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Reliable Wax Predictions for Flow Assurance

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Abstract

A number of wax models are currently in use by the oil industry which are based on parameters that were empirically determined to match available data for black oils. These data are often not very precise. The recently developed model of Coutinho is, however, based on high accuracy thermodynamic data.

The paper describes how the Coutinho model can be used in conjunction with conventional equations of state to perform wax equilibrium calculations for black oils. Examples are given showing how well the model can predict both wax appearance temperature and the amount of wax precipitated at varying temperatures with or without n-paraffin analyses. The examples include the effect of pressure on live oils.

Improved thermodynamic modelling of wax formation in turn allows better prediction of wax deposition rates for flow assurance.

Introduction

With the on-going trend to deep water developments, flow assurance has become a major technical and economic issue. The avoidance or remediation of wax deposition is one key aspect of flow assurance. The ability to predict wax deposition rates depends on a number of factors one of which is examined in this paper: the thermodynamic equilibrium between oil and wax.

Wax is a solid phase formed from the components of the oil that have the highest melting points. For temperatures of operational interest, i.e. above ~ 0 C, wax consists predominantly of the C₂₀₊ n-paraffins. A number of engineering models have been proposed for calculating oil-

wax equilibria, for example the work of Won [1], Hansen et al. [2], Erickson et al. [3], Pedersen [4], Rønningsen et al. [5], Lira-Galeana et al. [6] and Pan et al. [7]. The authors of all these models propose a number of correlations to predict the key thermodynamic parameters, but there is no direct experimental evidence to show that the assumptions made are correct. Instead the authors rely on experimental data for wax formation from oils to validate their models, predominantly measurements of wax appearance temperature (WAT). However, in a recent survey for Deepstar, Monger-McClure [8] suggested that uncertainties in WAT for good modern measurements may be ± 5 F. For older measurements the uncertainties can be considerably higher. Thus using data of this kind can only provide an approximate method to evaluate proposed models; it is not possible on this basis to discriminate in any detail between models.

In order to put wax calculations on a firmer footing, Coutinho and co-workers have developed a wax model that is directly based on high-quality laboratory data for the properties of liquid and solid hydrocarbons and their mixtures [9,10]. The model is summarised in the Appendix. Coutinho went on to show that the model accurately predicts the waxing behaviour of diesel fuels, jet fuels [11] and crude oils [12]. The Coutinho model exists in two variants, the Wilson and Uniquac wax models. The Wilson model is simpler to apply as it treats the wax phase as a single solid solution of n-paraffins. The Uniquac model is more realistic in that it predicts that the wax phase splits into a number of coexisting solid solution phases; experimental evidence confirms this to be the case [13]. Both variants require the n-paraffin distribution of the oil to be specified; however, in cases where this is not available, it can be estimated from the total wax content using a method devised by Coutinho and Daridon [12]. The method can therefore make optimum use of whatever data are available for a particular oil.

In order to calculate the correct equilibrium between oil and wax phases, it is obviously necessary to use an accurate thermodynamic description of the wax phase. However, it is equally important that to have an accurate thermodynamic model for the oil phase. In particular, the solution behaviour of the n-paraffins in the oil is a crucial controlling factor. This problem is usually ignored as conventional PVT modelling focuses on vapour-liquid equilibrium, i.e. the solution

behaviour of the light components on the oil.

Up till now, the Coutinho model has not been used with conventional equations of state for the fluid phases. In this work we investigated how to do this. To characterise the oil for wax calculations it was split it into two distributions, one for the n-paraffins and one for all other components. Using standard correlations such as the Twu method [14] to calculate the critical properties, we used the SRK equation [15] to find the activity coefficients for the n-paraffins. The activity coefficient of component f_{0i} can be derived from the equation of state fugacity coefficients as follows:

$$g_i = f_i / f_{0i} \quad (1)$$

where f_i is the fugacity coefficient of component i in the oil and f_{0i} is the fugacity coefficient of the hypothetical pure liquid component i at the same temperature and pressure. Figure 1 shows results for the n-paraffin activity coefficients for a typical crude oil. Coutinho and Daridon [12] have shown that good waxing results can be obtained by assuming the oil phase is an ideal solution; for an ideal solution, the log activity coefficients of all components are equal to zero. The figure shows that the equation of state deviates so extremely from the expected behaviour that no wax predictions are possible. A fundamental requirement is therefore to find a way to apply a conventional equation of state to give reasonable solution behaviour.

Figure 2 shows the calculated activity coefficients for the non-n-paraffins in the same oil. The calculated values are reasonable. Our investigations show that the cubic equations (SRK and PR) will only predict reasonable solution behaviour for SCN cuts assigned average properties to represent all the constituents of an oil. Any attempt to introduce realistic critical properties for the n-paraffins causes the solution model to fail as discussed above. In order to proceed, it is necessary to adopt an empirical approximation. The method we propose is to set up a distribution of components with average properties to represent the non-n-paraffins; we used the Riazi and Al-Sahhaf correlations [16] for molecular weight and specific gravity followed by the Twu correlations [14] for the critical properties. The n-paraffins are represented by a component from the non-n-paraffin distribution with the same molar density as the n-paraffin in question. Figure 3 shows the resulting n-paraffin activity coefficients again for the same oil; using this procedure, the n-paraffins form a near ideal mixture.

Applying the Model

To illustrate the performance of the Coutinho model, Oil 3 from the paper of Rønningsen et al. [17,18] was selected. The n-paraffin distribution was not measured for this sample, so the distribution was estimated using Coutinho and Daridon's method. Figure 4 gives a comparison between the results for the Wilson wax models using the equation of state methodology described above and the ideal solution assumption. The experimental values for amount of wax precipitated are the original nuclear magnetic resonance

(NMR) measurements quoted by Rønningsen et al. and values calculated by Coutinho and Daridon [12] from differential scanning calorimetry (DSC) traces for the same oil. The close agreement shows that the equation of state method is a practical way to proceed.

