

Reliable Wax Predictions for Flow Assurance

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Received March 29, 2005. Revised Manuscript Received January 25, 2006

A number of wax models currently in use by the oil industry 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 predictive local composition model is, however, a predictive, theoretically well-defined model based on high-accuracy thermodynamic data. The paper describes how the predictive local composition model can be used in conjunction with conventional cubic equations of state to perform wax equilibrium calculations for black oils. Examples are given that show how the model can predict both wax appearance temperature and the amount of wax precipitated at varying temperatures with or without detailed *n*-paraffin analyses. The examples presented include the effect of pressure on live oils. The improved thermodynamic modeling of wax formation will allow for better prediction of wax deposition rates for flow assurance.

Introduction

With the ongoing trend in 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 for predicting 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 et al.⁸ suggested that uncertainties in WAT for good modern measurements may be ± 5 °F. For older

measurements, the uncertainties can be considerably higher. Some recent works even question the possibility of the WAT being accurately measured by any foreseeable technique for most oils⁹ and recommend the use of other data to evaluate the wax precipitation potential of an oil.¹⁰ Using WAT data can only provide an approximate method for developing or evaluating proposed models. If a model is developed by empirically adjusting parameters to match a particular set of WAT data, the accuracy of any individual parameter is uncertain and the predictive capability of the model may be compromised. As new data become available, the original parameters may well require readjusting to accommodate the new information; it is noticeable that various researchers in the field have published a number of parameter revisions over time.^{2,4,5,6,7,11}

To put wax calculations on a sounder thermodynamic basis, Coutinho and co-workers adopted a different approach. They based their model on laboratory data for each aspect of wax thermodynamics. The key factors are the solution behavior of *n*-paraffin molecules in the oil phase, the thermophysical properties of the fusion of the *n*-paraffins (normal melting points and melting enthalpies) and the thermodynamics of solid solutions of *n*-paraffins, i.e., the wax phase itself. By breaking the problem down, it is possible to set up a model in which the accuracy of the individual assumptions and associated parameters can be reliably assessed by comparison with high-quality experimental data and the problem of internal cancellation of errors can be minimized. Where alternative formulations are proposed, it is possible to check that they give similar, reasonable predictions for all aspects of the waxing problem. The overall thermodynamics of wax–oil systems follows by

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(1) Won, K. W. *Fluid Phase Equilib.* **1989**, *53*, 377.

(2) Hansen, J. H.; Fredenslund, A.; Pedersen, K. S.; Rønningsen, H. P. *AIChE J.* **1988**, *34*, 1937.

(3) Erickson, D. D.; Niesen, V. G.; Brown, T. S. SPE 26604, Society of Petroleum Engineers' Annual Technical Conference and Exhibition, Houston, Oct 3–6, 1993.

(4) Pedersen, K. S. *SPE Prod. Facil.* **1995**, *2*, 46.

(5) Rønningsen, H. P.; Sømme, B. F.; Pedersen, K. S. In *Proceedings of Multiphase '97*, BHR Group, 1997.

(6) Lira-Galeana, C.; Firoozabadi, A.; Prausnitz, J. M. *AIChE J.* **1996**, *42*, 239.

(7) Pan, H.; Firoozabadi, A.; Fotland, P. *SPE Prod. Facil.* **1997**, *11*, 250.

(8) Monger-McClure, T. G.; Tackett, J. E.; Merrill, L. S. SPE 38774, Society of Petroleum Engineers' Annual Technical Conference and Exhibition, San Antonio, TX, Oct 5–8, 1997.

(9) Coutinho, J. A. P.; Daridon, J.-L. *Pet. Sci. Technol.* **2005**, *23*, 1113.

(10) Hammami, A.; Ratulowski, J.; Coutinho, J. A. P. *Pet. Sci. Technol.* **2003**, *21*, 345.

(11) Nichita, D. V.; Goual, L.; Firoozabadi, A. *SPE Prod. Facil.* **2001**, *16*, 250.

combining the thermodynamics of all the constituent parts of the problem. A detailed review of their work can be found elsewhere.¹²

Coutinho and co-workers went on to show that their model, the predictive local composition model, accurately predicts the waxing behavior of diesel and jet fuels^{13–17} and crude oils.^{18,19} The model exists in two variants, the Wilson²⁰ and Uniquac²¹ 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.²² Both variants require that the n -paraffin distribution of the oil be specified; however, in cases where it is not available, it can be estimated from the total wax content using a method devised by Coutinho and Daridon.¹⁹ The model can therefore make optimal use of whatever data are available for a particular oil.

It is normal practice in the oil industry to use cubic equations of state such as the Soave–Redlich–Kwong (SRK) or Peng–Robinson equations to describe the PVT properties of petroleum fluids. Because the aim of this work was to produce a practical model for use in wax deposition studies, it was important to retain the use of conventional equations of state for the fluids. We show how the predictive local composition model can be used for the description of a solid wax phase together with a cubic equation of state. Results for both dead and live oils are presented to illustrate the proposed model's ability to predict wax formation from crude oils.

Modeling

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 to have an accurate thermodynamic model for the oil phase. In particular, the solution behavior of the n -paraffins in the oil is a crucial controlling factor. This problem is usually ignored, as conventional PVT modeling focuses on vapor–liquid equilibrium, i.e., the solution behavior of the light components of the oil.

Until now, the predictive local composition model has been used only with equations of state coupled with an excess Gibbs energy mixing rule such as the linear combination of Vidal–Michelsen, commonly known as LCVM,^{12,17,18,23} but here we have used the conventional SRK equation. To characterize the oil for wax calculations, we split the oil into two distributions, one for the n -paraffins and one for all other components. Using standard correlations such as the Twu method²⁴ to calculate the critical properties, we substituted them into the SRK equation²⁵ to find

(12) Coutinho, J. A. P.; Pauly, J.; Daridon, J.-L. In *Computer Aided Property Estimation for Process/Product Design*; Gani, R., Kontogeorgis, G. M., Eds.; Elsevier: New York, 2004.

