

Computational Phase Behavior—Final Project

A short review on

Wax Deposition

Based on Chapter 11 of Phase Behavior of Petroleum Reservoir Fluids

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Executive Summary

This report serves as an introduction to the problem of wax formation and its thermodynamic modeling. Wax deposition in surface equipment and production pipelines gives rise to a wide variety of problems encountered in the petroleum industry and therefore proper modeling of deposition is very important. The major topics covered here are based on Chapter 11 of [1]; however, when necessary, the referenced papers are studied and summarized.

Introduction

Wax precipitation considerations

High viscosity and high yield stress for restarting flow

Especially at the beginning of the flow, since there is no wax layer acting as an insulation layer on the surface of the pipe wall, bulk temperature drops below WAT and causes solid wax formation in the oil phase. This causes alteration in oil phase viscosity. Not only does it make it higher but also, it changes the viscosity to be non-Newtonian. Consequently, high yield stress will be required to restart the flow.

Pigging frequency

Pigging is a method to mechanically remove the wax layer from the pipeline which can also be expensive. Therefore, the pigging frequency should be determined optimally. The pipeline pigging frequency is dependent upon the deposit strength which is mainly controlled by the deposit thickness and the deposit wax fraction. That is why a reliable modeling is required to predict wax deposition accurately.

Insulation layer design

Experiments have shown that temperature is the only dominant factor affecting wax precipitation. So, having temperature close to WAT and above is desirable. In subsea pipeline, an insulation layer around the pipe will be efficient as it helps to keep the temperature closer to the oil phase temperature. For optimally design an insulation layer, adequate information about wax precipitation rate should be available.

Wax Measurement

Differential scanning calorimetry

This method is used to detect wax appearance temperature and the temperature range in which wax precipitation occurs.

An oil phase containing wax molecules will be brought to a temperature above WAT. Then, its temperature will be reduced constantly (for example, $\frac{0.5^\circ}{\text{min}}$). This constant temperature reduction will happen through the release of heat which is, only, dependent on oil phase specific heat capacity. However, after reaching WAT, due to solidification process (exothermal process), more heat will be required to be released which ultimately is considered as an indication of wax appearance temperature. This increase in heat release (due to wax precipitation) will be eliminated at a certain temperature which is the lowest temperature in which precipitation occurs.

Modeling of Wax Precipitation

In 1991 a series of four papers were published on *wax precipitation from North Sea crude oils* by various authors [2]–[5]. These papers covered a wide variety of subjects, including analysis of 17 crude oil samples from the North Sea, measurements of wax precipitation temperature (WPT), measurement of solid phase as a function of temperature using pulsed NMR, and thermodynamic modeling. The experimental data presented in these papers have been used to evaluate the accuracy of various thermodynamic models afterward. The results of the wax weight percent as a function of temperature for the first four oils are presented in **Figure 1**. In this report, thermodynamic models are used to model the wax precipitation of oil 1 and the results are presented. The composition of this oil is shown in **Table 1**.