Figure 5 compares the Wilson wax model with the Uniquac wax model for Oil 3. The figure marks where the Uniquac model predicts the formation of additional wax phases. The simpler Wilson model gives only one wax phase but otherwise the results are similar.

In Figures 4 and 5, all the n-paraffins were individually included in the calculation. Usually it is desirable to reduce the number of components by lumping the SCN cuts into a smaller number of pseudocomponents. Figure 6 shows the result for Oil 3 using the Uniquac wax model with 15 n-paraffin pseudocomponents. Lumping the n-paraffins causes the wax precipitation curve to develop 'steps' corresponding to points where a new wax phase starts to form. We believe that this behaviour is an artifact of the lumped model. Figure 7 shows the effect of lumping the n-paraffins in Oil3 into 15 pseudocomponents using the Wilson wax model. The predicted amount of wax precipitated and the WAT increase slightly but the shape of the curve remains realistic. Lumping the non-n-paraffins has virtually no effect on the wax calculations.

The simplicity of the Wilson wax model combined with its stable behaviour when the n-paraffins are lumped makes it an excellent model for many engineering calculations. All subsequent examples are calculated with the Wilson wax model combined with above-mentioned procedure for applying the SRK equation to the oil phase. The Peng-Robinson equation can also be used with very similar results.

Results and Discussion

Dead Oils

The Rønningsen data are one of the largest collections of petroleum wax data in the public domain. It consists of wax precipitation curves for 13 different crude oils for which analyses are also reported. Figures 8-19 show the wax curves predicted by the model for most of the Rønningsen data apart from Oil 3 which has already been discussed. The experimental data were calculated by Coutinho and Daridon from the reported NMR traces for the oils; this is thought probably to be the most accurate way of obtaining the amount of wax precipitated [12]. As no measured n-paraffin distributions are available, it was necessary to estimate them in every case with the Coutinho and Daridon method. The results are entirely predictive; none of the calculated wax curves has been fitted to the data. The general agreement is excellent especially as the n-paraffin distributions are estimated. This result was already obtained by Coutinho and Daridon; the main difference in this work was that the oil was modelled with a conventional equation of state.

To obtain the most reliable wax calculations, it is best to use measured rather than estimated n-paraffins concentrations.

However, even though modern gas chromatograms can determine the n-paraffin part of each SCN cut at virtually no extra cost, this information is seldom reported. There are only a few examples in the public domain. Figure 20 shows the calculated and experimental wax curves for Oil 6 from Erickson et al. [3]. The reported analysis goes to C30 and includes the n-paraffin components. The n-paraffin distribution was then extrapolated to higher carbon numbers assuming an exponential decay. In this example the highest n-paraffin component is n-C55. Agreement is good apart from the location of the WAT. The reported value of 23 °C is about 11 °C lower than the calculated value.

WAT is the most difficult point on the precipitation curve to measure as it is theoretically the point where the first infinitesimally small amount of wax is formed. In practice it is only possible to detect a finite amount of wax; different experimental methods differ in their ability to detect small amounts of wax. WAT is also the most difficult point to calculate accurately as it is strongly influenced by the traces of the heaviest n-paraffins present in the oil. Bearing this in mind, the divergence between calculated and experimental WAT in Figure 20 is not surprising. At 23 °C, the model predicts that only 0.025wt% wax will precipitate from the oil which may well be on the limit of detection; the true WAT could well be higher.

Another example where n-paraffin content was measured is the oil Brut X reported by Calange [19]. The n-paraffin analysis goes to C40 and it was extrapolated as for the example from Erickson et al. Figure 21 gives the results. Agreement is excellent.

Live oils

A major benefit of the proposed model is that it uses an equation of state to describe the fluid phases. It can therefore be used to calculate oil-wax equilibria at elevated pressures. Above the bubble point, there is a two phase equilibrium between live oil and wax. As the pressure increases, the WAT also increases slightly. This is a simple thermodynamic effect that an increase in pressure always shifts the equilibrium in favour of the denser phase, here the wax phase.

Below the bubble point, a three phase gas-oil-wax equilibrium exists that must be calculated using a multiple phase equilibrium algorithm, e.g. the Multiflash algorithm discussed by Counsell et al. [20]. The phase behaviour is now far more complex. Besides the effect of pressure, the n-paraffin solubility in the oil is altered by the changing concentrations of light hydrocarbons in the oil phase.

There is a shortage of wax formation data for live oils. Recently Daridon et al. [21] reported data for two North Sea oils which included n-paraffin analyses. The uncertainty of these data is about 2K. Figure 22 shows the measured and calculated WATs for Oil B. The trend with pressure above the bubble point is well reproduced; the model results below the bubble point are also reasonable. The calculations are again a prediction and are not fitted to the data. Figure 23 shows the result for Oil A. The calculated trends are also in good

agreement with the data but all predicted WATs are slightly high although still within the error band suggested by Monger-McClure et al. [8]. As already remarked, WAT is very sensitive to the heaviest n-paraffins. To illustrate this: if the reported upper limit of the n-paraffin distribution for Oil A is reduced by a carbon number of 1 or 2, the dashed curves are obtained in Figure 23 which are in better agreement with experiment.

Figure 24 shows the results for the live oil A-1 reported by Hammami and Raines [22]. The reported n-paraffin analysis was not consistent with the total wax content, so in this case we used the Coutinho and Daridon method to estimate the n-paraffin distribution from the total wax content. The calculated WAT is about 3 °C lower than the value found by cross polar microscopy (CPM) and field data, but higher than the values found from SDS. The SDS method is less sensitive and detects the point where a finite amount of wax forms. The calculated line for 0.16wt% wax precipitation is in close agreement with the SDS data. Live oils A-2 and A-10 shown in Figures 25 and 26 are similar. For A-2 agreement is not quite so good; the SDS measurements correspond to 0.43wt% wax precipitation from the model. For A-10 the calculated WAT is 1.7 °C higher than the CPM measurement. The SDS measurements correspond to 0.19wt% wax precipitation from the model.