(13) Coutinho, J. A. P. *Energy Fuels* **2000**, *14*, 625.

(14) Coutinho, J. A. P.; Dauphin, C.; Daridon, J.-L. *Fuel* **2000**, *79*, 607.

(15) Mirante, F. I. C.; Coutinho, J. A. P. *Fluid Phase Equilib.* **2001**, *180*, 247.

(16) Coutinho, J. A. P.; Mirante, F.; Ribeiro, J. C.; Sansot, J. M.; Daridon, J.-L. *Fuel* **2002**, *81*, 963.

(17) Pauly, J.; Daridon, J.-L.; Sansot, J. M.; Coutinho, J. A. P. *Fuel* **2003**, *82*, 595.

(18) Daridon, J.-L.; Pauly, J.; Coutinho, J. A. P.; Montel, F. *Energy Fuels* **2001**, *15*, 730.

(19) Coutinho, J. A. P.; Daridon, J.-L. *Energy Fuels*, **2001**, *15*, 1454.

(20) Coutinho, J. A. P.; Stenby, E. H. *Ind. Eng. Chem. Res.* **1996**, *35*, 918.

(21) Coutinho, J. A. P. *Ind. Eng. Chem. Res.* **1998**, *37*, 4875.

(22) Chevallier, V.; Briard, A. J.; Petitjean, D.; Hubert, N.; Bouroukba, M.; Dirand, M. *Mol. Cryst. Liq. Cryst.* **2000**, *350*, 273.

(23) Pauly, J.; Daridon, J.-L.; Coutinho, J. A. P.; Lindeloff, N.; Andersen, S. I. *Fluid Phase Equilib.* **2000**, *167*, 145.

(24) Twu, C. H. *Fluid Phase Equilib.* **1984**, *16*, 137.

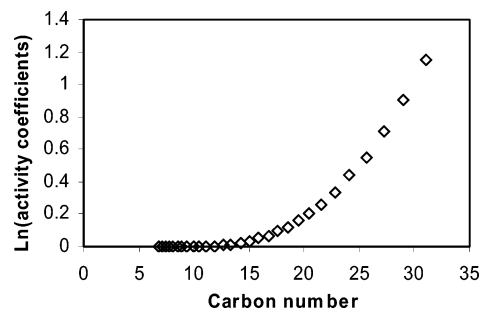


Figure 1. n -Paraffin activity coefficients in typical waxy oil (SRK model, Twu correlation).

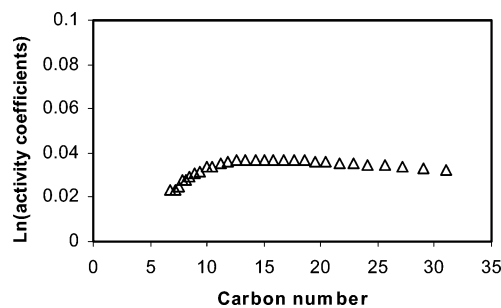


Figure 2. Non- n -paraffin activity coefficients in typical waxy oil (SRK model, Twu correlation).

the activity coefficients for the n -paraffins. The activity coefficient γ_i of component i can be derived from the equation-of-state fugacity coefficients as follows

$$\gamma_i = \phi_i / \phi_{oi} \quad (1)$$

where ϕ_i is the fugacity coefficient of component i in the oil and ϕ_{oi} is the fugacity coefficient of the hypothetical pure liquid component i at the same temperature and pressure. Figure 1 shows calculations of the n -paraffin activity coefficients for a typical crude oil. It has previously been shown that liquid mixtures of n -paraffins actually show small negative deviations from ideal mixing; i.e., G^E is slightly negative.²⁶ Although a modified Unifac model can provide a good description of the liquid phase,^{19,26} this model is not normally used for oil and gas applications and cannot be applied to live oils under high-pressure conditions such as those met in reservoirs and pipelines. For crude oils, Coutinho and Daridon¹⁹ showed that good results can be obtained by assuming that a dead oil forms an ideal solution. The same assumption was also made by Erickson et al.³ Figure 1 shows that the equation of state deviates so extremely from the expected behavior that reliable wax predictions are not possible. The overestimation of the liquid-phase nonideality must be corrected in order to proceed.

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 Peng–Robinson) will predict only reasonable solution behavior for single-carbon-number (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. To avoid the problem, it is necessary to adopt an empirical approximation. The method we propose here is to set up a distribution of components with average properties to represent the non- n -paraffins; we used the Riazi and Al-Sahhaf correlations²⁷ for molecular weight and specific gravity followed by the Twu correlations²⁴ for the critical properties. The n -paraffins are represented by a component from the non- n -paraffin distribution with the same molar density as that of the n -paraffin in question.

(25) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.

(26) Coutinho, J. A. P.; Andersen, S. I.; Stenby, E. H. *Fluid Phase Equilib.* **1995**, *103*, 23.

(27) Riazi, M. R.; Al-Sahhaf, T. A. *Fluid Phase Equilib.* **1996**, *117*, 217.

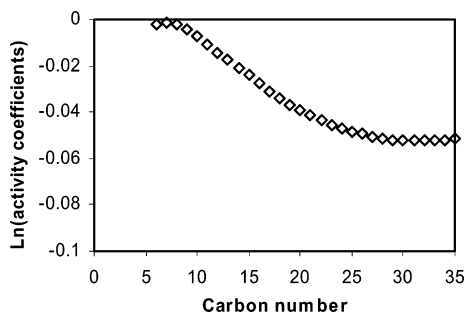


Figure 3. *n*-Paraffin activity coefficients in typical waxy oil (SRK model, Infochem characterization).

