Low-Pressure Modeling of Wax Formation in Crude Oils

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Organic deposition in the reservoir and pipelines is responsible for huge losses in profit in petroleum exploration. Among them, wax deposition is of particular concern in offshore and cold climate operation since they are temperature driven. A thermodynamic model able to anticipate the formation of wax in the oil from the knowledge of its properties would be a very valuable help for the design of transport facilities and the operation of reservoirs of potentially problematic oils. A new thermodynamic approach is proposed for the description of wax formation in crude oils at low pressures. This approach is based on the description of the solid−liquid equilibrium of the *n*-alkanes present in the fluid. It assumes an ideal liquid phase, allowing for the use of any characterization of the fluid, and describes the solid-phase nonideality using a predictive local composition model. The proposed model, unlike previous published models, is purely predictive since it uses only pure compound properties and the fluid composition to describe the wax formation. On the basis of the knowledge of the detailed composition of about 30 crudes from different origins, correlations are proposed to estimate the *n*-alkane content and distribution for waxy crudes. Using the proposed approach it was possible with very limited information on the composition to produce an excellent description of the experimental data available in the literature for different crudes.

Introduction

A considerable number of oils contain significant concentrations of *n*-alkanes above C20. Due to the low solubility of these compounds in hydrocarbon fluids, they precipitate from the crudes as they cool from the reservoir temperature down to ambient temperature during the transport in pipelines. The situation is particularly dramatic in off-shore explorations where the ambient temperature on the seabed is about 4 °C all year round both in North Sea and in the Gulf of Mexico. The paraffins that crystallize in the cold pipeline walls create deposit layers that increase the pressure drop, thus increasing transportation costs and reducing productivity, and often lead to the plugging of pipelines requiring mechanical pigging to clean the pipe and restore transport. The quest for a reliable thermodynamic model that could predict the conditions for wax formation in a given fluid to help in pipeline design and planning of transport operations has fuelled the research on this area for the last 15 years since the seminal work by Won.[1] A number of different thermodynamic models have been proposed to predict wax formation in crudes,[2−6] each with a different degree of success. The major problem with these models is that most of them are good for correlation of experimental data but lack the desirable predictive capacity, require too much data as input, or are too dependent on the oil characterization used to be reliable. This paper proposes the extension to crude oils of a predictive thermodynamic model that has proved very successful with synthetic mixtures and refined fuels.[7−10] It will be shown that with very little information a reliable description of wax formation for a wide range of crudes can be achieved.

Thermodynamic Model

Although the presence of microcrystalline waxes has been reported, most wax deposition problems are due to macrocrystalline waxes.[22,23,34] These are paraffinic waxes made up of large *n*-alkane molecules crystallized

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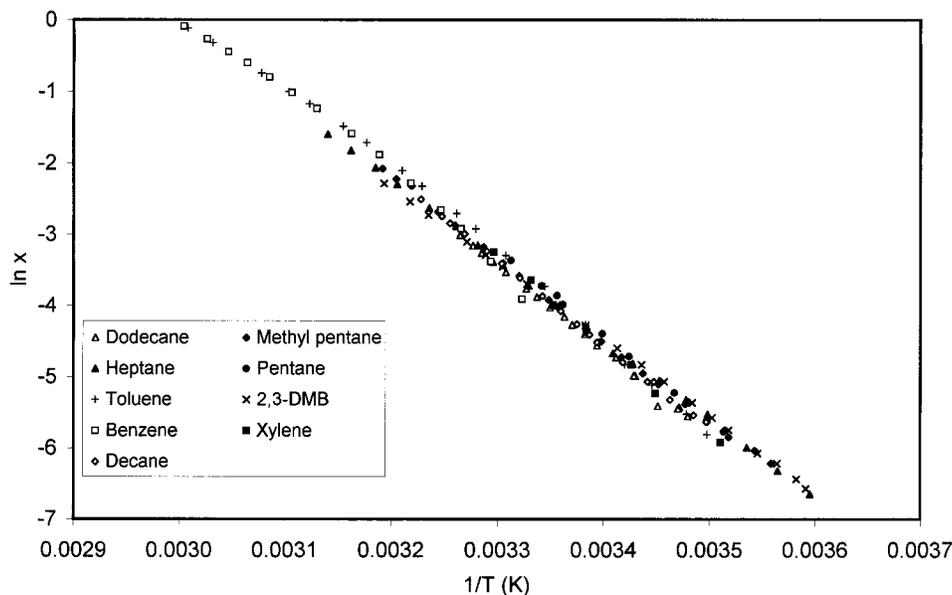
Figure 1. Experimental solubility of octacosane in different solvents.

