	6
Mix 5	0.763	1.009	0.673	6
Mix A*	0.171	0.232	0.155	8
Mix B*	0.112	0.205	0.107	9
Diesel S	0.465	0.357	0.262	4
Diesel NS	0.485	0.274	0.251	6
Average deviation	0.389	0.410	0.290	

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 crudes that have compositions poorly characterized and the equilibrium data usually reduces to the crystallization

Table 5
Solid content deviations (AAD)

System	Wilson	Modified UNIQUAC	UNIQUAC	Data points
Sol VI	2.844	0.643	1.453	9
Sol VII	0.914	1.537	0.634	8
Mix A	2.809	2.463	1.949	6
Mix B	2.591	1.032	0.811	6
Mix C	2.392	1.546	1.213	6
Bim 0	3.687	0.631	0.333	7
Bim 3	2.595	0.986	0.724	6
Bim 5	2.907	0.921	0.684	7
Bim 9	1.844	0.827	0.699	7
Bim 13	0.9868	0.7748	0.238	6
CD6–36	2.061	0.346	0.501	5
Mix 1	1.6793	2.387	1.105	6
Mix 2	3.538	5.039	2.535	6
Mix 3	0.862	1.661	0.706	6
Mix 4	1.234	1.480	1.148	6
Mix 5	0.666	1.491	0.377	6
Mix A*	0.668	0.906	0.655	8
Mix B*	0.481	1.063	0.289	9
Diesel S	6.772	2.341	2.691	4
Diesel NS	7.104	1.729	1.847	6
Average deviation	2.432	1.490	1.030	

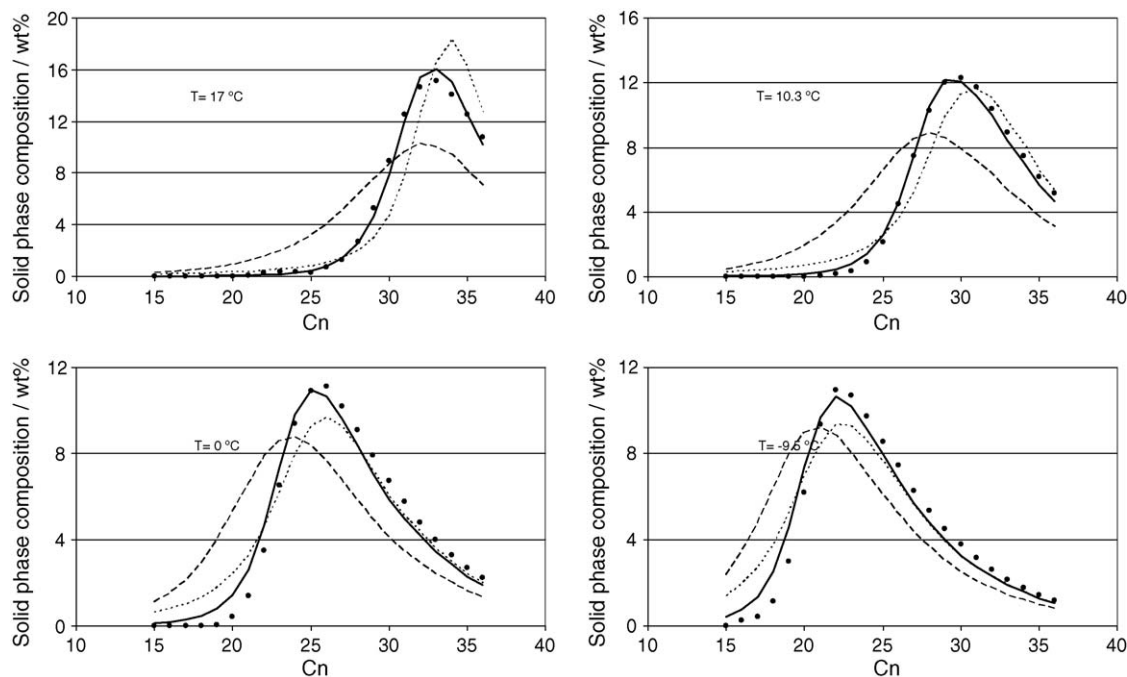


Fig. 1. Model results for the solid phase composition of a mixture of *n*-alkanes between C6 and C36 [13] at four different temperatures. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