Figure 3 shows the resulting *n*-paraffin activity coefficients for the same oil as that previously used in Figure 1. Using this procedure, the *n*-paraffins are now predicted to form a near ideal mixture with a small negative deviation.

When *n*-paraffins precipitate from concentrated solutions, they can form a solid solution that is a rotator phase. However, when wax precipitates from a real crude oil, the experimental evidence^{22,28,29} is that it only forms an orthorhombic solid solution. Thermodynamic data have been reported for the phase transitions of *n*-paraffins by Broadhurst.³⁰ These have been correlated by Coutinho and Daridon¹⁹ using equations of the asymptotic form advocated by Marano and Holder³¹ to give reasonable extrapolations for very high carbon numbers.

For *n*-paraffins with carbon numbers higher than that of tetracontane, *n*-C40, the normal melting point T_m can be correlated as a function of the carbon number, N

$$T_m = 421.63 - 1\,936\,412 \exp(-7.8945(N - 1)^{0.07194}) \text{ K} \quad (2)$$

and the enthalpy of melting ΔH_m as

$$\Delta H_m = 3779.1N - 12654 \text{ J/mol} \quad (3)$$

which leads to a Gibbs energy change of

$$\Delta G = \Delta H_m(T/T_m - 1) \quad (4)$$

where T is the absolute temperature. For pure *n*-paraffins between octane and tetracontane, the phase transition is more complex, as they form a rotator phase at the melting point. The melting temperature of this phase is still given by eq 2, but the enthalpy of fusion must now be obtained from the following correlation for the rotator phase

$$\Delta H_m = 3.55N^3 - 237.6N^2 + 7400N - 34\,814 \text{ J/mol} \quad (5)$$

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

$$T_r = 420.42 - 134\,784 \exp(-4.344(N + 6.592)^{0.14627}) \text{ K} \quad (6)$$

and the transition enthalpy ΔH_r can be obtained from a difference between eqs 3 and 5.

For these *n*-paraffins, the Gibbs energy change is now

$$\Delta G = \Delta H_m(T/T_m - 1) + \Delta H_r(T/T_r - 1) \quad (7)$$

Equation 7 is the correct expression to use for petroleum waxes, as the *n*-paraffin components are distributed between the oil phase

and an orthorhombic wax phase. In addition, at high pressures, a Poynting correction should be added to eqs 4 or 7; this is described in detail elsewhere.^{18,23,32,33}

Equations 1 and 6 give reasonable limits as the carbon number increases to very large values; the limits are close to the likely value for the melting point of polyethylene.³¹ However, the same is not true for the enthalpy of melting, eq 3, presumably because polyethylene does not form an orthorhombic crystalline structure.

It now seems accepted that the wax phase is a solid solution consisting mainly of *n*-paraffins, the behavior of which deviates significantly from ideal mixing. Using experimental data for solid solutions of *n*-paraffins, Coutinho and Stenby²⁰ showed that the wax solution behavior could be modeled by a form of the Wilson equation

$$G^E/RT = - \sum_i n_i^W \ln \left(\sum_j x_j^W \exp(\lambda_{ji} - \lambda_{ii}) \right) \quad (8)$$

where G^E is the excess Gibbs energy, R is the gas constant, and n_i^W and x_i^W are the mole numbers and mole fractions of component i in the wax phase, respectively. The Wilson parameters are estimated from

$$\lambda_{ii} = -\frac{1}{3}(\Delta H_{\text{sub},i} - RT) \quad (9)$$

where $\Delta H_{\text{sub},i}$ is the enthalpy of sublimation of component i obtained as the sum of the enthalpies of melting and vaporization at the normal melting point.²⁰ The expression for the cross-terms between components i and j is

$$\lambda_{ij} = \alpha_{ij} \min(\lambda_{ii}, \lambda_{jj}) \quad (10)$$

α_{ij} is a correction factor that takes into account end effects in the wax crystal.

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 in which a number of solid phases may arise.²² The experimental evidence suggests that the range of carbon numbers found within a single *n*-paraffin solid solution is no more than about 5–6. To represent this, Coutinho proposed an alternative expression for the wax phase on the basis of the Uniquac equation

$$G^E/RT = \sum_i n_i^W \left[\ln \left(\frac{r_i}{\sum_j x_j^W r_j} \right) + 3q_i \ln \left(\frac{q_i \sum_j x_j^W r_j}{r_i \sum_j x_j^W q_j} \right) - q_i \ln \left(\frac{\sum_j x_j^W q_j \exp(\lambda_{ji} - \lambda_{ii})}{\sum_j x_j^W q_j} \right) \right] \quad (11)$$

where the Uniquac parameters for component i are estimated from

$$q_i = 0.1N_i + 0.1141 \quad (12)$$

$$r_i = 0.1N_i + 0.0672 \quad (13)$$

where N_i is the carbon number of component i .

For the Uniquac model

$$\lambda_{ij} = \min(\lambda_{ii}, \lambda_{jj}) \quad (14)$$

The Uniquac wax equation predicts that the wax phase splits into

(28) Chevallier, V.; Provost, E.; Bourdet, J. B.; Bouroukba, M.; Petitjean, D.; Dirand, M. *Polymer* **1999**, *40*, 2121.

(29) Briard, A. J.; Bouroukba, M.; Petitjean, D.; Hubert, N.; Moise, J. C.; Dirand, M. *Fuel* **2005**, *84*, 1066.

(30) Broadhurst, M. G. *J. Res. Nat. Bur. Stand.* **1962**, *66A*, 241.

(31) Marano, J. J.; Holder, G. D. *Ind. Eng. Chem. Res.* **1997**, *36*, 1895.

(32) Pauly, J.; Daridon, J.-L.; Sansot, J. M.; Coutinho, J. A. P. *Fuel* **2003**, *82*, 595.

(33) Pauly, J.; Daridon, J.-L.; Coutinho, J. A. P.; Dirand, M. *Fuel* **2005**, *84*, 453.