in an orthorhombic structure.[11,12] The proposed model addresses solely these waxes. It considers the wax formation, from a thermodynamic point of view, as a solid−liquid equilibrium where the *n*-alkanes act as solutes and all the other compounds as solvents. It can thus be modeled using the general solid−liquid equilibrium equation that relates the composition in both phases with the nonideality of the phases and the thermophysical properties of the pure components. At low pressures, for each component *i*, the solid−liquid equilibrium equation can be written as[13]

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

Using the correlation for the pure component thermophysical properties based on the data by Broadhurst[14] presented in the Appendix and a flash algorithm, it is possible to estimate the temperature dependence of the

solid fraction, provided that adequate models for the nonideality of the solid and liquid phases are available.

Liquid-Phase Nonideality

In previous work, the liquid phase was described using a complex model that took into account the nonideality arising from entropic effects such as size and shape differences and free volume effects and energetic interactions between unlike molecules such as aromatics and aliphatics.[15] Although this model is very accurate in the description of the liquid-phase nonideality, it is impractical to use with crudes where a lumping procedure in pseudocompounds must be performed. Moreover, it would require a PNA (Paraffin, Naphthene, Aromatic) or a SARA (Saturated, Aromatic, Resin, Asphaltene) analysis to take into account the energetic interactions between unlike molecules. Although the solubility of an *n*-alkane on an aliphatic solvent presents negative deviations from ideality and positive deviations are found with an aromatic solvent, the solubility of *n*-alkanes in any hydrocarbon solvent does not deviate significantly from ideality, as shown in Figure 1, where the solubility of *n*-C28 in a number of aromatic and aliphatic solvents is presented. Negligible error is introduced by treating the liquid phase as ideal, and this simplification will allow a dramatic simplification in the model that is more than a mathematical simplification to the calculations as will be shown later. The liquid phase will then be taken as ideal.

Solid-phase g^E Model

The solid-phase nonideality will be described by the predictive UNIQUAC model.[7,8] This is a version of the original UNIQUAC where

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{Z}{2}\sum_{i=1}^n q_i x_i \ln\frac{\theta_i}{\Phi_i} -$$

$$\sum_{i=1}^n x_i q_i \ln\left[\sum_{j=1}^n \theta j \exp\left(-\frac{\lambda_{ij} - \lambda_{jj}}{q_i RT}\right)\right] \quad (2)$$

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with

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (3)$$

and using the definition for the structural parameters r and q proposed for the solid phase[8]

$$r_i = \frac{V_w}{109.2} \quad \text{and} \quad q_i = \frac{A_w}{15.0 \times 10^9} \quad (4)$$

where V_w and A_w are, respectively, the van der Waals volume and surface area of the molecules. Since the solid phase is composed exclusively of n-alkanes, the values of these parameters can be obtained from the correlations presented in the Appendix.