Rønningsen et al. report some measurements for a live oil (Oil 10 in [5]) as shown in Figure 27. Here there is a major discrepancy between experiment and the model. However, the experimental technique depends on measuring a discontinuity in pressure drop across a 1 micron filter. We expect that this method would not be very sensitive and could only detect the presence of a relatively large amount of wax. The calculated line for 1wt% wax precipitation corresponds with the measured points.

Importance for Wax Deposition

A major application of wax calculations for crude oils is flow assurance. Here the rate of wax deposition is the key factor. Industry standard methods are based on Fick's Law of diffusion to estimate the kinetics of the deposition process, (although the observed deposition rates are often inconsistent with the expected values for the diffusion coefficient [23]).

In order to perform a diffusion calculation, it is necessary to know the underlying thermodynamic driving force towards equilibrium. If this is not accurately known, the calculated deposition rate will also be inaccurate. The driving force not only depends on the value of the WAT, but also on the oil-wax equilibrium below the WAT. The Coutinho wax model has been shown to give reliable predictions of wax precipitation over a range of temperatures; it is therefore a very appropriate choice for the thermodynamic component for wax deposition modelling.

Conclusions

The Coutinho wax model is the only current engineering model for wax equilibrium calculations that is directly based on accurate thermodynamic data. It has been shown to predict

the waxing behaviour of diesel fuels, jet fuels and crude oils. This paper shows that the Coutinho model can be used in conjunction with conventional equations of state for the fluid. The model requires the n-paraffin distribution of the fluid, but if this is not available a method exists to estimate it. Using the Wilson version of the model, it is also possible to lump n-paraffins into a reduced number of pseudocomponents and still obtain reasonable results.

Flow assurance calculations require more than a thermodynamic model for wax precipitation; they also require a kinetic model to estimate the rate of wax deposition. However, accurate thermodynamics is a key requirement for deposition calculations as the thermodynamic driving force is a major factor controlling the kinetics. Developing a physically realistic description of the kinetics of the wax deposition process will be the subject of a future paper.

Nomenclature

G^E	Excess Gibbs energy
ΔG	Gibbs energy change
ΔH	Enthalpy change
n	Mole number
N	n-Paraffin carbon number
q	Uniquac model area parameter
r	Uniquac model volume parameter
R	Gas constant
T	Absolute temperature
x	Mole fraction
a	Wilson model binary correction parameters
g	Activity coefficient
f	Fugacity coefficient
I	Wilson/Uniquac interaction parameters

Superscripts:

O	Oil
W	Wax

Subscripts:

i, j	Component numbers
m	Normal melting point
tr	Solid phase transition point
sub	Sublimation

References

1. K. W. Won: 'Thermodynamic Calculation of Cloud Point Temperatures and Wax Phase Compositions of Refined Hydrocarbon Mixtures', *Fluid Phase Equil.*, **53**, 377, (1989).
2. J. H. Hansen, Aa. Fredenslund, K. S. Pedersen, H. P. Rønningsen: 'A Thermodynamic Model for Predicting Wax Formation in Crude Oils', *AIChEJ*, **34**, 1937, (1988).
3. D. D. Erickson, V. G. Niesen, T. S. Brown: 'Thermodynamic Measurement and Prediction of Paraffin Precipitation in Crude Oil', SPE 26604.
4. K. S. Pedersen: 'Prediction of Cloud Point Temperatures and Amount of Wax Precipitated' SPE 27629.
5. H. P. Rønningsen, B. F. Sømme, K. S. Pedersen: 'An Improved Thermodynamic Model for Wax Precipitation: Experimental Foundation and Application', *Multiphase '97*, BHR Group (1997).
6. C. Lira-Galeana, A. Firoozabadi, J. M. Prausnitz: 'Thermodynamics of Wax Precipitation in Petroleum Mixtures', *AIChEJ*, **42**, 239, (1996).
7. H. Pan, A. Firoozabadi, P. Fotland: 'Pressure and Composition Effect on Wax Precipitation: Experimental Data and Model Results', SPE 36740.
8. T. G. Monger-McClure, J. E. Tackett, L. S. Merrill: 'DeepStar Comparisons of Cloud Point Measurement & Paraffin Prediction Methods', SPE 38774.
9. J. A. P. Coutinho, E. H. Stenby: 'Predictive Local Composition Models for Solid/Liquid Equilibrium in n-Alkane Systems: Wilson Equation for Multicomponent Systems', *Ind. Eng. Chem. Res.*, **35**, 918, (1996).
10. J. A. P. Coutinho: 'Predictive UNIQUAC: A New Model for the Description of Multiphase Solid-Liquid Equilibria in Complex Hydrocarbon Mixtures', *Ind. Eng. Chem. Res.*, **37**, 4875, (1998).
11. J. A. P. Coutinho: 'A Thermodynamic Model for Predicting Wax Formation in Jet and Diesel Fuels', *Energy & Fuels*, **14**, 625, (2000).
12. J. A. P. Coutinho, J.-L. Daridon: 'Low-Pressure Modeling of Wax Formation in Crude Oils', *Energy & Fuels*, **15**, 1454, (2001).
13. J. A. P. Coutinho: 'Predictive Local Composition Models: NRTL and UNIQUAC and their Application to Model Solid-Liquid Equilibrium of n-Alkanes', *Fluid Phase Equil.*, **158-160**, 447, (1999).
14. C. H. Twu: 'An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal Tar Liquids', *Fluid Phase Equil.*, **16**, 137, (1984).
15. G. Soave: 'Equilibrium Constants from a Modified Redlich-Kwong Equation of State', *Chem. Eng. Sci.*, **27**, 1197, (1972).
16. M. R. Riazi, T. A. Al-Sahhaf: 'Physical Properties of Petroleum Fractions and Crude Oils', *Fluid Phase Equil.*, **117**, 217, (1996).
17. H. P. Rønningsen, B. Bjørndal, A. B. Hansen, W. B. Pedersen: 'Wax Precipitation from North Sea Crude Oils. 1. Crystallization and Non-Newtonian Flow Properties', *Energy & Fuels*, **5**, 895, (1991).
18. K. S. Pedersen, P. Skovborg, H. P. Rønningsen: 'Wax Precipitation from North Sea Crude Oils. 4. Thermodynamic Modeling', *Energy & Fuels*, **5**, 924, (1991).
19. S. Calange: 'Modélisation Thermodynamique Compositionnelle de la Cristallisation des Bruts Paraffiniques', Ph.D. thesis, Institut Français du Pétrole, Paris, (1996).
20. J. F. Counsell, R. A. S. Moorwood, R. Szczepanski: 'Calculating Multiphase Equilibrium', *VLE '90*, Aston University, Birmingham, U. K., (1990).
21. J.-L. Daridon, J. Pauly, J. A. P. Coutinho, F. Montel: 'Solid-Liquid-Vapor Phase Boundary of a North Sea Waxy Crude: Measurement and Modeling', *Energy & Fuels*, **15**, 730, (2001).
22. A. Hammami, M. Raines: 'Paraffin Deposition from Crude Oils: Comparison of Laboratory Results to Field Data' SPE 38776.
23. T. S. Brown, V. G. Niesen, D. D. Erickson: 'Measurement and Prediction of the Kinetics of Paraffin Deposition', SPE 26548.
24. J. Pauly, J.-L. Daridon, J. A. P. Coutinho, N. Lindeloff, S. I. Andersen: 'Prediction of Solid-Fluid Phase Diagrams of Light Gases-Heavy Paraffins up to 200 MPa using an Equation of State- G^E Model', *Fluid Phase Equil.*, **167**, 145, (2000).