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 to the Wilson model, it predicts slightly lower amounts of wax precipitated and slightly lower WAT, although the differences are not large. However, for engineering applications, the Wilson model has the advantage of being easier to use because it treats the wax as a single phase. In this work, we used the correction factor α_{ij} in the Wilson model to bring the results as close as possible to those from the Uniquac model while retaining the convenience of treating the wax as a single phase. The expression used was

$$\alpha_{ij} = 1 - 8 \times 10^{-7} |\Delta H_{\text{sub},i} - \Delta H_{\text{sub},j}| \quad (15)$$

Phase Equilibria

To apply the model, it is necessary to compute the equilibrium between the wax and the fluid phases. From the equations above coupled with a standard cubic equation of state for the fluid phases, it is possible to compute the Gibbs energy of any phase. For example, the Gibbs energy of the wax phase is found by summing the Gibbs energies of the liquid n -paraffins (given by the fluid-phase equation of state) plus their Gibbs energies of fusion and then adding the excess Gibbs energy for the wax phase. Equilibrium occurs for the phase distribution in which the Gibbs energy is at a minimum. The fugacity coefficients ϕ_i of component i can be derived as follows

$$\ln \phi_i = \frac{\partial}{\partial n_i} \left(\frac{G - G^{\text{id}}}{RT} \right) \quad (16)$$

where n_i is the mole number of component i , G is the Gibbs energy of the phase in question and G^{id} is the Gibbs energy of an ideal gas phase of the same composition, temperature, and pressure. The fugacities are then defined as

$$f_i = p x_i \phi_i \quad (17)$$

It can be shown that at equilibrium, the fugacities of each component have the same value in all the coexisting phases. In general, there is the possibility of any combination of the following phases: vapor, hydrocarbon liquid, and wax. If water is present, an aqueous liquid phase can also form; if the Uniquac wax model is used, there may be several wax phases. To solve this potentially complex problem, we used the *Multiflash* multiphase equilibrium program.³⁴ The algorithm uses a phase-stability test³⁵ and a phase-split procedure³⁶ as described by Michelsen; both procedures require that the fugacities of a phase can be calculated as a function of its composition. The phase stability test can determine if it is possible to split a new phase off from an existing phase, i.e., the formation of a new phase is found to lower the Gibbs energy. The phase split procedure finds the equilibrium point for a given set of coexisting phases by adjusting the phase fractions and compositions until the fugacities of the components are the same in all the phases, i.e., the Gibbs energy is at a minimum. The algorithm can be summarized as follows:

- (1) Start with a single phase (e.g., oil phase) with a composition set equal to the overall fluid composition.
- (2) Apply the phase stability test to detect if a new phase may form.
- (3) If no new phase forms, stop, as the solution has been found.
- (4) If a new phase forms, apply the phase-split procedure to find the equilibrium point.
- (5) If the phase fraction of a phase goes to zero, eliminate it.
- (6) Go back to Step 2.

(34) Counsell, J. F.; Moorwood, R. A. S.; Szczepanski, R.; VLE '90, Aston University, Birmingham, U.K., June 1990.

(35) Michelsen, M. L. *Fluid Phase Equilib.* **1982**, *9*, 1.

(36) Michelsen, M. L. *Fluid Phase Equilib.* **1982**, *9*, 21.

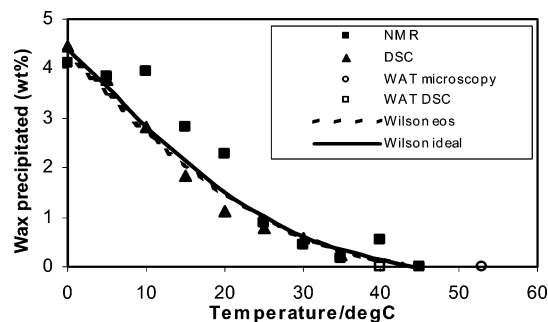


Figure 4. Wilson + EOS wax model compared with ideal mixing.

The algorithm predicts which phases must be present and in what amounts for any overall composition, pressure, and temperature. It has the advantage that the solution is completely rigorous, i.e., it follows entirely from the expressions for the Gibbs energies of the phases assumed in model.

Results and Discussion

Dead Oils. Much of the experimental effort in wax studies has gone into measuring WAT; for a discussion of the experimental issues see refs 8–10.^{8–10} Generally, cross-polar microscopy (CPM) is now considered to be one of the most accurate techniques for measuring WAT. In fact, the whole wax precipitation curve is a better indicator of wax deposition tendency, but less has been published on this problem. Apart from CPM, most of the methods of measuring WAT can also be used; commercial laboratories frequently use differential scanning calorimetry (DSC), as it is relatively inexpensive.

The Rønningsen data^{37,38} 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 compositional analyses are also reported. These data have been used to evaluate the performance of the proposed model concerning the prediction of wax formation.

To illustrate various possibilities for applying the proposed model, oil 3 from the paper of Rønningsen et al. was selected. The n -paraffin distribution was not measured for this sample, so the distribution was estimated using the method previously proposed.¹⁹ 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.¹⁹ (In all figures, wax precipitation is expressed as percentage of total fluid.) The experimental values for the amount of wax precipitated are the original nuclear magnetic resonance (NMR) measurements quoted by Rønningsen et al. and values calculated from DSC traces for the same oil. The close agreement between the equation-of-state (EOS) approach and the method previously used by Coutinho and Daridon¹⁹ shows that the method proposed on the basis of the use of an equation of state to describe the liquid phase 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

(37) Rønningsen, H. P.; Bjørndal, B.; Hansen, A. B.; Pedersen, W. B. *Energy Fuels* **1991**, *5*, 895.

(38) Pedersen, K. S.; Skovborg, P.; Rønningsen, H. P. *Energy Fuels* **1991**, *5*, 924.