213 point, usually named cloud point or WAT (wax appearance temper- 221
 214 ature). For crudes the only data set with some equilibrium 222
 215 data below the WAT, in spite of the limited compositional char- 223
 216 acterization, is the study for a number of crudes presented by 224
 217 Rønningsen et al. [39]. It has been used as benchmark by most 225
 218 wax formation models. Here predictions by the studied models 226
 219 will be compared against these data. All the other data available 227
 220 has been measured by the authors in previous stages of their 228

studies in wax formation during the last 10 years. Most data 221
 concerns synthetic mixtures with well-defined composition and 222
 of variable complexity. Data sets range from binaries and ternaries 223
 in a solvent up to mixtures of 10–30 *n*-alkanes. Besides these 224
 well-defined systems, data for two diesels previously studied by 225
 the authors were also used. The low pressure data used in this 226
 model evaluation is reported in Table 1. For the high pressures 227
 the data used is summarized in Table 2. 228

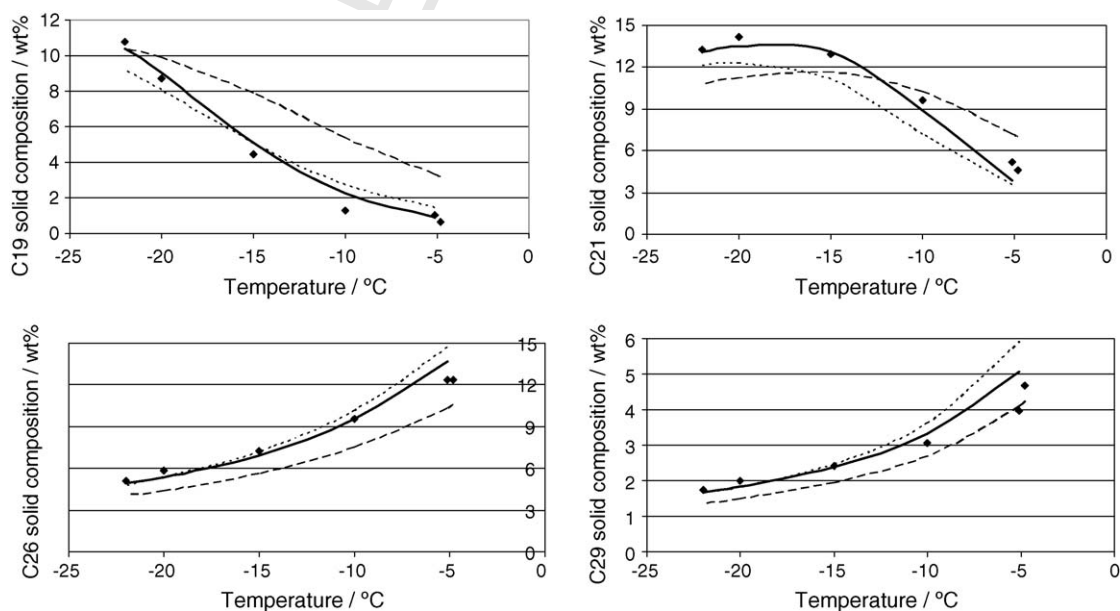


Fig. 2. Model results for the solid phase composition of *n*-alkanes for Diesel NS [8]. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

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

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^N |X_{\text{exp } i} - X_{\text{clci}}| \quad (23)$$