Appendix

Coutinho and co-workers have investigated the thermodynamics of oil-wax equilibria over a number of years [9,10]. In order to achieve a greater level of confidence in the predicted results, they have broken the problem down and investigated each aspect of wax formation by making use of high-accuracy thermodynamic data for mixtures of n-paraffins in both the oil and the wax phase. In this way, all assumptions in the model can be justified.

There are three main factors controlling the thermodynamics of wax formation. These are the solution behaviour of the n-paraffin molecules in the oil phase, the solid transition properties (normal melting point, enthalpy of melting, etc.) of each n-paraffin and the solution behaviour of the n-paraffins in the wax phase.

Coutinho suggests that when wax precipitates from a real crude oil, the n-paraffins solidify to form an orthorhombic solid solution. Using available thermodynamic data for phase transitions for n-paraffins with a carbon number of 42 or more, the normal melting point can be correlated as:

$$T_m = 421.63 - 1936112.63 \exp(-7.8945(N-1)^{0.07194}) \quad (\text{A1})$$

and the enthalpy of melting as:

$$\Delta H_m = 1000(3.7791N - 12.654) \quad (\text{A2})$$

where N is the carbon number. This leads to a Gibbs energy change of:

$$\Delta G = \Delta H_m (T_m / T - 1) \quad (\text{A3})$$

where T is the absolute temperature. For n-paraffins below a carbon number of 42 (but above one of 8) the phase transition is more complicated. At the melting point they form a rotator phase. The melting temperature is again given by Equation A1 but the enthalpy of fusion must be obtained from the following correlation:

$$\Delta H_m = 1000(-0.00355N^3 + 0.2376N^2 - 3.6209N + 18.5391) \quad (\text{A4})$$

A second solid phase transition from rotator to orthorhombic phase then occurs at a slightly lower temperature. The transition temperature is given by:

$$T_r = 420.42 - 134784.42 \exp(-4.344(N + 6.592)^{0.14627}) \quad (\text{A5})$$

and the transition enthalpy by:

$$\Delta H_r = 1000(0.00355N^3 - 0.2376N^2 + 7.4N - 34.814) \quad (\text{A6})$$

The Gibbs energy change is now:

$$\Delta G = \Delta H_m (T_m / T - 1) + \Delta H_r (T_r / T - 1) \quad (\text{A7})$$

In addition at high pressures, a small correction term should be added to Equations A3 or A7 which is described in [24].

After systematic investigation, Coutinho concluded that the wax phase is a solid solution of mainly n-paraffins that deviates significantly from ideal mixing. Using experimental data for solid solutions of n-paraffins, he showed that the wax solution behaviour could be modelled by a form of the Wilson equation:

$$G^E / RT = -\sum_i n_i^W \ln \left(\sum_j x_j^W \exp(\mathbf{I}_{ji} - \mathbf{I}_{ii}) \right) \quad (\text{A8})$$

where G^E is the excess Gibbs energy, R is the gas constant,

n_i^W and x_i^W are the mole number and mole fraction of component i in the wax phase and the Wilson parameters are estimated from:

$$\mathbf{I}_{ii} = -\frac{1}{3}(\Delta H_{sub,i} - RT) \quad (\text{A9})$$

where $\Delta H_{sub,i}$ is the enthalpy of sublimation of component i ; reference [9] details how the enthalpy of sublimation can be calculated. The expression for the cross-terms is:

$$\mathbf{I}_{ij} = \mathbf{a}_{ij} \min(\mathbf{I}_{ii}, \mathbf{I}_{jj}) \quad (\text{A10})$$

\mathbf{a}_{ij} is a correction factor close to unity. (See below.)