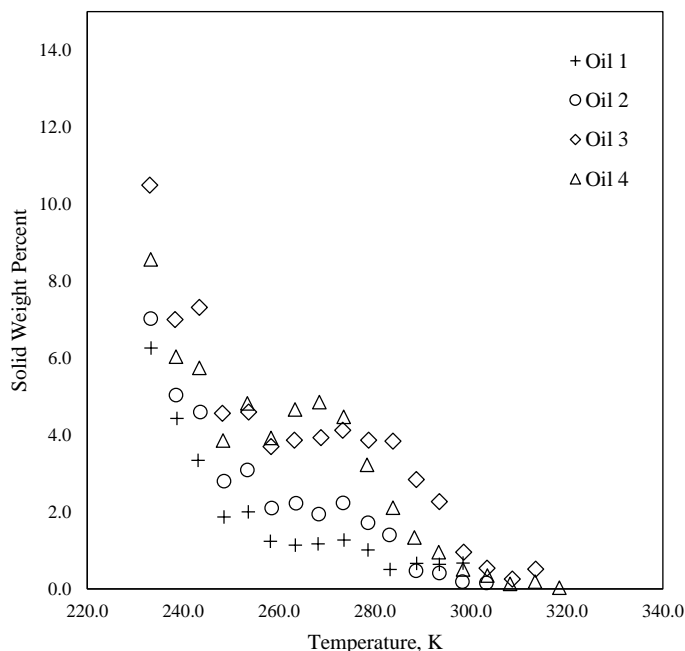


Figure 1—Solid precipitation as a function of temperature for oils 1 through 4 [2]

Thermodynamics

The change in the Gibbs free energy for a pure component is

$$\Delta G_i^f = \Delta H_i^f - T\Delta S_i^f$$

Table 1—Molar Composition of Oil 1

| Comp. | Mole % | MW | Comp. | Mole % | MW | Comp. | Mole % | MW |
|-------|--------|-------|-------|--------|-------|-------|--------|-------|
| C1 | 1.139 | 16.0 | C10 | 5.414 | 132.0 | C21 | 1.936 | 281.0 |
| C2 | 0.507 | 30.1 | C11 | 4.323 | 148.0 | C22 | 2.039 | 293.0 |
| C3 | 0.481 | 44.1 | C12 | 4.547 | 159.0 | C23 | 1.661 | 307.0 |
| iC4 | 0.563 | 58.1 | C13 | 5.289 | 172.0 | C24 | 1.616 | 320.0 |
| C4 | 0.634 | 58.1 | C14 | 4.720 | 185.0 | C25 | 1.421 | 333.0 |
| iC5 | 1.113 | 72.2 | C15 | 4.445 | 197.0 | C26 | 1.233 | 346.0 |
| C5 | 0.515 | 72.2 | C16 | 3.559 | 209.0 | C27 | 1.426 | 361.0 |
| C6 | 2.003 | 86.2 | C17 | 3.642 | 227.0 | C28 | 1.343 | 374.0 |
| C7 | 5.478 | 90.9 | C18 | 3.104 | 243.0 | C29 | 1.300 | 381.0 |
| C8 | 8.756 | 105.0 | C19 | 2.717 | 254.0 | C30+ | 13.234 | 624.0 |
| C9 | 7.222 | 117.7 | C20 | 2.597 | 262.0 | | | |

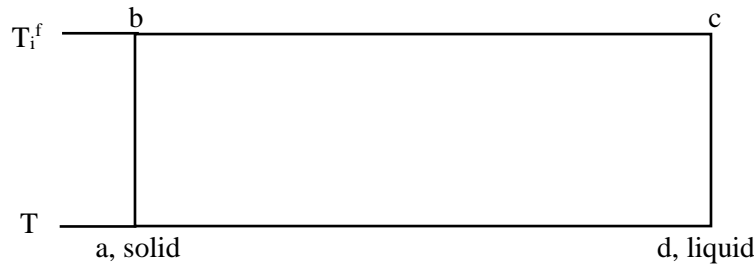


Figure 2—Hypothetical melting process at temperature T

Here f refers to fusion which describes the melting of the pure component i . At melting temperature ($T \neq T_i^f$) the change in Gibbs free energy is zero and therefore the change in the enthalpy can be readily calculated. If the melting of the component i occurs at temperatures other than the melting temperature of this component ($T \neq T_i^f$), one can use the hypothetical melting process shown in **Figure 2**. The change in the enthalpy on the path ad is equal to the summation of the changes in the enthalpy on the paths ab , bc , and cd :

$$\Delta H_{ad} = \Delta H_{ab} + \Delta H_{bc} + \Delta H_{cd} = \Delta H_i^f + \int_T^{T_i^f} \Delta C_{pi} dT$$

where ΔC_{pi} is the difference between the heat capacity of component i at solid and liquid phases. This equation is useful because ΔH_i^f is available for each component. Using similar concept for entropy, one can calculate the change in the Gibbs free energy on the path ad as follows:

$$\Delta G_{ad} = \Delta H_i^f \left(1 - \frac{T}{T_i^f} \right) + \int_T^{T_i^f} \Delta C_{pi} dT - \int_T^{T_i^f} \frac{\Delta C_{pi}}{T} dT$$

