

A THERMODYNAMIC MODEL TO PREDICT WAX FORMATION IN PETROLEUM FLUIDS

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Abstract - Some years ago the authors proposed a model for the non-ideality of the solid phase, based on the Predictive Local Composition concept. This was first applied to the Wilson equation and latter extended to NRTL and UNIQUAC models. Predictive UNIQUAC proved to be extraordinarily successful in predicting the behaviour of both model and real hydrocarbon fluids at low temperatures. This work illustrates the ability of Predictive UNIQUAC in the description of the low temperature behaviour of petroleum fluids.

It will be shown that using Predictive UNIQUAC in the description of the solid phase non-ideality a complete prediction of the low temperature behaviour of synthetic paraffin solutions, fuels and crude oils is achieved. The composition of both liquid and solid phases, the amount of crystals formed and the cloud points are predicted within the accuracy of the experimental data.

The extension of Predictive UNIQUAC to high pressures, by coupling it with an EOS/G^E model based on the SRK EOS used with the LCVM mixing rule, is proposed and predictions of phase envelopes for live oils are compared with experimental data.

Keywords: Paraffins, wax deposition, solid-liquid equilibrium, thermodynamic modelling, crude oils

INTRODUCTION

Crystallisation and deposition of paraffinic waxes during production, transport and use of both crudes and refined products are responsible for losses of billions of dollars yearly to petroleum industry in prevention, maintenance and repair costs. They cause reduction of production, well shut-in, plugging of pipelines and require increased man power and extensive use of chemicals to fight the problem.

The best way to deal with this problem would be to predict its occurrence and act preventively. A reliable thermodynamic model, able to predict wax formation in a fluid submitted to a given environmental condition, using only information on the fluid composition would be a powerful tool to prevent wax formation through a more adequate design of the process and process equipment for use with potentially troublesome fluids.

Some of such models have been proposed in the last decade with different degrees of success (Won,

1986; Hansen et al., 1989, Pedersen et al., 1991; Erikson et al., 1993, Pedersen, 1995; Lira-Galeana et al., 1996). Although some of them are currently used in the oil industry (Erikson et al., 1993, Pedersen, 1995) they still aren't satisfactory. From a theoretical point of view, most of them are based on wrong hypothesis in what concerns the nature of the solid phase. Some authors assume to have one or multiple pure solid phases (Lira-Galeana et al., 1996, albeit a pseudo compound), others accepting to have solid solution treat it as an ideal solid phase (Erikson et al., 1993). Certain models consider the co-precipitation of aromatics and naphthenics adjusting accordingly the pure component thermophysical properties (Pedersen et al., 1991) and all models fail to clearly state the crystalline habit of the solid material. From the engineer point of view, all these models lack reliability and quite a number of them also do not have the predictive character that would be required. In spite of the industrial favour that some of these models have known, it is necessary an improvement of both the basic assumptions and theory behind the modelling and their predictive capabilities.

This article describes a thermodynamic model for prediction of wax formation in hydrocarbon fluids at low and high pressures.

THERMODYNAMIC MODEL

The wax is assumed to be formed just by n-alkanes crystallising from a hydrocarbon fluid as orthorhombic crystals in solid solutions (Coutinho et al., 1996; Coutinho, 1998). This is supported by experimental evidence reported on the literature (Misra et al., 1995; Chevallier et al., 2001). The algorithm of resolution of the Rachford-Rice equations applied to multiphase systems proposed by Leibovici and Neoschil (1995) was 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 phase stability analysis used was proposed by Heidemann (Abdel-Ghani et al., 1994). 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.

The thermodynamical description of wax formation is accomplished using the general solid-liquid equilibrium equation that relates the

composition in both phases with the non-ideality of the phases and the pure component thermophysical properties (Prausnitz et al., 1999):