The Wilson wax model gives good results but has the limitation that it predicts that the wax always remains as a single solid solution. However, waxes consist of many crystals each one of which is a separate solid solution. The experimental evidence suggests that the range of carbon numbers found within a single n-paraffin solid solution is no more than about 56. In order to represent this, Coutinho proposed an alternative expression for the wax phase based on the Uniquac equation:

$$G^E / RT = \sum_i n_i^W \left[\ln \left(\frac{r_i}{\sum_j x_j^W r_j} \right) + 3q_i \ln \left(\frac{q_i \sum_j x_j^W r_j}{r_i \sum_j x_j^W q_j} \right) - q_i \ln \left(\frac{\sum_j x_j^W q_j \exp(\mathbf{I}_{ji} - \mathbf{I}_{ii})}{\sum_j x_j^W q_j} \right) \right] \quad (\text{A11})$$

where the Uniquac parameters for component i are estimated from:

$$q_i = 0.1N + 0.1141 \quad (\text{A12})$$

$$r_i = 0.1N + 0.0672 \quad (\text{A13})$$

For the Uniquac model:

$$\mathbf{I}_{ij} = \min(\mathbf{I}_{ii}, \mathbf{I}_{jj}) \quad (\text{A14})$$

The Uniquac wax equation predicts that the wax phase splits into a number of separate solid solution phases with limited ranges of n-paraffin carbon number. In this respect, the Uniquac wax model is more physically realistic. Generally the Uniquac model seems to give slightly more accurate results; compared with the Wilson model, it predicts slightly lower amounts of wax precipitated and slightly lower WAT. However, for engineering applications, the Wilson model has the advantage of being easier to use as it treats the wax as a single phase. In this work we used the correction factor \mathbf{a}_{ij} in the Wilson model to bring the results as close as possible to those from the Uniquac model. The expression used was:

$$\mathbf{a}_{ij} = 1 - 8 \times 10^{-7} \left| \Delta H_{sub,i} - \Delta H_{sub,j} \right| \quad (\text{A15})$$

The final aspect of wax modelling is to obtain an accurate representation of the solution behaviour of the n-paraffins in the oil phase. Coutinho investigated the thermodynamics of liquid mixtures of n-paraffins and found that they show small negative deviations from ideal mixing; i.e. G^E is slightly negative. Originally he used the Unifac model to describe the oil phase; however, this model is not normally used for oil and gas applications. For crude oils, Coutinho and Daridon showed that good results can be obtained by assuming that a dead oil

forms an ideal solution. This assumption was also made by Erickson et al. In the absence of further experimental evidence, the ideal mixing assumption is the most practical way to proceed.

An ideal solution is one for which $G^E = 0$. By definition, the activity coefficient of component i is:

$$\ln \mathbf{g} = \frac{\partial}{\partial n_i} \left(\frac{G^E}{RT} \right) \quad (\text{A16})$$

Thus for an ideal solution, all the activity coefficients are equal to unity.

To apply the model it is necessary to compute the oil-wax equilibrium. This occurs when the activities of all n-paraffin components are equal in both phases:

$$x_i^O \mathbf{g}_i^O = x_i^W \mathbf{I}_i^W \quad (\text{A17})$$

where superscripts O and W denote the oil and wax phases respectively. \mathbf{g}_i^O is obtained from the equation of state for the oil using Equation 1. For the wax phase, the activity coefficients (relative to the oil phase) are made up of the solid transition Gibbs energy change defined by Equation A7 plus the contribution from the excess Gibbs energy of the wax phase as defined either by Equation A8 or A11:

$$\ln \mathbf{g}^W = \frac{\Delta G}{RT} + \frac{\partial}{\partial n_i^W} \left(\frac{G^E}{RT} \right) \quad (\text{A18})$$

A standard phase equilibrium algorithm is used to find the conditions where Equation A17 is satisfied.

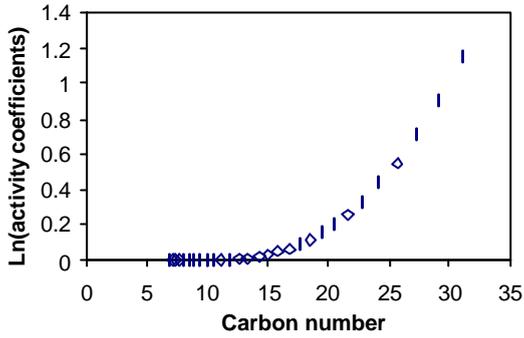


Figure 1. N-paraffin activity coefficients in typical waxy oil (SRK model, Twu correlation)

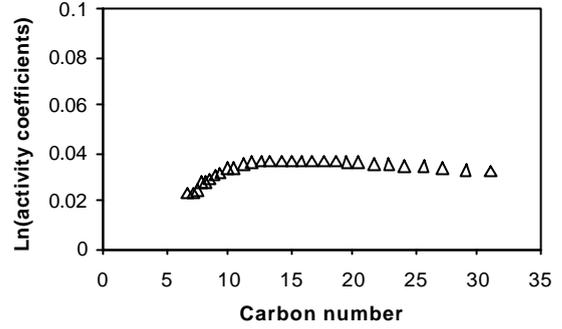


Figure 2. Non-n-paraffin activity coefficients in typical waxy oil (SRK model, Twu correlation)

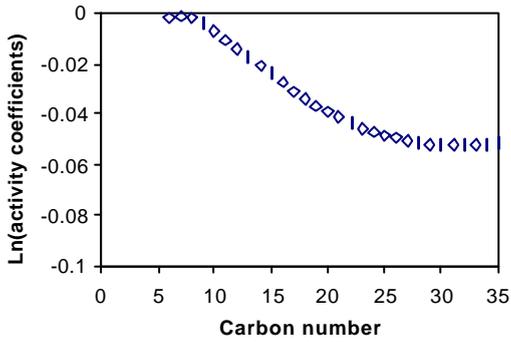


Figure 3. N-paraffin activity coefficients in typical waxy oil (SRK model, Infochem characterisation)