The assessment of the local composition is based on the values of the interaction energies between pairs of molecules, λ_{ij}. The predictive local composition concept[8] provides a predictive approach for the estimation of the interaction energies used. The pair interaction energies between two identical molecules are estimated from the enthalpy of sublimation of an orthorhombic crystal of the pure component

$$\lambda_{ii} = -\frac{2}{Z}(\Delta_{sub}H_i - RT) \quad (5)$$

z being the coordination number with a value of 6. The enthalpy of sublimation, $\Delta_{sub}H = \Delta_{vap}H + \Delta_{fus}H + \Delta_{t2}H$, is calculated at the melting temperature of the pure component. The heat of vaporization, $\Delta_{vap}H$, is calculated using the PERT2 correlation by Morgan and Kobayashi.[16]

The pair interaction energy between two nonidentical molecules is given by

$$\lambda_{ij} = \lambda_{jj} \quad (6)$$

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

The thermodynamic model proposed is thus a purely predictive model in that it uses in the calculation of the phase behavior nothing but pure component properties.

Petroleum Characterization

The approach used in this model considers that the petroleum comprises two types of compounds: n-alkanes that may crystallize to form a solid phase and will be the solute and all the other compounds that may be present in the oil and that will act as the solvent.

n-Alkanes. A number of investigations by our team attempting to study the solid−liquid behavior of n-alkane solutions indicate that in general the n-alkanes exhibit independent behavior and that an accurate description of their solid−liquid behavior cannot be obtained unless each n-alkane is considered individually.[9,17−20] The goal of the n-alkanes characterization is

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to develop a description of the n-alkanes distribution as close as possible to the original oil. The distribution of n-alkane concentrations can be described by two quantities: the total wax (n-alkane) content of the oil and the n-alkane decay that in most oils is basically an exponential decay. These can be obtained in a number of ways. The most immediate is a HTGC analysis that would provide both the total n-alkane content and its distribution. The total wax content can also be obtained from precipitation with acetone or other solvents at low temperature, or from a correlation involving some known property of the oil. The total wax content correlates well with the average molecular weight for paraffinic waxy crudes according to:

$$n\text{-alkanes (C20+)[wt \%]} = 0.070 \times \text{Mw-8.3} \quad (7)$$

as shown in Figure 2. A correlation of broader applicability, including asphaltenic crudes and gas condensates, could be obtained if other information was available, such as a SARA analysis, but it will be always a question of optimizing the quality of the prediction with the amount of information required.

The decay of the n-alkanes in oils is an exponential decay as is well documented in the literature.[21−22] It will be defined here as the ratio between the mass fractions of two neighbor n-alkanes

$$\alpha = \frac{wC_n}{wC_{n-1}} \quad (8)$$

If the n-alkane compositions are available from a HTGC analysis, they can be used directly, but the n-alkane decay can be estimated from TBP (True Boiling Point) or simulated distillation data if available up to at least C30. A comparison between the decays of the Cn fractions from simulated distillations and the true n-alkane decays for a large number of oils available in the literature shows that the decay of the n-alkane distribution is somewhat faster than the decay for the simulated distillation. This is explained by the increasing number of isomers with carbon number. The average n-alkane decay has a value of $\alpha = 0.88$ (standard deviation of 0.03) and the simulated distillation decay an average value of $\alpha = 0.91$ (standard deviation of 0.02) for about 25 oils from literature. The n-alkane decay can thus be estimated as

$$\alpha_{n-\text{alkanes}} = \alpha_{\text{sim,dist}} - 0.03 \quad (9)$$

if some simulated distillation information is available. If no information at all is available, the average decay value of $\alpha = 0.88$ can be used, with due care, to generate the n-alkane distribution.