We assume that the calculation is performed at a reference pressure, p_{ref} , and all the components of the above equation are available at that pressure. Also, using the relationship between Gibbs free energy and fugacity for real fluids we know:

$$\Delta G_{ad} = RT \ln \left(\frac{f_i^{\circ L}(p_{ref})}{f_i^{\circ S}(p_{ref})} \right)$$

where $f_i^{\circ L}$ and $f_i^{\circ S}$ are the reference fugacities of component i in liquid and solid states. Combining the last two equations and assuming that all calculations are at p_{ref}

$$f_i^{\circ S} = f_i^{\circ L} \exp \left(-\frac{\Delta H_i^f}{RT} \left(1 - \frac{T}{T_i^f} \right) - \frac{1}{RT} \int_T^{T_i^f} \Delta C_{pi} dT + \frac{1}{RT} \int_T^{T_i^f} \frac{\Delta C_{pi}}{T} dT \right)$$

While this equation is written for pure components, the liquid and solid fugacities of a component in the mixture can be calculated using

$$f_i^L = x_i^L \gamma_i^L f_i^{\circ L}$$

$$f_i^S = x_i^S \gamma_i^S f_i^{\circ S}$$

where the terms γ_i^L , γ_i^S and x_i^L , x_i^S are the fugacity coefficients and mole fractions of component i . By combining these two equations with the above equation and by considering the fact that the liquid and solid phase fugacities of a component are equal at equilibrium we get:

$$\frac{x_i^L}{x_i^S} = \frac{\gamma_i^S}{\gamma_i^L} \exp \left(-\frac{\Delta H_i^f}{RT} \left(1 - \frac{T}{T_i^f} \right) - \frac{1}{RT} \int_T^{T_i^f} \Delta C_{pi} dT + \frac{1}{RT} \int_T^{T_i^f} \frac{\Delta C_{pi}}{T} dT \right)$$

By solving the above equation, one can calculate the fraction of each component in each phase as a function of temperature and predict the onset of solid phase formation as well as solid weight percent as a function of temperature. The main challenge remained to solve the above equation is to find an estimation of the fugacity coefficients.

Results

Method of Won

Won used regular solution theory to describe the nonidealities in the solid and liquid phase [6], [7]. Won assumed that the liquid and solid phase heat capacities are equal. With that assumption the thermodynamic model reduces to

$$\frac{x_i^L}{x_i^S} = \frac{\gamma_i^S}{\gamma_i^L} \exp \left(-\frac{\Delta H_i^f}{RT} \left(1 - \frac{T}{T_i^f} \right) \right)$$

Also, he used the regular solution theory to calculate the activity coefficients as follow:

$$\begin{aligned} \ln \gamma_i^L &= \frac{V_i^L (\bar{\delta}^L - \delta_i^L)^2}{RT}, \ln \gamma_i^S = \frac{V_i^S (\bar{\delta}^S - \delta_i^S)^2}{RT} \\ \bar{\delta}^L &= \sum_{i=1}^N \Phi_i^L \delta_i^L, \bar{\delta}^S = \sum_{i=1}^N \Phi_i^S \delta_i^S \\ \Phi_i^L &= \frac{x_i^L V_i^L}{\sum_{j=1}^N x_j^L V_j^L}, \Phi_i^S = \frac{x_i^S V_i^S}{\sum_{j=1}^N x_j^S V_j^S} \\ \delta_i^L &= \sqrt{\frac{\Delta H_i^{vap} - RT}{V_i^L}}, \delta_i^S = \sqrt{\frac{\Delta H_i^{vap} - \Delta H_i^f - RT}{V_i^S}} \end{aligned}$$