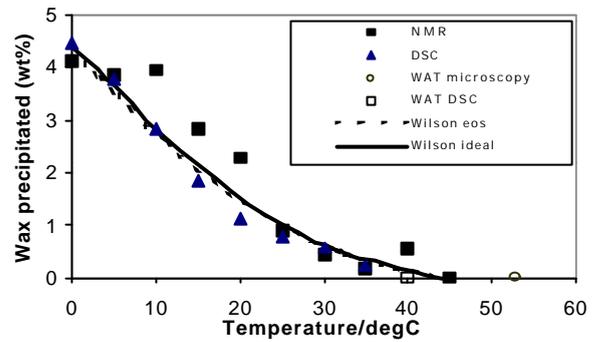


Figure 4. Wilson + EOS wax model compared with ideal mixing

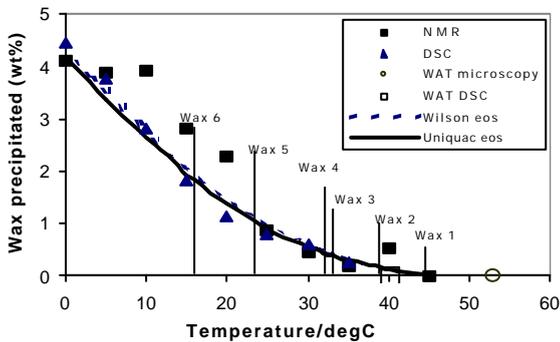


Figure 5. Wilson & Uniquac + EOS wax models compared

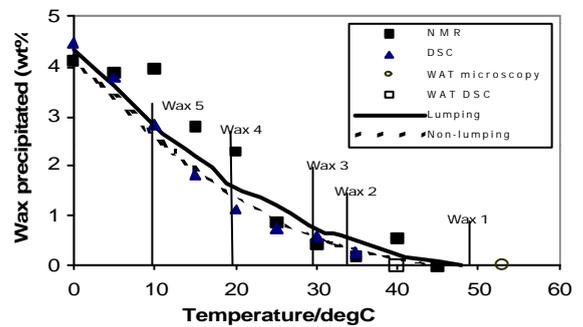


Figure 6. Uniquac + EOS wax model with and without lumping

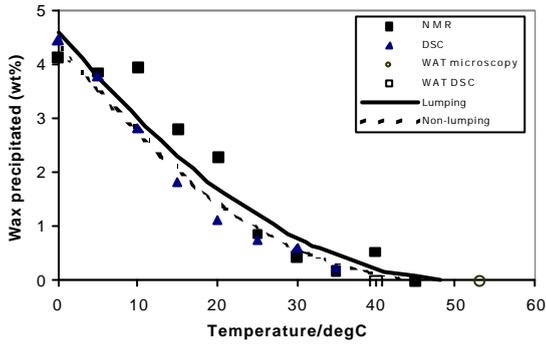


Figure 7. Wilson + EOS wax model with and without lumping

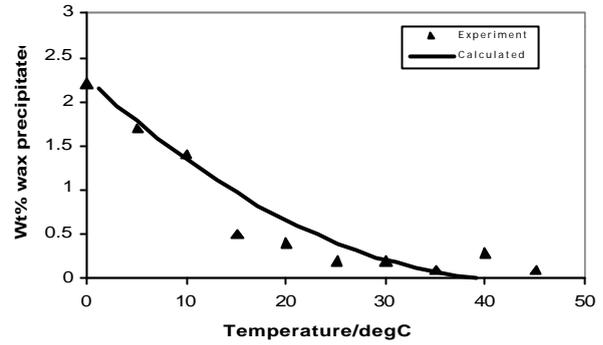


Figure 8. Rønningsen Oil 2

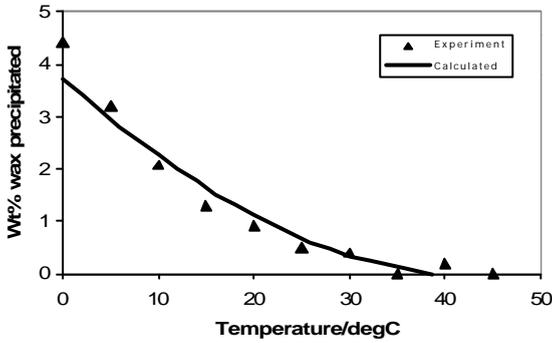


Figure 9. Rønningsen Oil 4

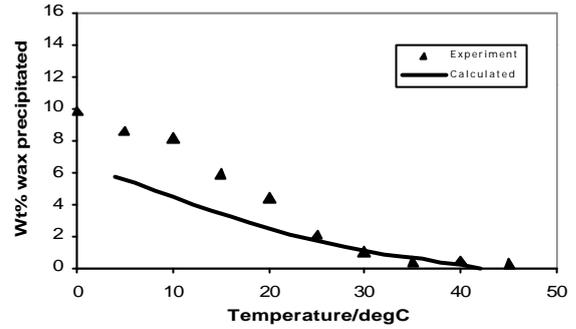


Figure 10. Rønningsen Oil 5