Solvent. Ideally, a model to describe the phase behavior of a petroleum fluid should be independent, or at least as weakly dependent as possible, of the characterization procedure used. One of the major advantages of this model is that it is actually independent of the characterization procedure used as long as the n-alkane compositions are adequately described. Any solvent characterization can thus in principle be used. The explanation for that is related with the discussion above on the liquid-phase ideality. As shown the solubility of n-alkanes is independent of the solvent
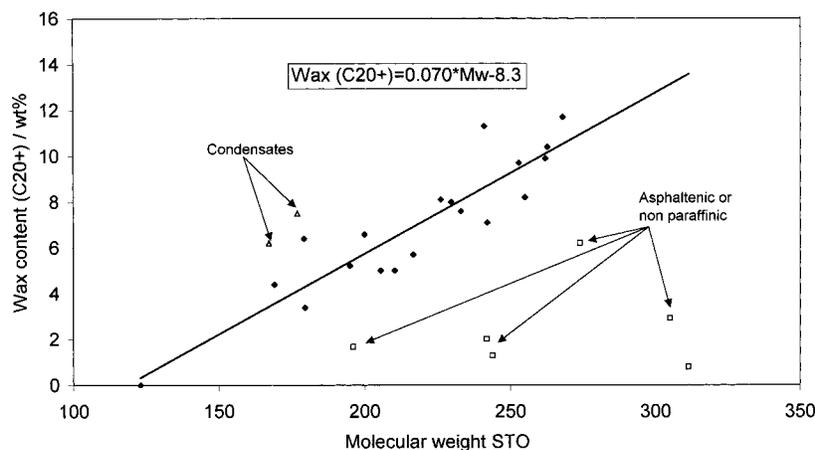
Figure 2. Correlation of C20+ wax content with the oil average molecular weight.
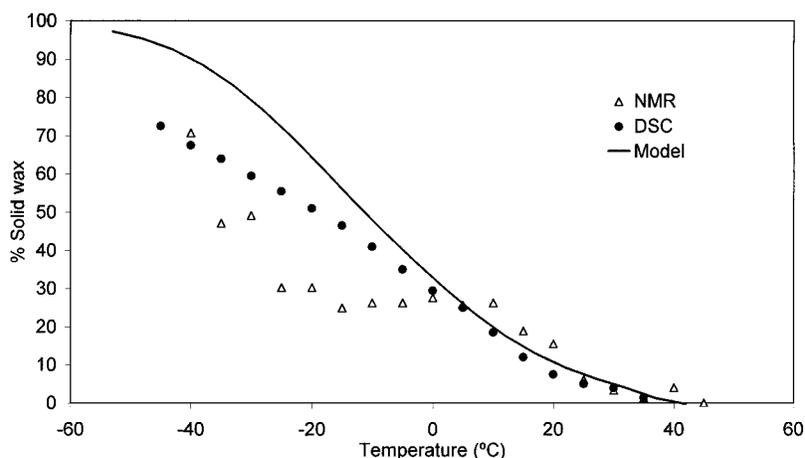
Figure 3. Comparison between experimental DSC and NMR measurements and model predictions for Rønningsen's oil 3.

nature. It is thus inconsequential which and how many pseudocompounds are chosen to describe the solvent as long as the molar fractions of the *n*-alkanes and the total-solvent are not changed relative to those of the original oil. For this purpose, the only constraint is that the average molecular weight of the oil is conserved in the characterization procedure. For a matter of simplicity, a single pseudocompound will be used in this work in the description of the fluids.

Results

No matching data are available in the literature for the temperature dependence of wax formation and some of the data are not reliable. Often, very little information is available for the oil composition. This limitation leads to the development of a model that uses a minimum amount of information on the oil composition. A number of systems that could be used to test the model against were compiled from the literature. Among these are the well-known Rønningsen data[23] for 17 North Sea oils, for which detailed information on composition and behavior is available. These have been used by different authors to test their models.[2,3,6] These data will also be used in this work for testing the proposed model after a previous discussion on their quality.

Rønningsen et al. used NMR to determine the amount of wax forming in the oils in the temperature range from −40 to 45 °C. NMR is far from being a very accurate technique for measuring amounts of solid, and the