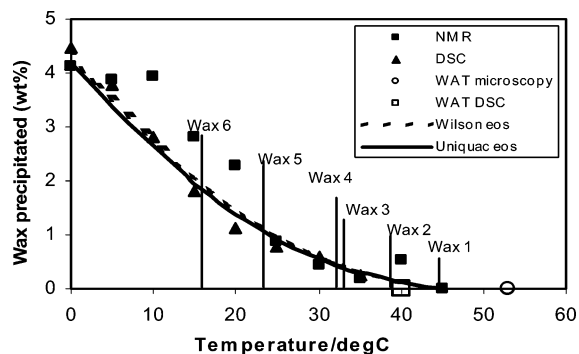


Figure 5. Wilson & Uniquac + EOS wax models compared.

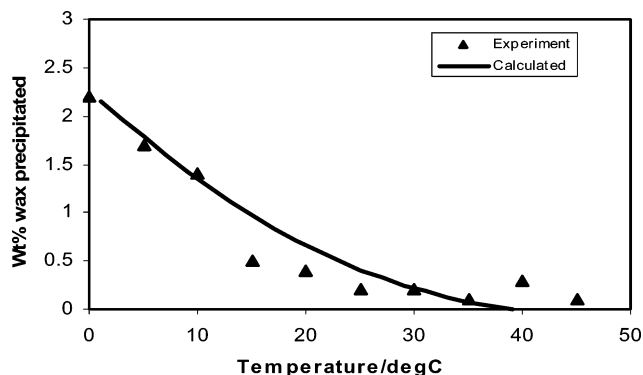


Figure 8. Rønningsen oil 2.

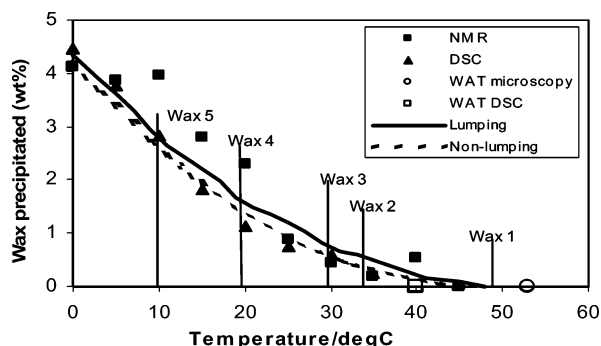


Figure 6. Uniquac + EOS wax model with and without lumping.

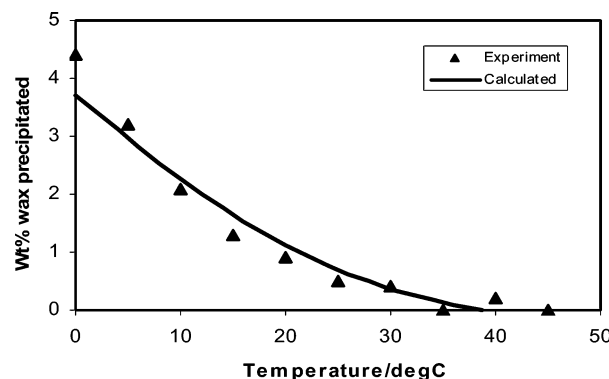


Figure 9. Rønningsen oil 4.

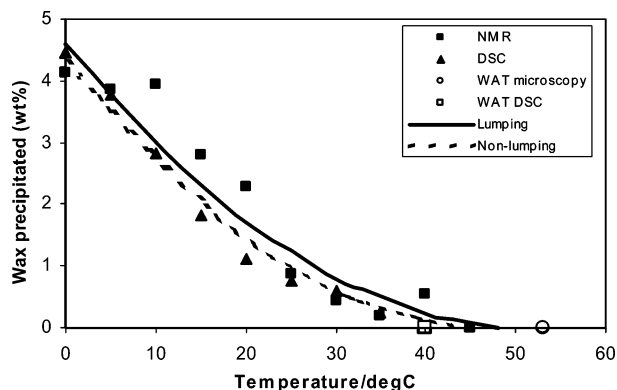


Figure 7. Wilson + EOS wax model with and without lumping.

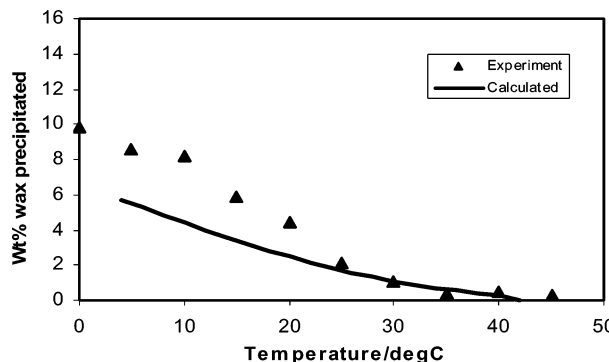


Figure 10. Rønningsen oil 5.

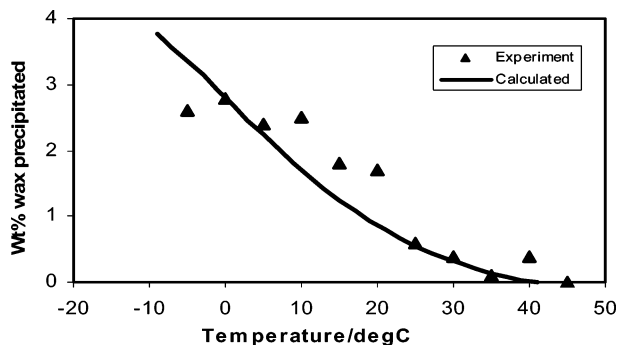


Figure 11. Rønningsen oil 7.

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; this behavior is an artifact of the lumped model. Figure 7 shows the effect of lumping the *n*-paraffins in oil 3 into 15 pseudocomponents using the Wilson wax model. The predicted amount of wax precipitated and 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 behavior 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 the above-mentioned procedure for using the SRK equation to describe of the oil phase. The Peng–Robinson equation can alternatively be used with very similar results.