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

The heat capacities term of this equation was found negligible and thus is not used in the modelling. The correlations used for the paraffins heat and temperature of phase transitions are based on the data by Broadhurst (1962) and derived following the Marano and Holder (1997) approach:

$$T_{fus,i} [K] = 421.63 - 1936412 \exp \exp(-7.8945(C_{ni}-1)^{0.07194}) \quad (2)$$

$$T_{t2,i} [K] = 420.42 - 134784 \exp \exp(-4.344(C_{ni}+6.592)^{0.14627}) \quad (3)$$

and

$$\Delta_{tot} H_i [kJ/mol] = 3.7791 C_{ni} - 12.654 \quad (4)$$

$$\Delta_{fus} H_i [kJ/mol] = 0.00355 C_{ni}^3 - 0.2376 C_{ni}^2 + 7.400 C_{ni} - 34.814 \quad (5)$$

with

$$\Delta_{t2} H = \Delta_{tot} H - \Delta_{fus} H \quad (6)$$

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 Liquid Phase Non Ideality

The liquid phase non-ideality is described by a version of the UNIFAC model. It can be written as:

$$\ln \gamma_i = \ln \gamma_i^{res} + \ln \gamma_i^{comb-fv} \quad (7)$$

The residual term, $\ln \gamma^{res}$, describing the energetic interactions between unlike molecules, such as aromatics and aliphatics, is given by modified UNIFAC (Fredenslund et al., 1975 and 1977; Larsen et al., 1987), while the size difference effects and free volume contributions, $\ln \gamma^{comb-fv}$, are described by the Flory-free volume equation (Coutinho et al., 1995):

$$\ln \gamma_i^{comb} = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} \quad \text{with} \quad \Phi_i = \frac{x_i S_i}{\sum_j x_j S_j} \quad (8)$$

where V_i is the molar volume and V_{wi} is the van der Waals volume of component i estimated using the Bondi method (Bondi, 1968) (or alternatively using the UNIFAC volume parameters r (Fredenslund et al., 1975)).

The Solid Phase Non Ideality - Predictive UNIQUAC

For the solid phase non-ideality the Predictive UNIQUAC model is used (Coutinho, 1998; Coutinho, 1999). This is a version of the original UNIQUAC (Abrams and Prausnitz, 1975) where

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{Z}{2} \sum_{i=1}^n q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_{i=1}^n x_i q_i \ln \left[\sum_{j=1}^n \theta_j \exp \left(-\frac{\lambda_{ij} - \lambda_{jj}}{q_i RT} \right) \right] \quad (9)$$

with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (10)$$

using a new definition for the structural parameters r and q . The correlations for the r and q values with the paraffin chain length are:

$$r_n = 0.1C_n + 0.0672 \quad (11)$$

$$q_n = 0.1C_n + 0.1141 \quad (12)$$

The core of the model is the predictive local composition concept (Coutinho et al., 1996; Coutinho and Stenby, 1996). It provides an estimation of the interaction energies values, λ_{ij} , used by these models. The pair interaction energies between two identical molecules are estimated from the heat of sublimation of an orthorhombic crystal of the pure component,

$$\lambda_{ii} = -\frac{2}{Z} (\Delta_{sub} H_i - RT) \quad (13)$$

where Z is the coordination number with a value of 6 for orthorhombic crystals. The heat of sublimation,

$\Delta_{sub} H = \Delta_{vap} H + \Delta_{fus} H + \Delta_{t2} H$, 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 (1994).

The pair interaction energy between two non-identical molecules is given by $\lambda_{ij} = \lambda_{ji}$ where j is the n -alkane with the shorter chain of the pair ij .

The thermodynamic model proposed is thus a purely predictive model, requiring for the calculation of the phase behaviour nothing but pure component properties

FLUID CHARACTERISATION

For real fluids, where generally a detailed composition is not available, a fluid characterisation is required. The model only needs a good knowledge of the paraffins composition to describe the phase behaviour of a fluid at low temperature. This can either be obtained from chromatographic measurements or generated from other sort of information. All the individual paraffins with concentrations larger than 0.05% (w/w) are considered, although less sensitivity it is required and only paraffins in concentrations higher than 0.5% (w/w) should be used if the total paraffins content is large enough (>15%). No

pseudo-components are used in the paraffins description.

All the other compounds, acting as solvent, are described by pseudo-components, their number depending on the amount of information available. If a PNA distribution is known, 2 pseudo components, one aromatic and the other naphthenic or isoparaffinic may be considered. However, since the solubility of the paraffins in aromatic or non-aromatic solvents is similar, a single pseudo-component can be used if no PNA distribution is available. The pseudo-components are chosen to match the average molecular weight of the fluid, if this is known, or some other readily available property.

RESULTS

Low Pressures

Since real petroleum fluids are rather complex, with a great deal of uncertainty about the composition and the interactions between the different chemical compounds of the mixture, they are not suited for the development of a model. Therefore, to test the thermodynamic model proposed above, complex synthetic mixtures were used to emulate the wax formation at low temperatures of real petroleum fluids.