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

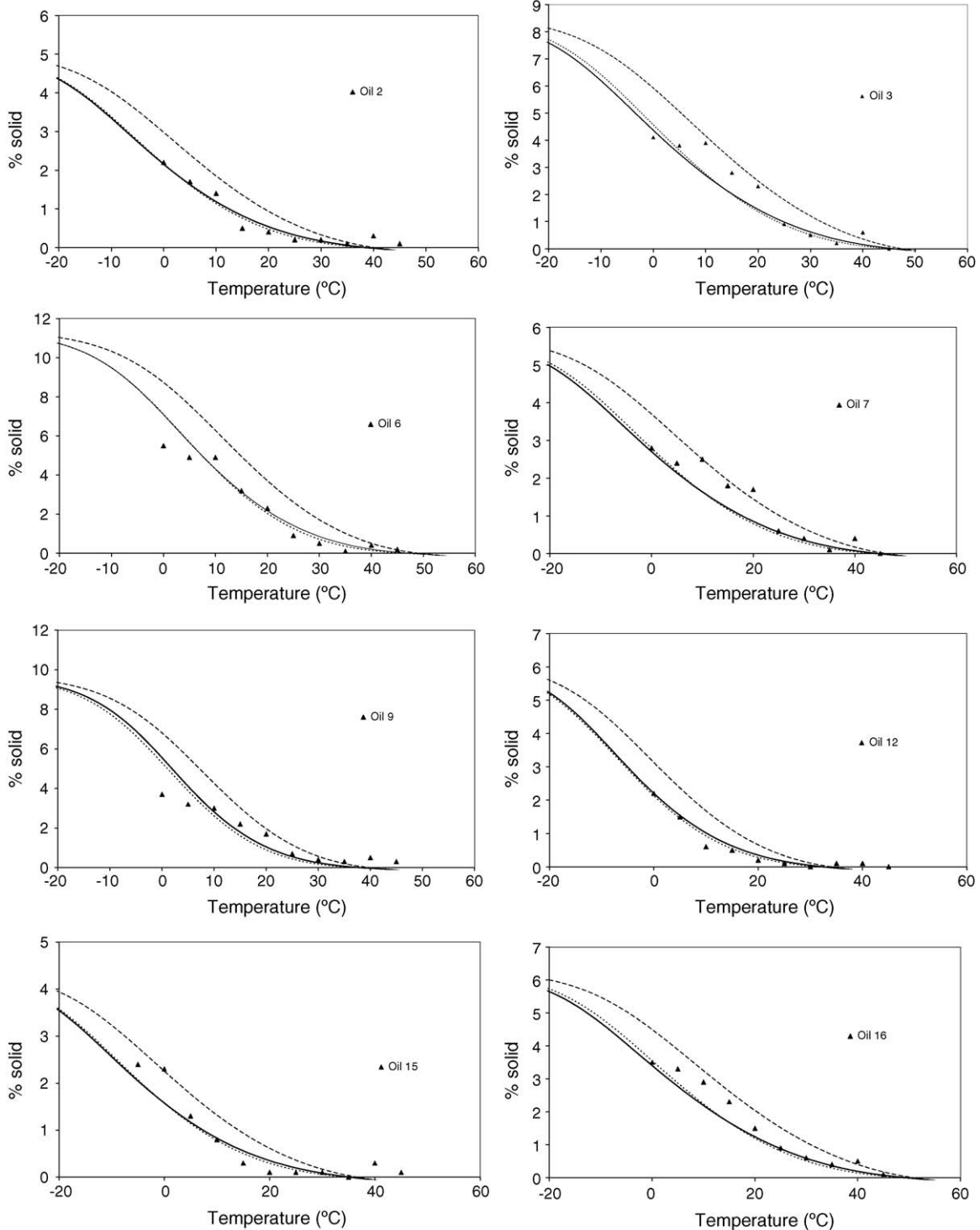


Fig. 3. Model results for some of the Rønningens oils [39]. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