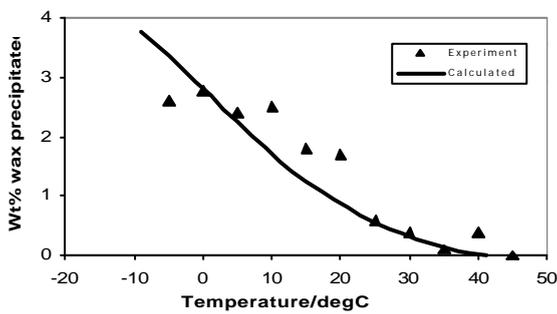


Figure 11. Rønningsen Oil 7

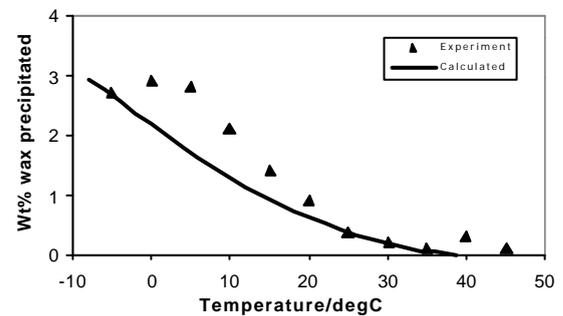


Figure 12. Rønningsen Oil 8

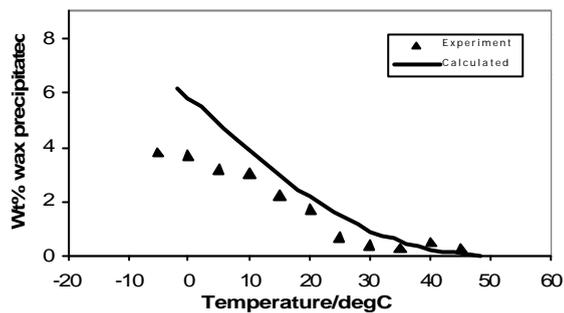


Figure 13. Rønningesen Oil 9

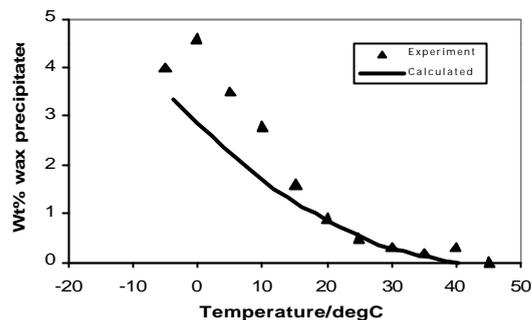


Figure 14. Rønningesen Oil 10

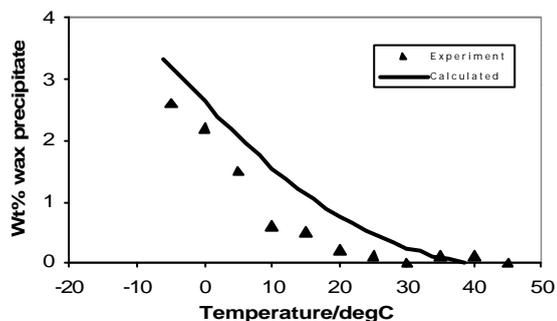


Figure 15. Rønningesen Oil 12

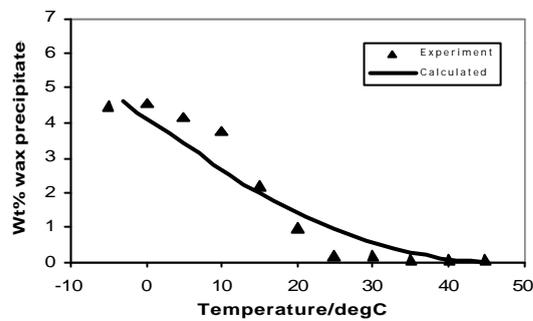


Figure 16. Rønningesen Oil 14

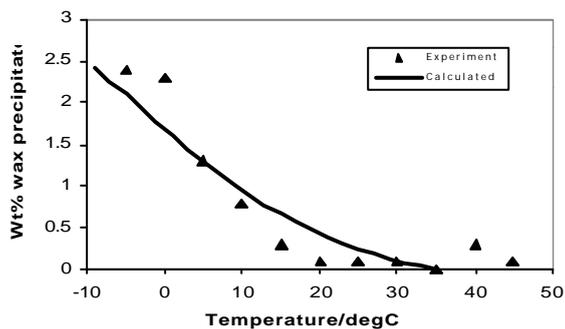


Figure 17. Rønningesen Oil 15

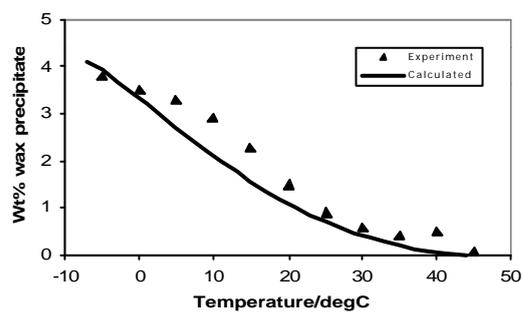


Figure 18. Rønningesen Oil 16

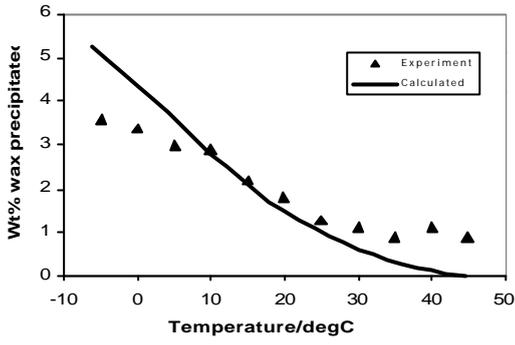


Figure 19. Rønningesen Oil 17