Data for a number of these mixtures with different paraffin distributions were measured by the authors in both aromatic and aliphatic solvents (Coutinho and Ruffier-Meray, 1997; Pauly et al., 1998; Dauphin et al., 1999). The proposed model was extensively tested against experimental data and compared with the predictions of models by other authors (Pauly et al., 1998). The predictions of the proposed model were superior to all other available models for the wax appearance temperatures, fraction of solids and composition of liquid and solid phases. Results for a mixture of n-paraffins ranging between C20 and C30 in decane are presented in Fig. 1. A comparison between the model predictions and the set of data measured for one of the systems is presented in Figs. 2 to 4. The mixture has a paraffin distribution ranging from n-C18 to n-C27 and decane as solvent (Pauly et al., 1998). Typically, as shown in the figures, the model results are within the experimental uncertainty.

As discussed above no limitations are imposed on the number of solid phases estimated by the model.

Although both experimental evidence (Craig et al., 1998; Chevalier et al., 1999 and 2001) and model results indicate the presence of more than one solid phase, the experimental technique used is not able to measure the composition of each solid phase present. Only the global composition of the solid phases can be determined and it is against this data that the model results are compared.

The uncertainty that existed before the recent results by Dirand about the presence of multiple solid phases (Chevallier et al., 1999 and 2001), their composition and the ability of the model to describe them, led to a new work (Dauphin et al., 1999). Equilibrium data were measured for systems with an exponential decay continuous distribution of n-alkanes ranging from octadecane to hexatriacontane dissolved in decane in a concentration of about 35 wt%. To force the appearance of multiple solid phases some middle alkanes were taken from the heavy n-paraffin distribution thus generating from the continuous distribution named Bimodal some true bimodal distributions named Bimodal-n where n is the number of n-alkanes removed from the distribution. This produces a bimodal distribution where two distinct solid phases form. Both the temperature at which the second solid phase appears and the composition of the phases can be determined. Model results for these bimodal distributions are presented in Figs. 5 and 6. Although the experimental data are very unusual, it can be noticed that the appearance of a second solid phase is very well described both in temperature as in composition.

These results show not only that the model can well deal with multiphase behaviour but also give a good indication about its potentiality to be applied to oil or fuel blends where these bimodal distributions may occur.

The work with synthetic mixtures clearly indicates that the model can describe the wax formation in complex hydrocarbon solutions. The remaining question was about the real fluids. Whether new phenomena would arise that would make wax formation in real fluids more complicated than in the model solutions, or whether the uncertainty in compositions would create difficulties in the modelling. To answer these problems, a study of a diesel at two different moments of the production process was carried out in collaboration with Petrogal (Coutinho et al., 2000). An analytical protocol was defined to achieve a perfect quantification of the paraffins and phase equilibrium

measurements similar to those used for the model mixtures were performed. The model behaved surprisingly well. The quality of the phase behaviour description was similar to those obtained for the synthetic mixtures. Some examples are presented in Figs. 7 to 9. A confirmation of these results was obtained with the modelling of the existing literature data for a number of fuels ranging from Jet to Diesel fuels. Results for the description of the solid deposit fraction with the temperature are shown in Fig. 10 (Coutinho, 2000).

Although data available in the open literature for crude oils is scarce and often unreliable, there is a set of data by Rønningsen et al. (1991) that is rather complete in what concerns the description of the oil composition and the measurements of amount of wax forming and has been widely used to test theoretical models. Predictive UNIQUAC model was compared with the data presented by Rønningsen for the 17 different oils with excellent results for all

cases. Results for oils 6 and 16 are presented in Figures 11 and 12. Only data above 270 K was used for two reasons: first of all, the measurement of the wax content takes into account only n-alkanes above C22 (Burger et al., 1981) and thus it is not possible to incorporate in the model composition for n-alkanes lower than C22 and these start precipitating at around 270 K; moreover, comparing the Rønningsen's data for the wax formed measured by DSC (Hansen et al., 1991) and NMR (Pedersen et al., 1991) they agree well down to 270 K but seem to disagree at temperatures below that value. This may be related with the fact that the NMR was not thermostated and thus measurements at very low temperatures may be suffering from temperature gradients developing inside the cell. The quality of the prediction for these oils clearly illustrates the capabilities of the model when it comes to the description of the low temperature behaviour of crudes