Figures 8–19 show the wax curves predicted by the model for most of the other oils reported by Rønningsen. As no measured *n*-paraffin distributions are available, it was necessary as before for oil 3 to estimate them in every case using the

method proposed by Coutinho and Daridon.¹⁹ The results are entirely predictive; none of the calculated wax curves has been fitted to the data. The general agreement is good considering the *n*-paraffin distributions are estimated.

To obtain the most reliable wax calculations, it is best to use measured rather than estimated *n*-paraffin concentrations. However, even though modern gas chromatograms can deter-

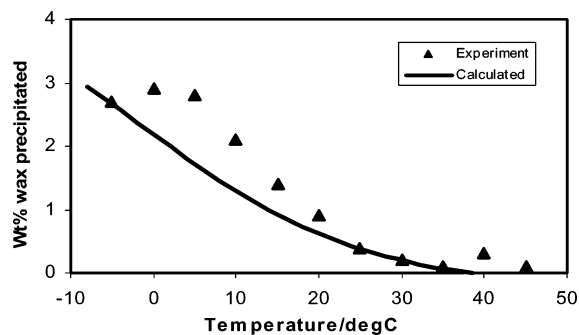


Figure 12. Rønningens oil 8.

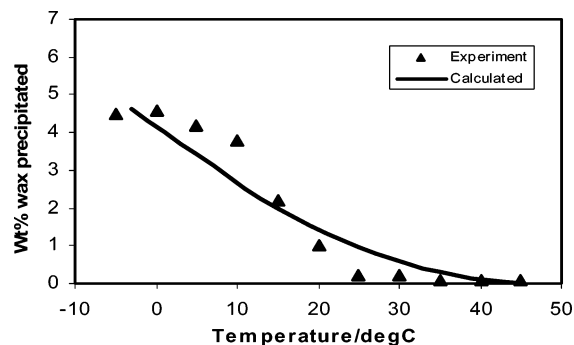


Figure 16. Rønningens oil 14.

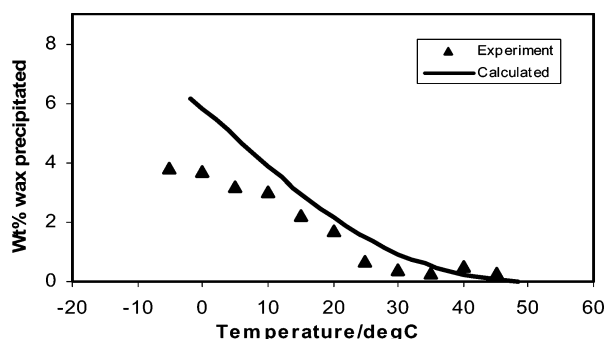


Figure 13. Rønningens oil 9.

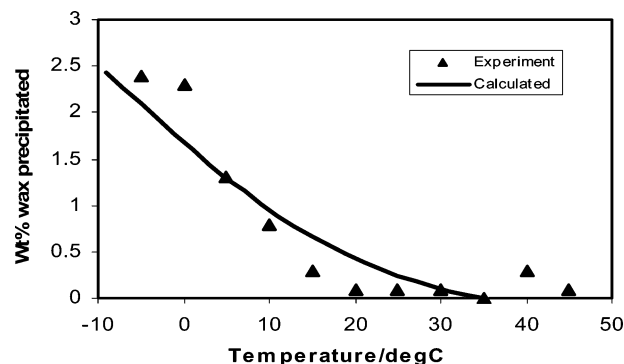


Figure 17. Rønningens oil 15.

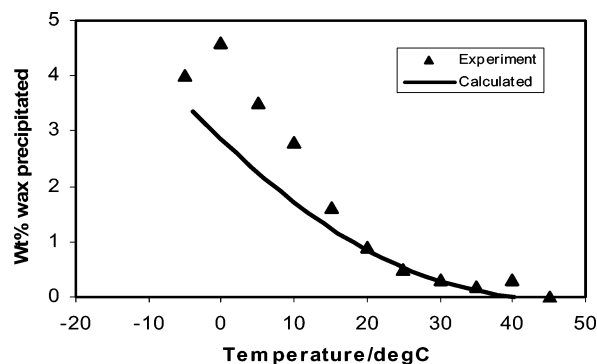


Figure 14. Rønningens oil 10.

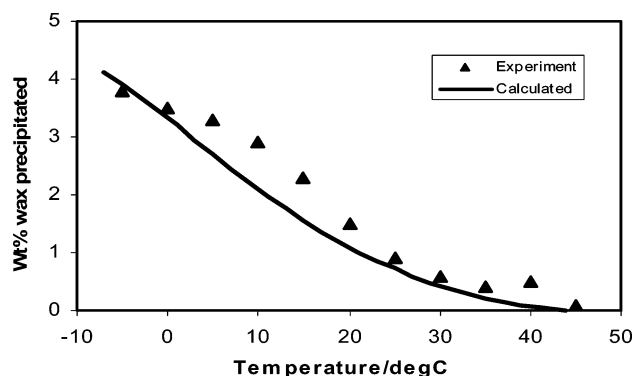


Figure 18. Rønningens oil 16.

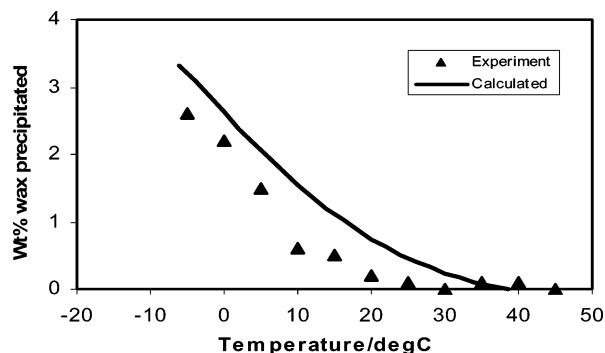


Figure 15. Rønningens oil 12.