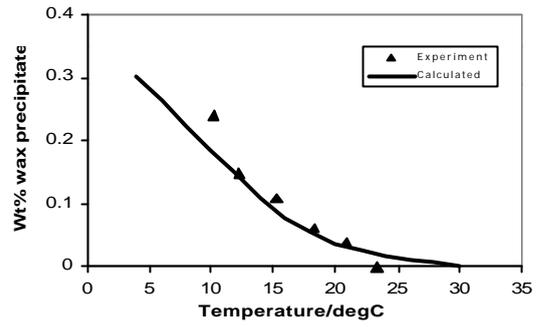


Figure 20. Erickson et al. Oil 6

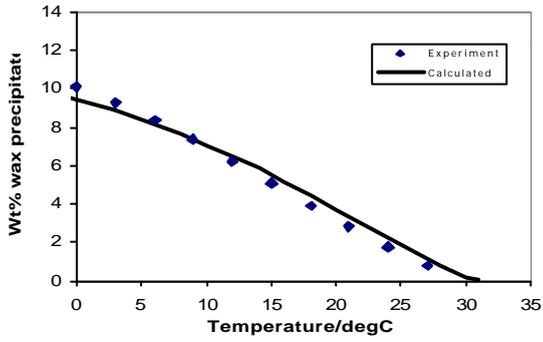


Figure 21. Calange Brut X

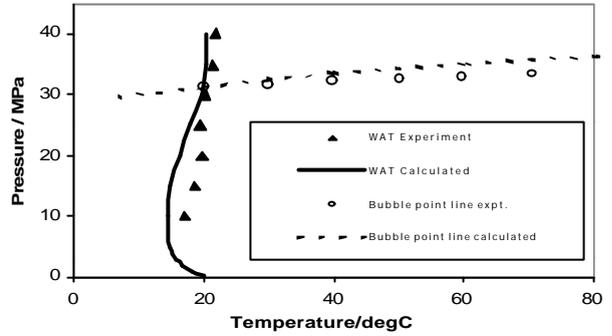


Figure 22. Daridon et al. Oil B

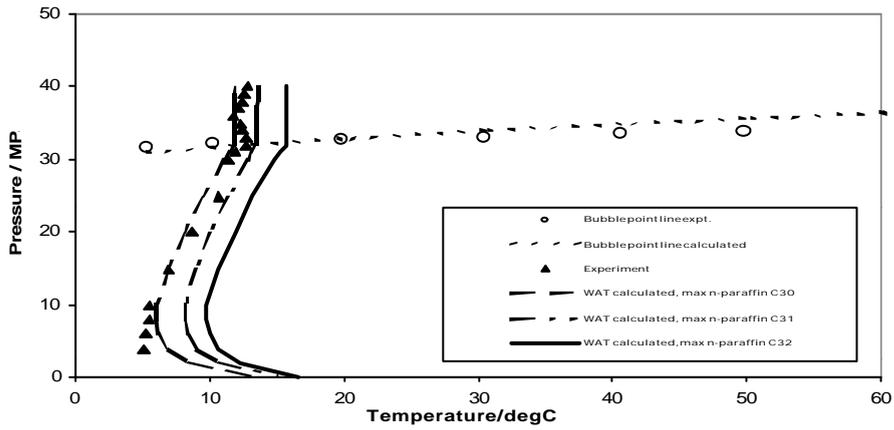


Figure 23. Daridon et al. Oil A

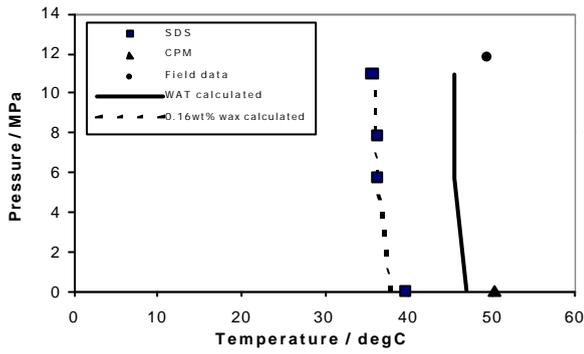


Figure 24. Hammami and Raines Oil A - 1

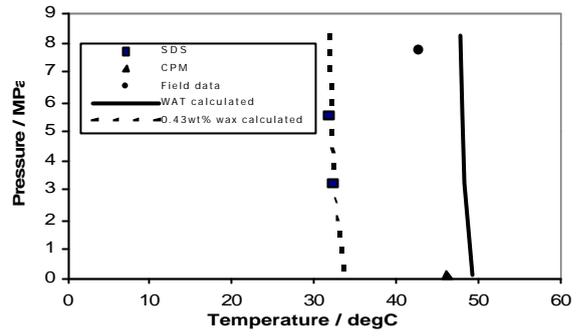


Figure 25. Hammami and Raines Oil A - 2

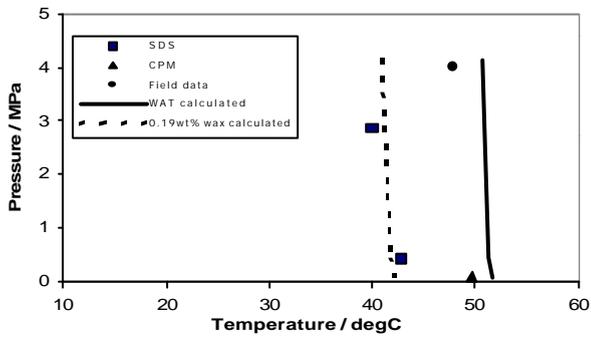


Figure 26. Hammami and Raines Oil A - 10

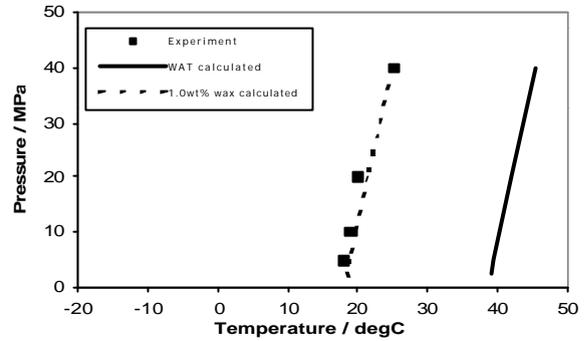


Figure 27. Rønningesen et al. [5] Oil 10