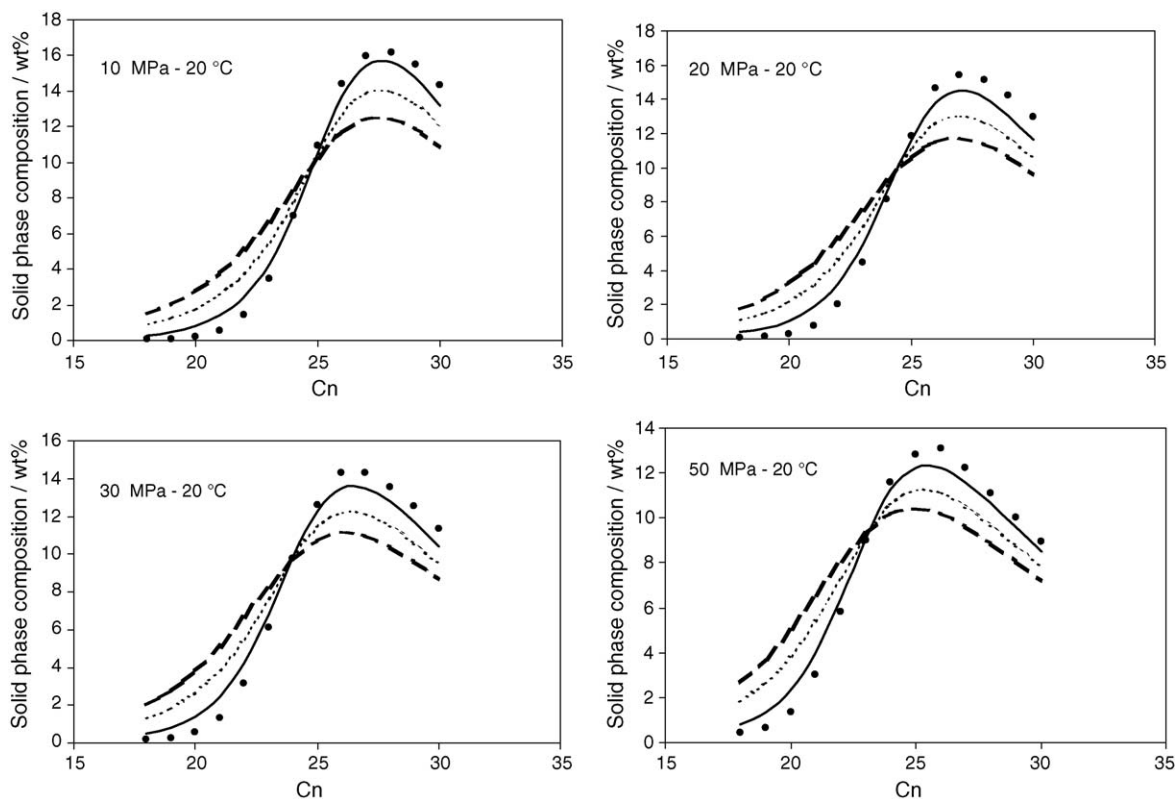


Fig. 4. Model results for the solid phase composition of a mixture of decane + *n*-alkanes between C18 and C30 [41] at four different pressures. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

238 Table 3 reports the deviations for the liquid phase composition,
 239 Table 4 for the solid phase composition, and Table 5 for the solid
 240 content.

241 The results suggest that Wilson provides a better description
 242 of the experimental data than modified UNIQUAC for the sys-
 243 tems with a number of *n*-alkanes lower than 6 such as Mix 1–5,
 244 Mix A*, Mix B* and Bim 13. Sols I–V from Ref. [4] although
 245 not presented here also display a similar behavior. For the other
 246 more complex systems, with a larger number of *n*-alkanes, the
 247 description of modified UNIQUAC is consistently better than
 248 Wilson. This was one of the limitations of the models previ-
 249 ously proposed. The UNIQUAC model seems to overcome this
 250 problem providing a consistent description of both simple and
 251 complex systems. It provides a lower deviation than Wilson for
 252 simple systems and also a better description of complex systems
 253 than modified UNIQUAC.

254 Another problem with the Wilson and modified UNIQUAC
 255 models was the overestimation of the precipitation of the light
 256 alkanes. These models underestimated the non-ideality of the
 257 light paraffins in the solid phase predicting their precipitation
 258 at higher temperatures above the experimental and in higher
 259 quantities than experimentally observed. The UNIQUAC model
 260 severely reduces this problem as shown in Fig. 1 for the mixture
 261 ‘CD6–36’ [13] where the solid phase composition is presented at
 262 four temperatures using the three models. Both Wilson and mod-
 263 ified UNIQUAC overestimate the solid phase composition of the
 264 light *n*-alkanes leading to important deviations to the experimen-
 265 tal data. This is particularly important at temperatures removed

266 from the cloud point. The UNIQUAC model, although still dis-
 267 playing some overestimation of the light *n*-alkanes precipita-
 268 tion for the lower temperatures, produces a much superior descrip-
 269 tion of the experimental solid phase composition that for most
 270 cases is within the experimental uncertainty.

271 The UNIQUAC model seems to be superior to both Wilson
 272 and modified UNIQUAC. These models present global average
 273 deviations 50% larger for the liquid phase and at least twice
 274 as larger for the solid composition and solid content than UNI-
 275 QUAC for the well-defined systems studied.