scatter in the experimental data is a symptom of that problem. Moreover, their NMR apparatus was not thermostated. The samples were equilibrated at a given temperature, and the quality of the measurement would rely on the promptness of the measurement to prevent temperature changes. It is reasonable to assume that the further the sample temperature is from ambient temperature, the larger the error will be. Rønningsen and co-workers also measured wax formation using DSC.[24] This is altogether a more well-established and reliable technique to measure low-temperature phase behavior of oils.[25] Using the approach proposed before for DSC data analysis,[26,27] it was possible to compare the two techniques and assess the quality of the NMR data. A comparison for oil 3 is presented in Figure 3, and similar results can be obtained for all the other oils. Basically, they show good agreement with the NMR data above 0 °C despite the scattering in the NMR data. The constant value for the NMR wax deposition below this temperature that raised so many interpretations[2,6] seems to be a simple problem of poor experimental data. That such behavior is not present in the DSC data for the same oils nor on any other oil measured by different techniques reported in the literature only supports this assumption. The data by Rønningsen will be used only for temperatures above 0 °C.

Although there seem to be good reasons to believe that NMR data below 0 °C are not reliable, another problem exists with Rønningsen's data that prevents modeling
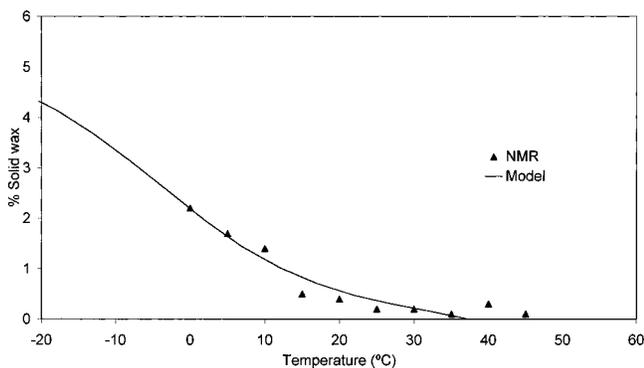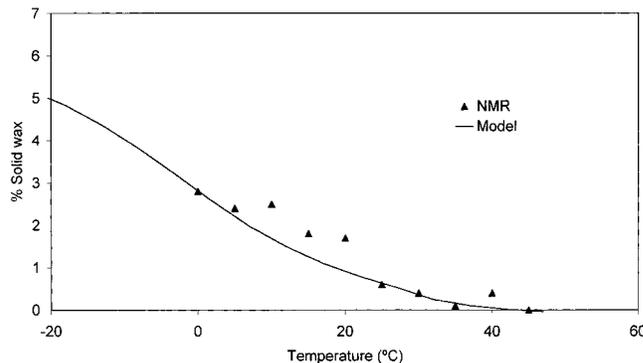
Figure 4. Comparison between NMR measurements and model predictions for Rønningsen's oil 2.

below that temperature using the DSC data. Neither the *n*-alkane content nor the distribution of the C20− fraction is available. The acetone precipitation technique used gives only the C20+ *n*-alkanes.[28] On the other hand, the *n*-alkane distribution only follows an exponential decay for *n*-alkanes larger than C20. For the *n*-alkanes below C20, no specific variation can be found, and their composition cannot be obtained by extrapolation from the heavier alkanes or from TBP or simulated distillation data. The *n*-alkane composition below C20 is not accessible unless a GC analysis of the fluid is available. This is not the case for these data. It can be shown both from experimental data and from model results[9,17−20,29] that C20 starts precipitating at around 0 °C while all the lighter compounds are still in the liquid phase. The knowledge of the *n*-alkane compositions only above C20 allows the modeling above 0 °C but makes it impossible below this temperature since the compositions of the light *n*-alkanes that will be crystallizing are not known, nor can they be estimated reliably. For both these reasons, the poor quality of Rønningsen's data below 0 °C and the lack of information on the light *n*-alkanes composition, the modeling of Rønningsen's data will be done only above 0 °C. Data from other authors with a more detailed composition analysis, allowing for prediction well below 0 °C, will also be presented.