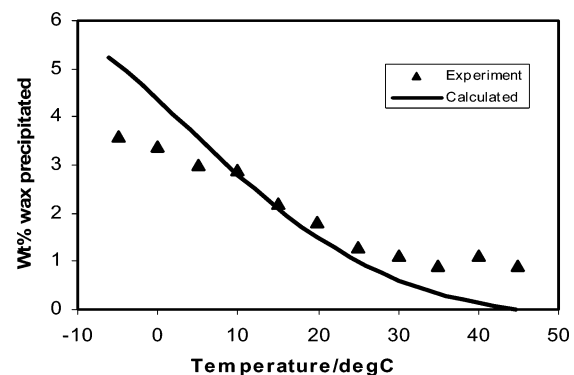


Figure 19. Rønningens oil 17.

mine 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 *n*-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 considered is *n*-C55. Agreement is good aside 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

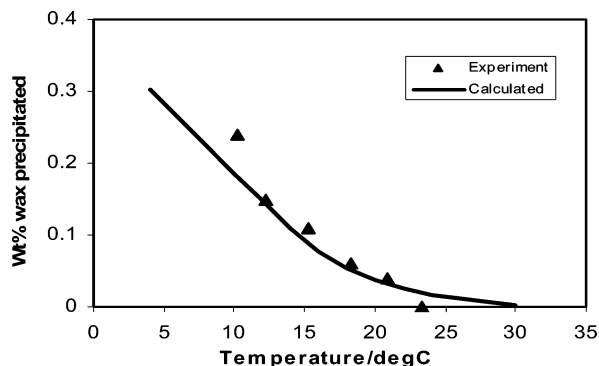


Figure 20. Erickson et al. oil 6.

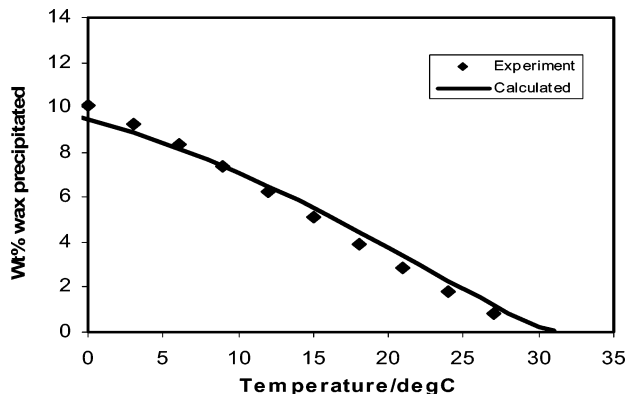


Figure 21. Calange Brut X.

calculate accurately as it is strongly influenced by the traces of the heaviest *n*-paraffins present in the oil. Bearing this in mind, we are not surprised by the divergence between calculated and experimental WAT in Figure 20. At 23 °C, the model predicts that only 0.025 wt % wax will precipitate from the oil, which may well be on the limit of detection; the true WAT could well be higher.^{8–10}

Another example where *n*-paraffin content was measured is the oil Brut X reported by Calange.³⁹ The *n*-paraffin analysis goes to *n*-C40 and it was extrapolated as for the example from Erickson et al. The results reported in Figure 21 show excellent agreement.

Live Oils. A major benefit of the proposed model is that it uses an equation of state to describe the fluid phases. It is therefore not only compatible with most commercial oil simulators but can also be used to calculate oil–wax equilibria at high 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; an increase in pressure always shifts the equilibrium in favor 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.³⁴ The phase behavior is now far more complex: besides the direct 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.¹⁸ reported data for two North Sea oils that included *n*-paraffin analyses; the uncertainty of these data is about 2 K. 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

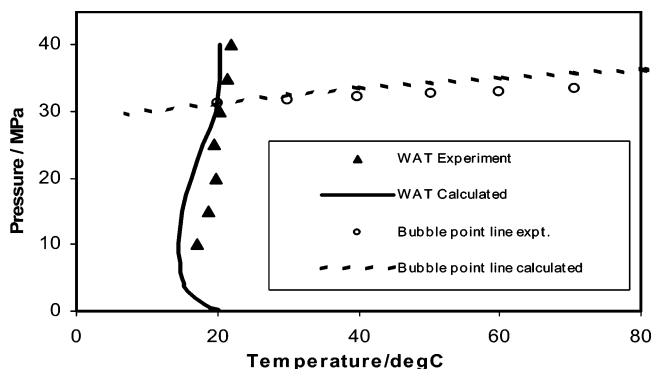


Figure 22. Daridon et al. oil B.

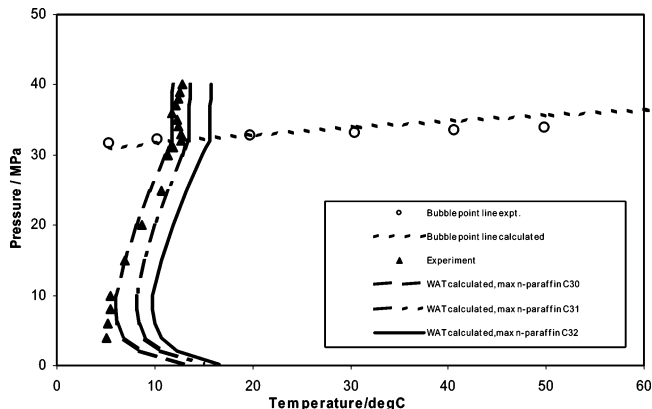


Figure 23. Daridon et al. oil A.