In the above set of equations, ΔH_i^{vap} is the molar heat of vaporization for component i and Φ_i^L and Φ_i^S are the volume fractions of component i in liquid and solid phases which is calculated using V_i , molar volume of component i . δ_i^L and δ_i^S represent the activity coefficient of component i in solid liquid and solid phase. He also presented the following correlations for the calculation of ΔH_i^f , T_i^f , and V_i^L , V_i^S

$$\Delta H_i^f = 0.1426 M_i T_i^f$$

$$T_i^f = 374.5 + 0.02617 M_i - \frac{20172}{M_i}$$

$$V_i^L = V_i^S = \frac{M_i}{d_{i,25}^L}$$

$$d_{i,25}^L = 0.8155 + 0.6273 \times 10^{-4} M_i - \frac{13.06}{M_i}$$

The last formula is the liquid phase density of component i at 25°C. The thermodynamic model must be solved for x_i^L , x_i^S . Since the fugacity coefficients on the right hand side are functions of these two components, an iterative procedure must be adopted. This is shown schematically in **Figure .**

Won himself did not have access to experimental data to validate his model; however, Pedersen et al. used his model along with the experimental data from the North Sea. The results for the Won method is showed in **Figure 3**. This figure is regenerated using the method of Won and the MATLAB code presented in **Appendix A** which corresponds to the flowchart of Figure and the data and correlations presented in the literature, some of which were explained earlier ([2], [3]). The results of the Won method are *not satisfactory*. This model clearly overestimates the wax precipitation (same behavior was observed for other 17 oil samples [3]).

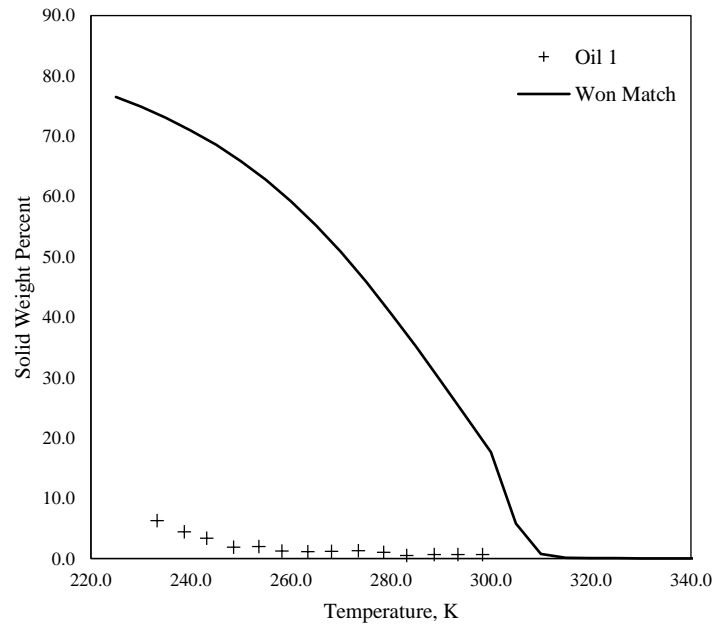


Figure 3—Solid precipitation as a function of temperature using the method of Won.