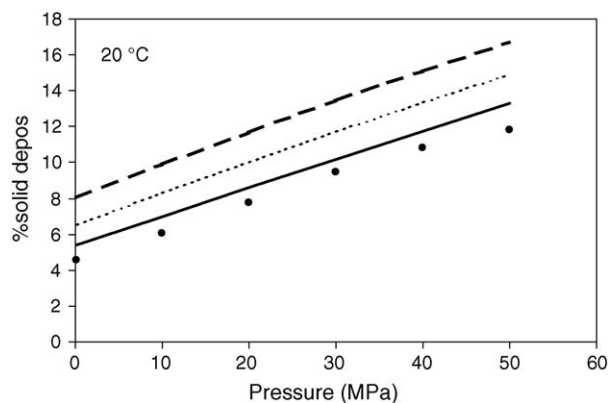


Fig. 5. Model results for the amount of solid deposit (wt.%) vs. the pressure for a mixture of decane + *n*-alkanes between C18 and C30 [41] at 20 °C. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

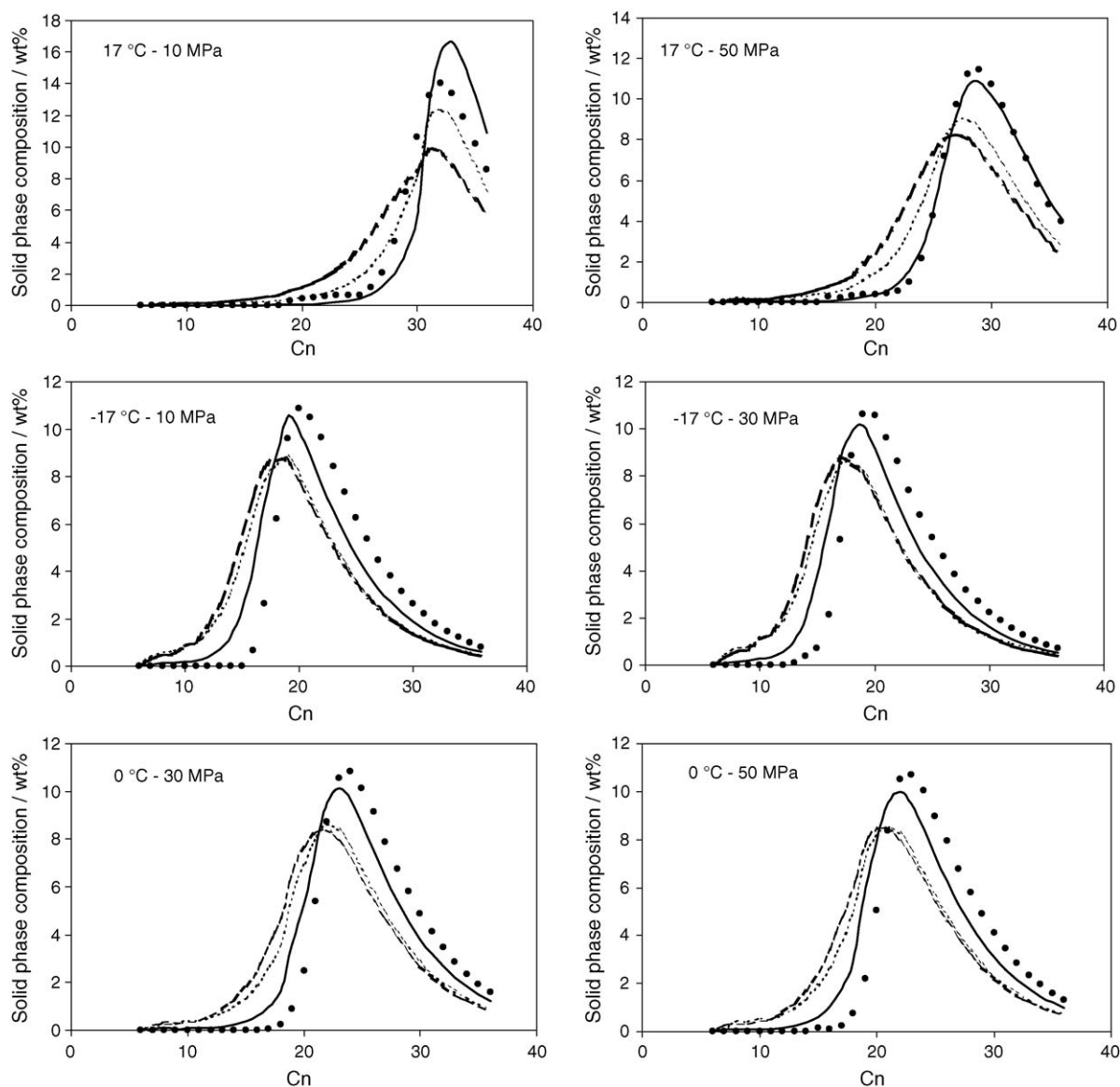


Fig. 6. Model results for the solid phase composition of a mixture of *n*-alkanes between C6 and C36 [13] at different conditions of *T* and *P*. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

276 The models had their behavior also compared for real sys-
 277 tems. For this purposed two diesels [8] and the crudes by
 278 Rønningsen et al. [39] were used. For the diesels the *n*-alkane
 279 composition was well-known but not the non-*n*-alkane fraction
 280 that acts as solvent. For the crudes no detailed compositional
 281 information was available and the generation of a *n*-alkane
 282 distribution following an approach previously suggested [14] was
 283 done. For the diesels the deviations are presented in Tables 3–5.
 284 The deviations of UNIQUAC are roughly half of those presented
 285 by Wilson and two thirds of those from modified UNIQUAC.
 286 The results presented for the solid phase composition of four
 287 *n*-alkanes of diesel NS in Fig. 2 clearly display the advantages
 288 of the UNIQUAC model over the two other models providing a
 289 superior description of the composition of the four *n*-alkanes
 290 in the entire temperature range studied.

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

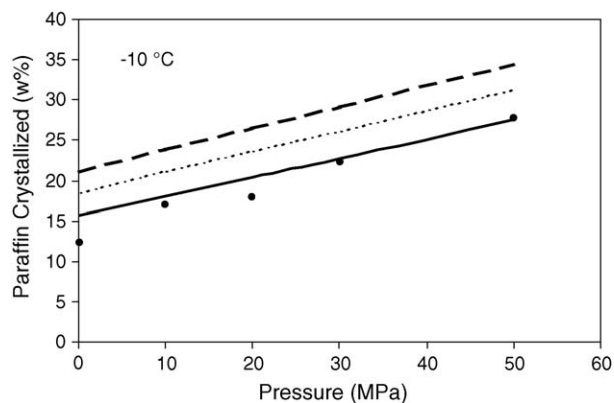


Fig. 7. Model results for the amount of solid deposit (wt.%) vs. the pressure for a Diesel NS [8] at $-10\text{ }^{\circ}\text{C}$. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