Figure 3 shows a comparison between experimental NMR and DSC data with predictions using the model and characterization procedure proposed above. The description of the experimental data is very good above 0 °C. Below this temperature, NMR data are no longer reliable, and a discrepancy between the model and DSC data due to the poor characterization of the C20− fraction also appears. Since the model fluid has no crystallizable compounds below C20, while these are present in the real fluid, the information from the model and DSC are no longer comparable. The predicted solid fraction below 0 °C refers only to C20+ compounds, while the DSC measured solid fraction takes into account all the crystallizable compounds present in the fluid. This result clearly shows the validity of the discussion about the limitations to the use of Rønningsen's data above 0 °C. Predictions for other crudes are reported in Figures 4−7. Similar results could be presented for all the Rønningsen's oils. Data from other authors, although scarce, could also be found in the literature. Figure 8 shows the result for an oil by Erikson et al.[30] (oil 6), and Figure 9 shows the results
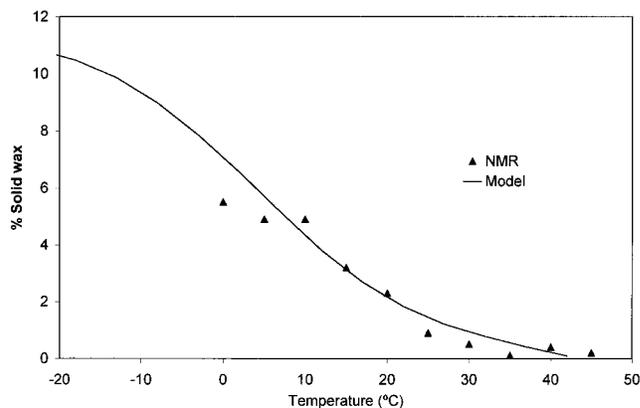
Figure 5. Comparison between NMR measurements and model predictions for Rønningsen's oil 6.
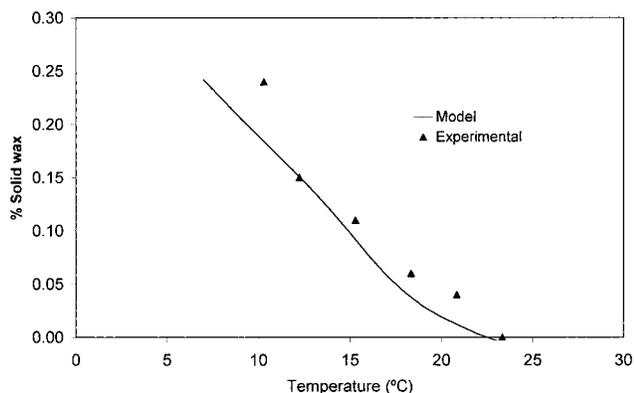

Figure 6. Comparison between NMR measurements and model predictions for Rønningsen's oil 7.
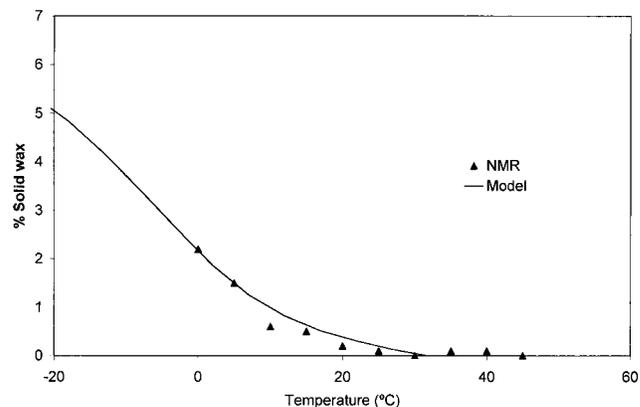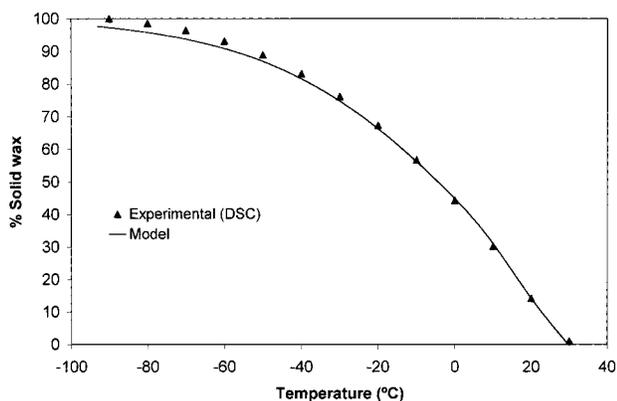