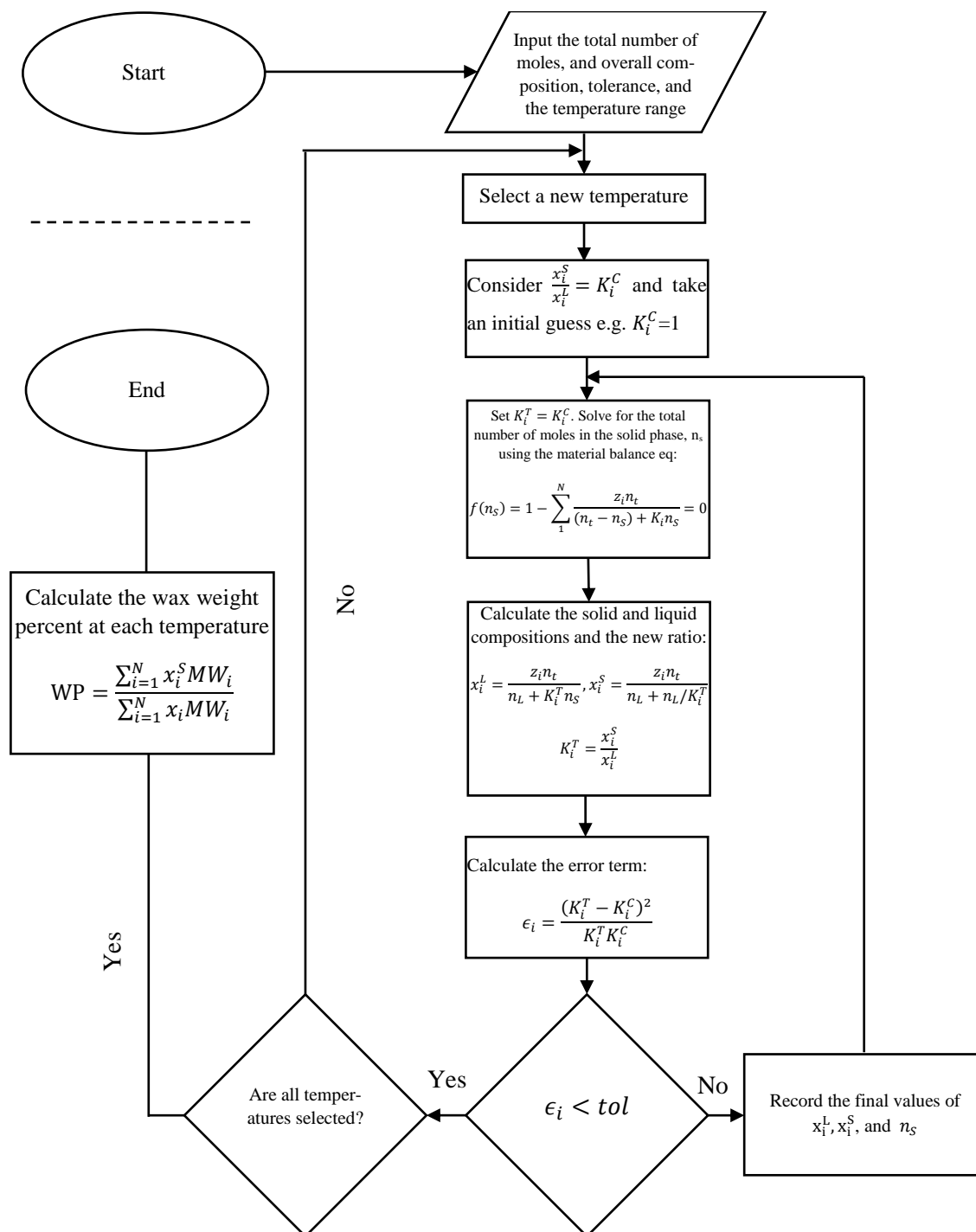


Figure 4—Flowchart for the calculation of liquid-solid equilibrium

Method of Pedersen

Pedersen attributed this to several factors and tried to mitigate this problem by fixing each factor. These factors are (1) the solubility parameter, δ_i^L , δ_i^S , (2) the melting enthalpy of components, ΔH_i^f , and (3) the solid and liquid phase heat capacities, C_p^S , C_p^L .

Pedersen claimed that the solubility parameters calculated in the method of Won are based on literature values for normal paraffins. To take into account the effect of branched paraffins, naphthenes, and aromatics, he used the following set of equations for the solubility parameters:

$$\delta_i^L = 7.41 + a_1(\ln C_N - \ln 7)$$

$$\delta_i^L = 8.5 + a_2(\ln C_N - \ln 7)$$

For C_7 , these equations give values of solubility parameter in accordance with the method of Won. For heavier components, these equations yield larger solubility parameters which was proposed to be in accordance with literature data. a_1 , and a_2 are fitting parameters and must be calculated using by fitting the model to experimental data.