293 experimental data itself are too important. Results are presented
 294 for eight of the crudes in Fig. 3. The two UNIQUAC mod-
 295 els present similar results for the amount of precipitated wax
 296 and are essentially equivalent. Both provide a description of the
 297 experimental data much superior to the Wilson model that over-
 298 estimates the total wax precipitating from the crudes.

299 4.2. High pressure results

300 Predictions by the three models under investigation were
 301 compared against the experimental high pressure data for a selec-
 302 tion of systems reported in Table 2. Results for these systems
 303 are presented in Figs. 4–9.

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

315 The Wilson and modified UNIQUAC models also predict
 316 a higher amount of solid deposit versus the pressure than the
 317 experimentally observed as shown in Figs. 5 and 7. This situa-
 318 tion, which was one of major problems of the initial model

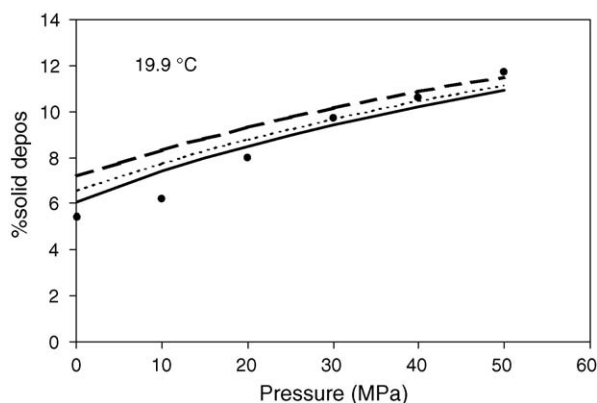


Fig. 9. Model results for the amount of solid deposit (wt.%) vs. the pressure for a multi paraffin wax (MPW) mixture with *n*-alkanes between C20 and C42 in C14 [42] at 19.9 °C. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

319 developed by Pauly et al. [30], seems to be solved by using the
 320 predictive UNIQUAC model here proposed. Moreover the slope
 321 of the deposition curve versus pressure which was already per-
 322 fectly described is not affected by changing the G^E model used
 323 for description of the non-ideality of the solid phase.