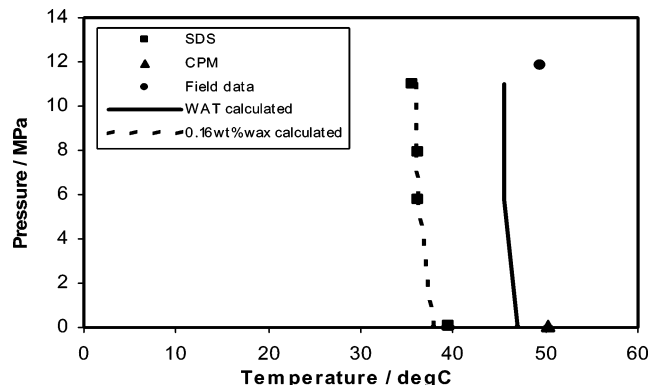


Figure 24. Hammami and Raines oil A-1.

are also good. 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, the calculated WAT is very sensitive to the heaviest *n*-paraffins. To illustrate this, if we reduce the reported upper limit of the *n*-paraffin distribution for oil A by a carbon number of 1 or 2, we obtain the dashed curves in Figure 23, which are in better agreement with experimental values.

Figure 24 shows the results for the live oil A-1 reported by Hammami and Raines.⁴⁰ The reported *n*-paraffin analysis was not consistent with the total wax content, so in this case, we used the same method as that discussed above to estimate the *n*-paraffin distribution from the total wax content. The calculated WAT is about 3 °C lower than the value found by CPM and field data but higher than the values found from Hammami and

(39) Calange, S. Ph. D. Thesis, Institut Français du Pétrole, Paris, 1996.

(40) Hammami, A.; Raines, M. SPE 38776, 1997.

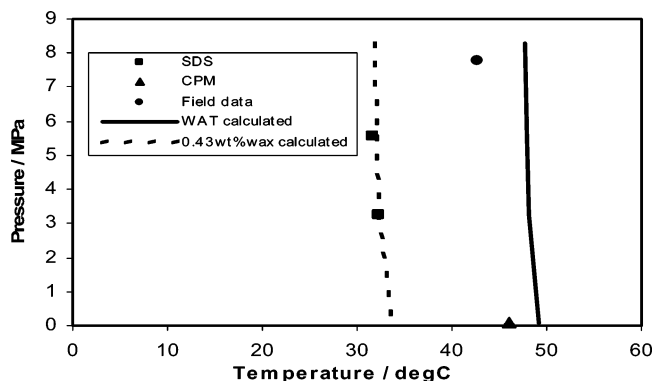


Figure 25. Hammami and Raines Oil A-2.

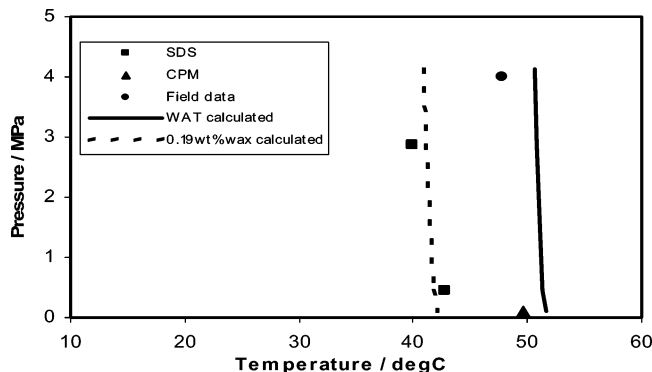


Figure 26. Hammami and Raines oil A-10.

Raines' laser-based solids detection system (SDS). The SDS method is less sensitive and detects the point where a finite amount of wax forms. The calculated line for 0.16 wt % 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 0.43 wt % wax precipitation from the model. For A-10, the calculated WAT is 1.7 °C higher than that for the CPM measurement. The SDS measurements correspond to 0.19 wt % wax precipitation from the model.

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

Importance for Wax Deposition. A major application of wax calculations for crude oils is flow assurance, for which the rate of wax deposition is a key factor. Industry standard methods

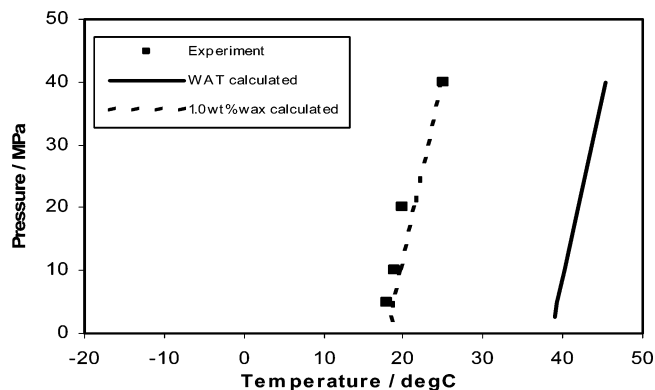


Figure 27. Rønningsen et al.⁵ oil 10.

are based on Fick's law of diffusion for estimating the kinetics of the deposition process (although the observed deposition rates are often inconsistent with the expected values for the diffusion coefficient⁴¹).

To perform a diffusion calculation, it is necessary to know the underlying thermodynamic driving force toward equilibrium. If this is not accurately known, the calculated deposition rate will be proportionally inaccurate. The driving force does not depend on the value of the WAT, but mostly on the shape of the precipitation curve below the WAT. The wax model proposed here 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 modeling.

Conclusions

The predictive local composition model is directly based on accurate, laboratory-determined thermodynamic data; it has been found to accurately predict the waxing behavior of diesel fuels, jet fuels, and crude oils. This paper shows how the model can be used in conjunction with conventional equations of state for the fluid phases. The model requires the *n*-paraffin distribution of the fluid, which can be obtained from gas chromatography or estimated from the available data. 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. Developing a physically realistic description of the kinetics of the wax deposition process will be the subject of a future paper.

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(41) Brown, T. S., Niesen, V. G., Erickson, D. D., SPE 26548, Society of Petroleum Engineers' Annual Technical Conference and Exhibition, Houston, Oct 3–6, 1993.