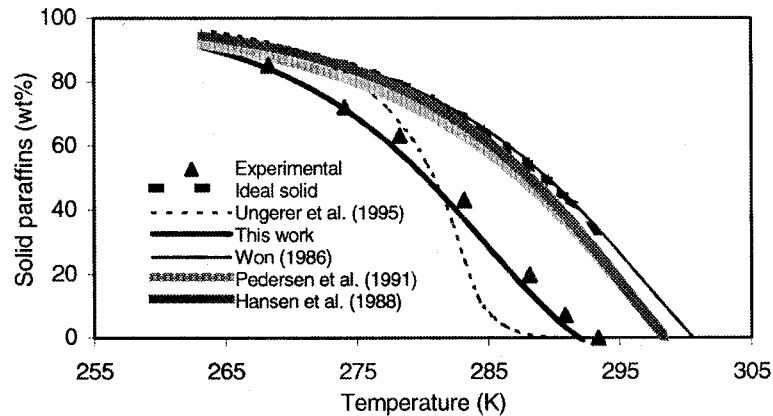


Figure 1: Comparison of the performance of Predictive UNIQUAC model (Coutinho, 1998 and 1999) with other literature models for the solid phase non-ideality.

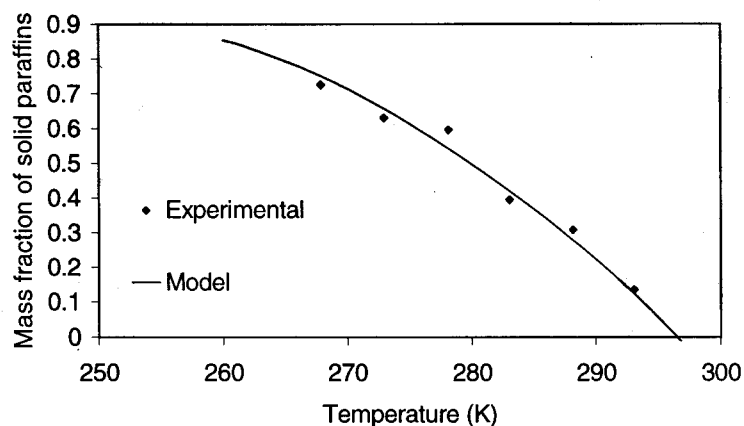


Figure 2: Experimental data and predicted results for the mass fraction of solid paraffins for mixture F (Pauly et al., 1998).

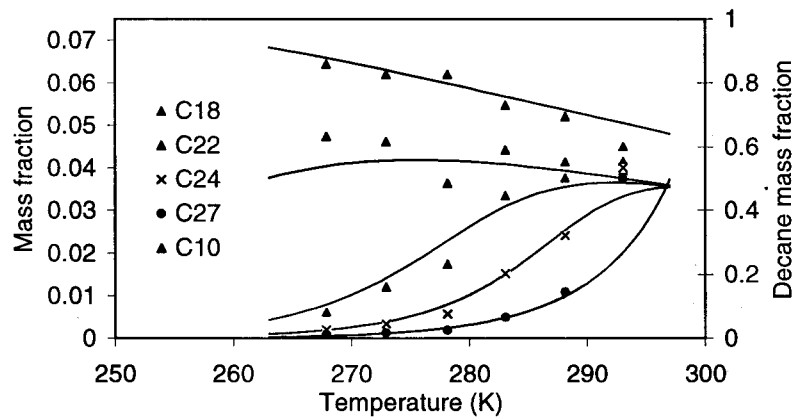


Figure 3: Experimental data and predicted results for the liquid phase composition of mixture F (Pauly et al., 1998).

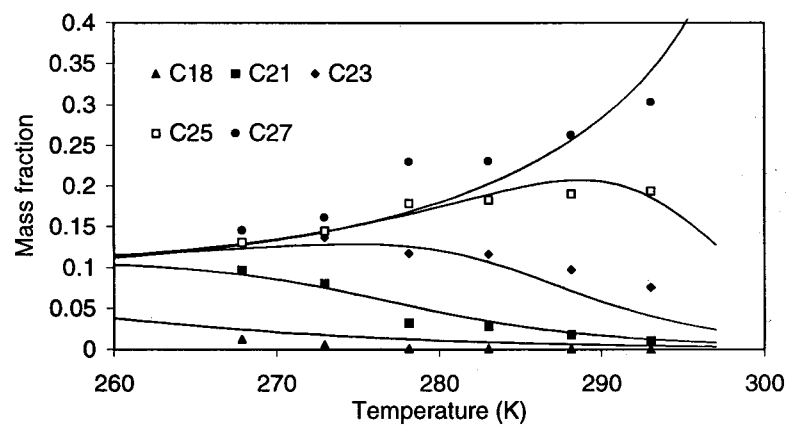


Figure 4: Experimental data and predicted results for the solid phase composition of mixture F (Pauly et al., 1998).