324 5. Conclusions

325 The predictive UNIQUAC model here proposed is shown to
 326 be superior than the other predictive local composition models

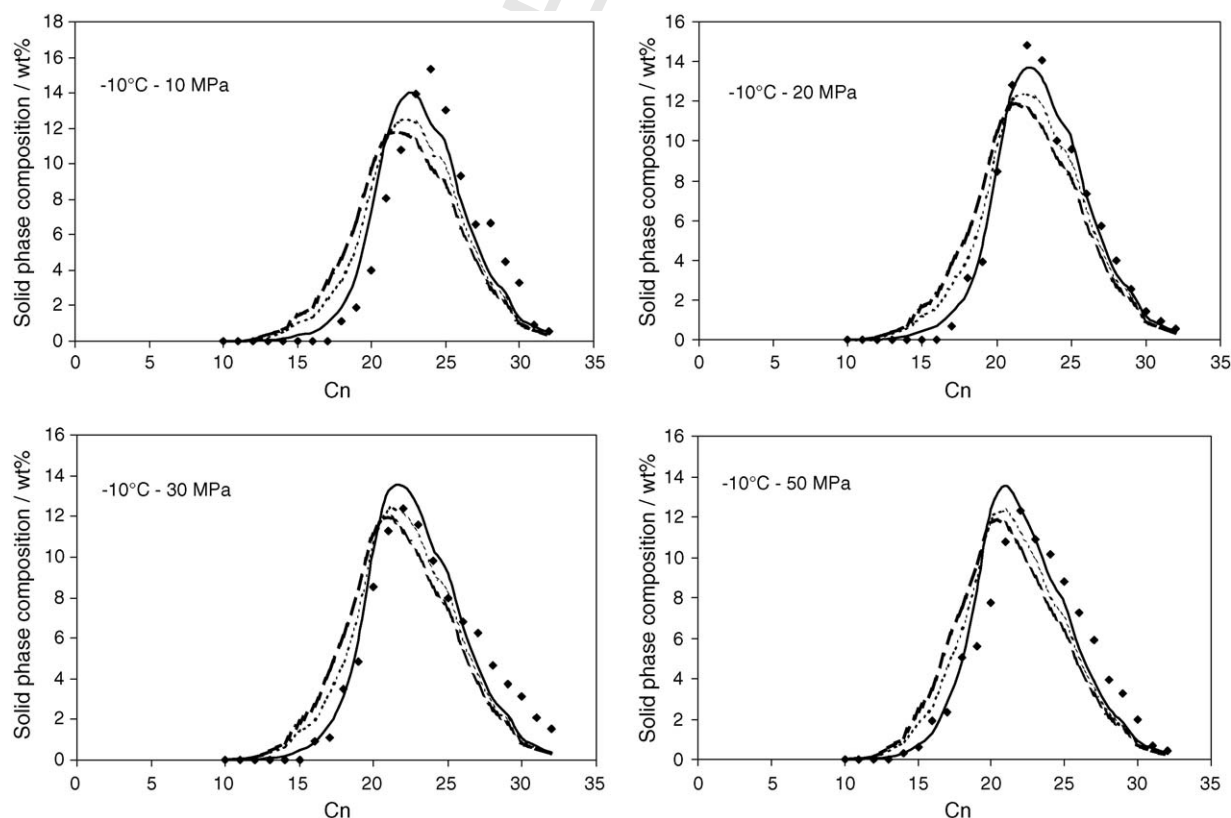


Fig. 8. Model results for the solid phase composition of the *n*-alkanes for Diesel NS [8] at four different pressures. Full line: UNIQUAC; dotted line: modified UNIQUAC; dashed line: Wilson.

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.

Uncited reference

[21].

Acknowledgment

Financial support from INTERREG IIIB, FEDER and FCT (Project POCTI/CTM/60288/2004) is gratefully acknowledged.

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