Figure 7. Comparison between NMR measurements and model predictions for Rønningsen's oil 12.

for Brut X.[5] The behavior of the latter was measured by DSC, and detailed information for the C20− fraction was available that allows a prediction of the wax formation down to −100 °C. The predictions provide an excellent description of the experimental data showing that the model can well be applied to very low temperatures, provided that compositional information is available.

Other data can be found in the literature; e.g., Erickson et al.[30] report deposition curves for other oils, but no information about their composition is provided. In these cases, when no composition information is available, it is possible to use the total wax content and *n*-alkane distribution to correlate the experimental data. This is done in Figure 10 for oil 3 by Pan et al.,[31] where a total wax content of 17.5 wt % was used to correlate

Figure 8. Comparison between experimental measurements and model predictions for Erikson's oil 6.
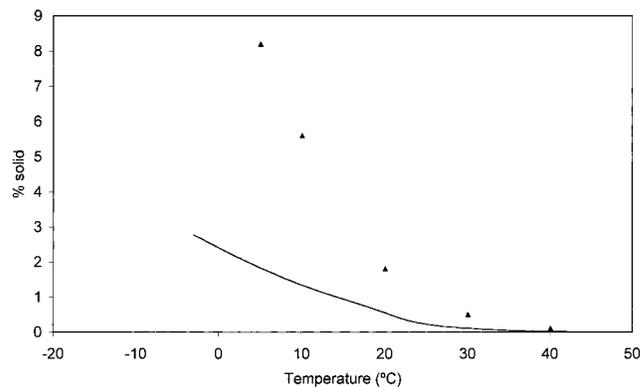

Figure 9. Comparison between experimental measurements and model predictions for Calange's Brut X.
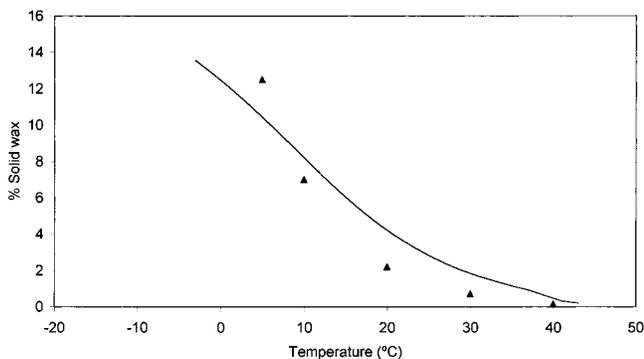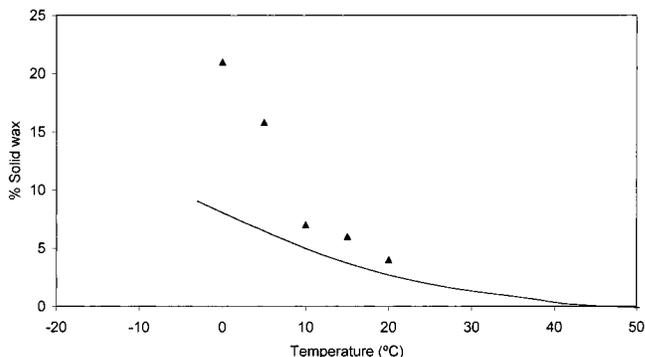

Figure 10. Comparison between experimental measurements and model predictions for Pan's oil 3.

Figure 11. Comparison between experimental measurements and model predictions for Pan's oil 2.