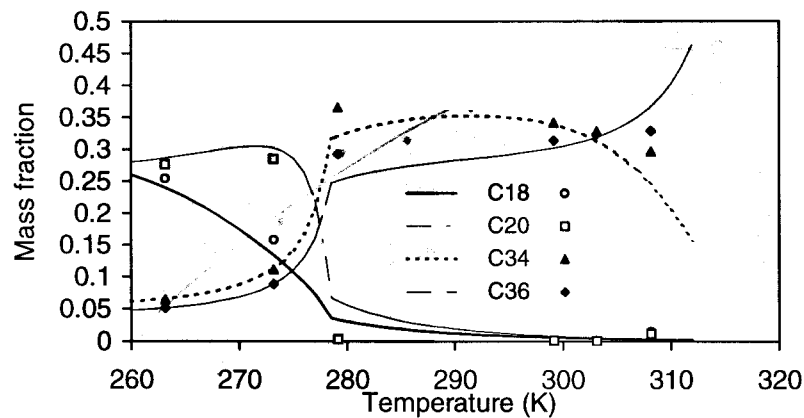


Figure 5: Wax composition versus temperature for system *Bimodal 13* (Dauphin et al., 1999). Lines are model prediction and points the experimental data.

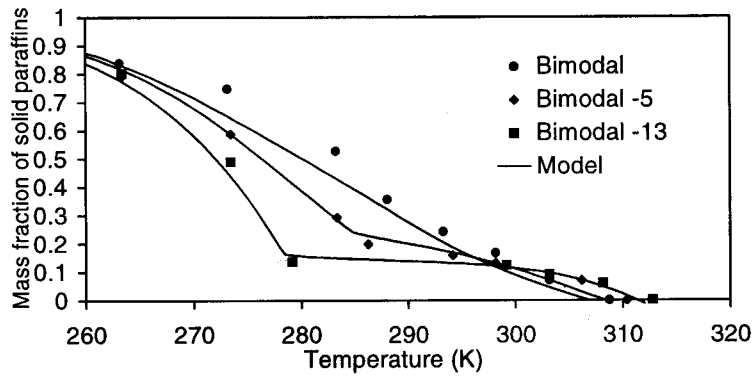


Figure 6: Comparison between experimental data and calculated overall percentage of paraffins crystallized (Dauphin et al., 1999).

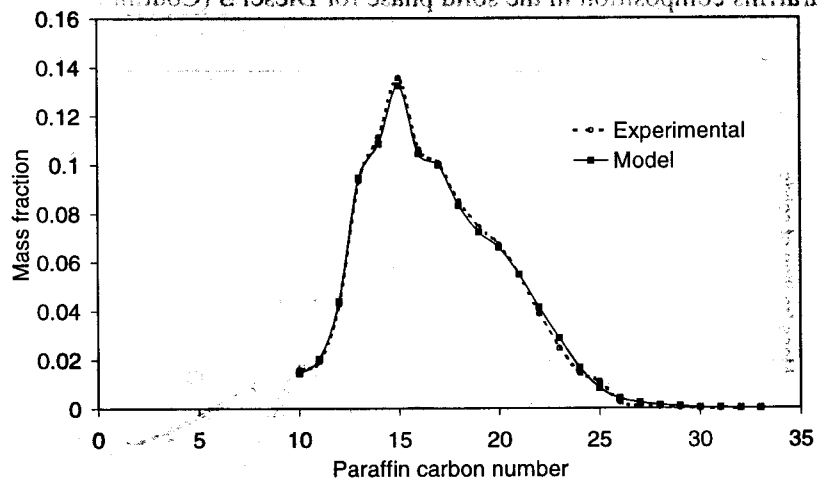


Figure 7: Experimental data and model predictions for the composition in paraffins in the liquid phase at 14 °F for Diesel NS (Coutinho et al., 2000).

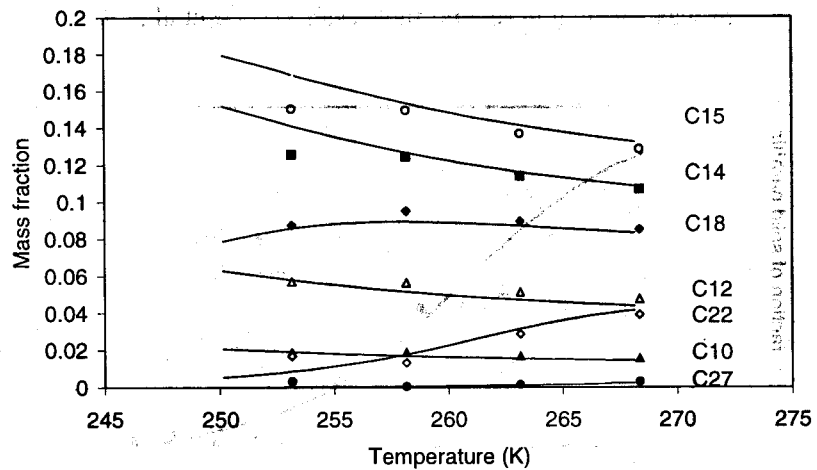


Figure 8: Experimental data and model predictions for the temperature dependence of the paraffins composition in the liquid phase for Diesel S (Coutinho et al., 2000).

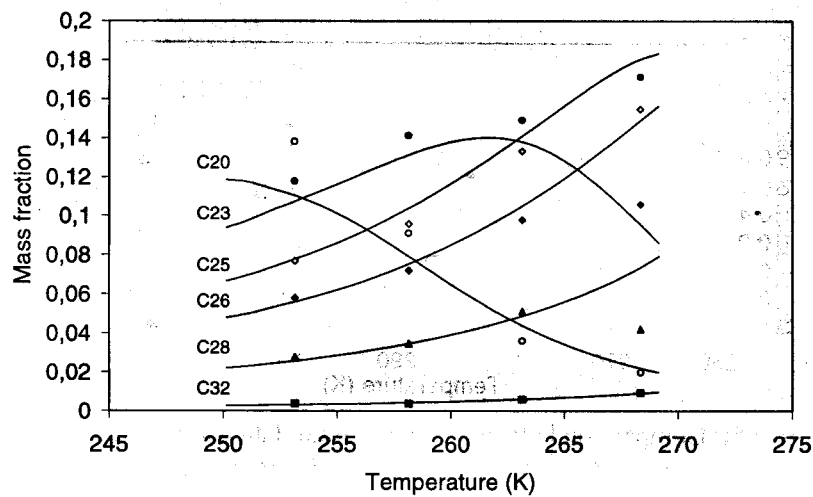


Figure 9: Experimental data and model predictions for the temperature dependence of the paraffins composition in the solid phase for Diesel S (Coutinho et al., 2000).

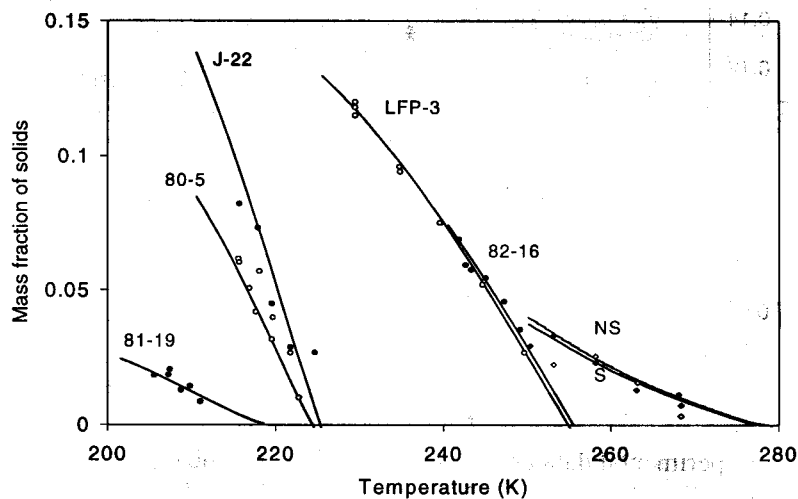


Figure 10: Experimental data and model predictions for the fraction of wax forming in several fuels (van Winkle et al., 1987).