Figure 12. Comparison between experimental measurements and model predictions for Majeed's oil.

the experimental data. However, correlation of experimental data is a dangerous procedure, as experimental data are often not reliable, as was already discussed for Rønningsen's data and will be shown for two other oils. Figure 11 shows the results for oil 2 by Pan et al.[31] Wax fractions were measured by high-speed centrifugation, and since a detailed composition was available, the predictions can be compared with the measured wax fractions. The model severely underestimates the experimental solid fraction, and it is clear that the experimental solid fractions are strangely high since at 5 °C they are already 80% of the total C10−C63 *n*-alkane content reported. It is admissible to think this may be an oil with a microcrystalline wax that cannot be described by the proposed model, given the high concentration of nonnormal paraffins reported. Nevertheless a good description of the wax appearance tem-

perature is achieved. Similar results were obtained for Majeed et al.[32] presented in Figure 12. The wax fraction was also measured by high-speed centrifugation but, in this case, without correction for the trapped liquid.[28] Again, the model under predicts the experimental data, but an experimental value of 21 wt % of solids formed at 0 °C seems to be too large and indicates that complete liquid separation was not achieved.

The results show that the proposed model and characterization can describe the measured precipitation curves within reasonable experimental accuracy, provided that some information on the total wax content and *n*-alkane distribution in the oil is available. It has also been shown that fitting of experimental data can be performed with the proposed model if the total *n*-alkane content or the *n*-alkane distributions are tuned, but to obtain meaningful results attention should be paid to the quality of the experimental data.

Conclusions

A thermodynamic model and a characterization procedure for crude oils is proposed for the description of wax formation in crudes at atmospheric pressure. The proposed model, unlike previous published models, is purely predictive in that it uses only pure compound properties and the fluid composition to describe wax formation. It needs very little information on the fluid composition, requiring basically some information on the *n*-alkane distribution, although it can work based on some judicious estimates. The model treats the liquid phase as an ideal phase and thus does not need any information on the nature of the solvent. Any characterization procedure can be used with the proposed

model as long as a reasonable description of the individual *n*-alkane composition is assured. Comparisons of the model with experimental data for crudes available in the literature show that it can produce excellent predictions of wax formation in a wide range of crudes from different parts of the world, and if enough information on the lower compounds is available, predictions at very low temperatures can be performed with the same quality.

Appendix

Thermophysical Properties Correlations. The correlations used for the heat and temperature of phase transitions of paraffins are based on the data by Broadhurst.[14] Following Marano and Holder's approach[33]

$$T_{\text{fus,i}}[K] = 421.63 - (421.63 + 1935991)$$
$$\exp(-7.8945(C_{ni} - 1)^{0.07194}) \quad \text{(A.1)}$$

$$T_{\text{t2,i}}[K] = 420.42 - (420.42 + 134364)$$
$$\exp(-4.344(C_{ni} + 6.592)^{0.14627}) \quad \text{(A.2)}$$

and

$$\Delta_{\text{tot}}H_i[\text{kJ/mol}] = 3.7791\,C_{ni} - 12.654 \quad \text{(A.3)}$$

$$\Delta_{\text{fus}}H_i[\text{kJ/mol}] = 0.00355\,C_{ni}^3 - 0.2376\,C_{ni}^2 +$$
$$7.400\,C_{ni} - 34.814 \quad \text{(A.4)}$$

with

$$\Delta_{\text{tot}}H = \Delta_{\text{fus}}H + \Delta_{\text{t2}}H \quad \text{(A.5)}$$

where C_{ni} is the number of carbon atoms in *n*-alkane i. These equations are valid from pentane up to at least *n*-$C_{100}H_{202}$ 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*-C9 and *n*-C41, inclusive.

Correlations for the Structural Parameters. The correlations for the structural parameters r and q with the paraffin chain length used are

$$r_{ni} = 0.1\,C_{ni} + 0.0672 \quad \text{(A.6)}$$

$$q_{ni} = 0.1\,C_{ni} + 0.1141 \quad \text{(A.7)}$$

Nomenclature

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

Greek letters

α	*n*-alkane decay defined by eq 8
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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