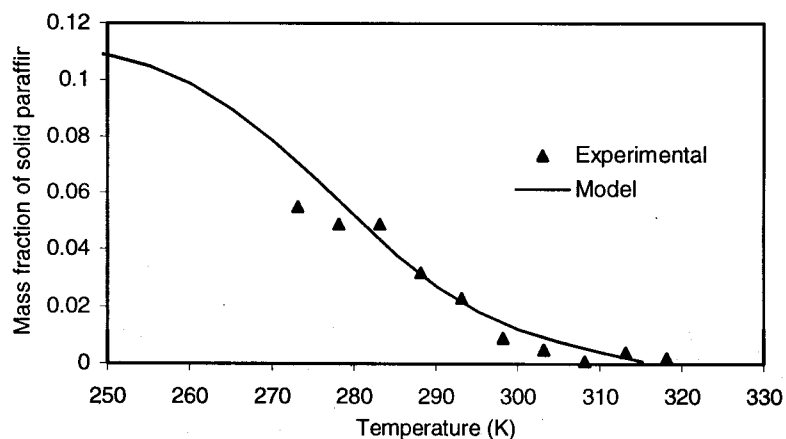


Figure 11: Comparison between experimental data and model predictions for the fraction of wax forming in Oil 6 (Rønningsen et al., 1991).

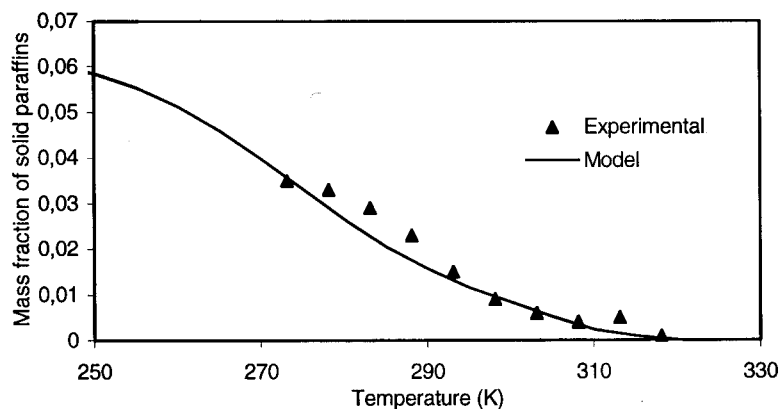


Figure 12: Comparison between experimental data and model predictions for the fraction of wax forming in Oil 16 (Rønningsen et al., 1991).

Extension to High Pressures

The strongest point of the model is the excellent description of the solid phase non-ideality. It relies, however, on an excess free energy model that was developed for low pressures, while much interest in the petroleum industry addresses the high pressure behaviour in a reservoir or during off shore transportation, where pressures can be very high and multiphase behaviour (GLSE) arise. The influence of the light ends in the solubility of the heavy fraction is well known (Ruffier-Meray et al., 1993 and 1997; Brown et al., 1994). It is thus essential to be able to simultaneously describe the solubility of the hydrocarbon gases in the liquid phase with pressure, as well as the influence of the pressure in the non-ideality of the phases.

The description of the fluid phases fugacity at high pressures will be done using a cubic equation of state (EOS). Due to the superior description of the pure compound fugacities the SRK-EOS was chosen (Hartono et al., 1999). A very poor description of the fugacities for hydrocarbon mixtures is obtained using the van der Waals one fluid mixing rules (Kontogeorgis et al., 1998). Although this is not a problem for VLE calculations using a Phi-Phi approach due to error compensation, in a gamma-phi approach the differences in fugacities descriptions between the solid and fluid phases introduced a large

error in the calculations. To minimize this deviation the LCVM mixing rule (Boukouvalas et al., 1994 and 1997) was chosen because it provides the best description of asymmetric hydrocarbon mixtures fugacities (Voutsas et al., 1995; Kontogeorgis et al., 1998).

Using SRK-EOS with the LCVM mixing rule for the description of the fluid phases properties, and introducing in the Poynting term a correction for the solid phase excess volume to take into account the dependence of the solid phase non-ideality with pressure (Pauly et al., 2000), an excellent phase behaviour description is obtained for both fluid-fluid and solid-fluid phase boundaries as shown in Fig. 13.

Phase envelopes for the waxy phase are even more rare in the open literature and less reliable than data at low pressures. Data acquisition at high pressures is more difficult and typically is based only on cloud points unlike data at low pressures where wax fractions can be assessed as well. A phase envelope for a live oil from North Sea was measured in our laboratory (Gaubert, 1995) and the result is compared with the model predictions in Fig. 14. As can be seen an excellent description of the experimental data is obtained for this live oil using the extension of the Predictive UNIQUAC model to high pressures.

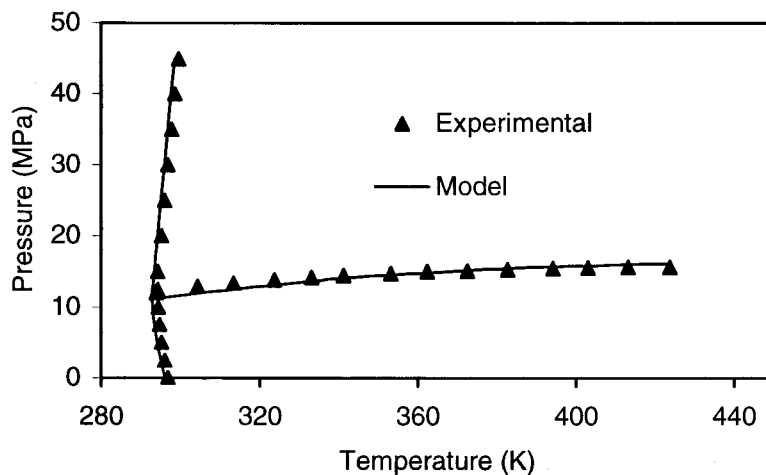


Figure 13: Measured and calculated phase envelope of the C₁-C₁₀-multi-paraffin system C (Pauly et al., 1998).

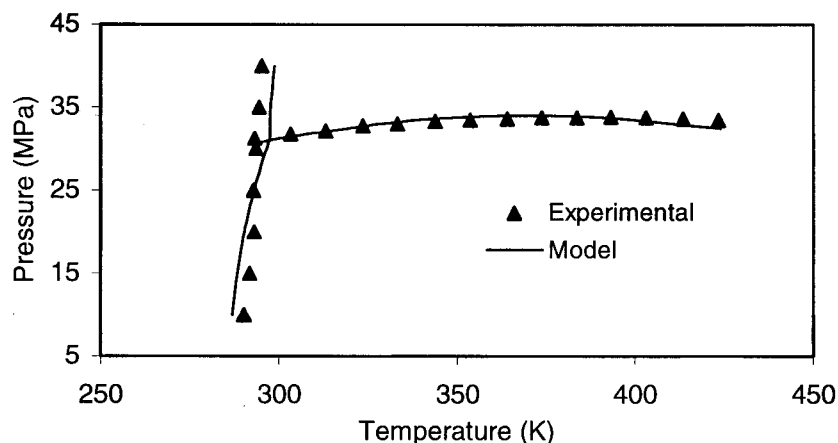


Figure 14: Measured and calculated phase envelope for a live oil from North Sea (FL2, Gaubert, 1995).

CONCLUSIONS

A predictive model for non-ideality of the solid phase is proposed. It is based on a standard model for chemical and petroleum engineering, the UNIQUAC model. It was shown how it provides excellent descriptions of the phase behaviour of both synthetic mixtures and real fluids at low pressures.

The extension of the model to high pressures was also discussed. Using an EOS/G^E model for the fluid phases and introducing the excess volume of the solid solution to account for the effects of the

pressure in the solid phase non ideality, an excellent description of both fluid-fluid and solid-fluid phase boundaries is achieved, even for live oils.

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NOMENCLATURE

A_w	van der Waals area
Cn	n-alkane with n carbon atoms or number of carbon atoms of that n-alkane
g	Gibbs free energy
H	enthalpy
q	UNIQUAC structural parameter
r	UNIQUAC structural parameter
R	universal gas constant
T	temperature
V	molar volume
V_w	van der Waals volume
x	molar fraction
Z	coordination number

Greek Letters

γ	activity coefficient
λ	pair interaction energy

Subscripts

i	component i
j	component j
fus	fusion
sub	sublimation
t2	solid phase transition

Superscripts

E	excess property
l	liquid phase
s	solid phase

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