For the melting enthalpies, Pedersen suggested that while the melting enthalpies used in the method of Won is for normal paraffins, petroleum waxes contain many components that have chemical natures different than normal paraffins resulting in much lower melting enthalpies than that of normal paraffins. They suggested to fix this problems using a multiplier as follows:

$$\Delta H_i^f = a_3 \Delta H_{o,i}^f$$

where $\Delta H_{o,i}^f$ is the original enthalpies used in the method of Won and a_3 is a fitting parameter to be determined. Finally, based on experimental data, the assumed that the heat capacity differences, ΔC_{pi} , is a linear function of temperature and proportional to the molecular weight:

$$\Delta C_p^i = a_4 MW_i + a_5 MW_i T$$

where a_4 and a_5 are fitting parameters and are to be determined by fitting the model into experimental data. Using least square fit method and by fitting the model to all the available experimental data the reported the values of $0.5914 \left(\frac{\text{cal}}{\text{cm}^3}\right)^{0.5}$, $5.763 \left(\frac{\text{cal}}{\text{cm}^3}\right)^{0.5}$, 0.5148 , $0.3033 \frac{\text{cal}}{\text{g.K}}$, $-4.635 \times 10^{-4} \frac{\text{cal}}{\text{g.K}^2}$ for a_1 through a_5 , respectively. The results are presented in

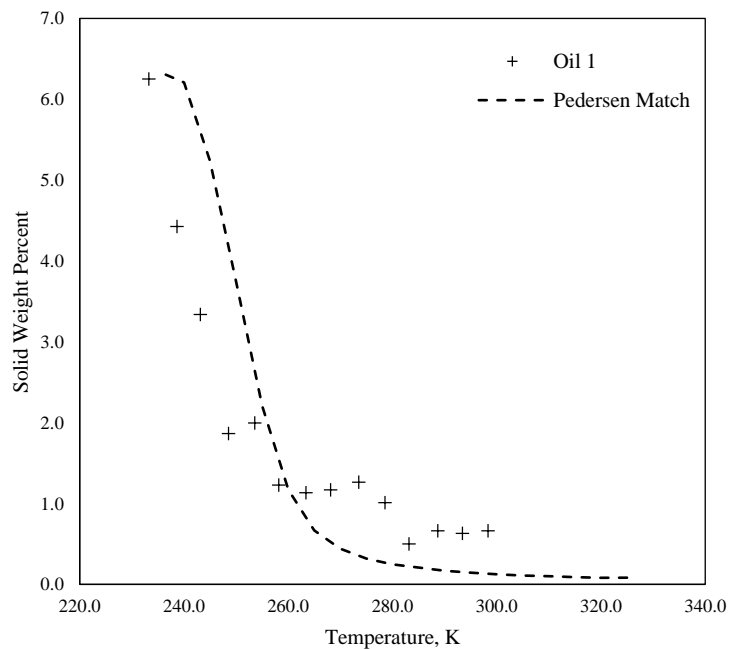


Figure 5—Solid precipitation as a function of temperature using the method of Pedersen.

Figure . For the purpose of this illustration, we made slight changes in the fitting parameters reported by Pedersen to improve the quality of our match. The discrepancies are associated with the fact that Pedersen used the data for up to 60 components while only the data for 30 components are reported in the paper. Nonetheless, it is clear that the method of Pedersen provides the means to improve the match through the use of regression methods.

Other Methods

The majority of the thermodynamic studies of wax focus on the liquid-solid phase equilibrium. In this section, a comprehensive approach will be discussed that successfully targets three phase equilibrium while the proposed modeling approach will, best, fit the experimental data without having to use any fitting parameters to tune the modeling results with experimental data. The proposed approach is based on the assumption that precipitated wax consists of several solid phases; each solid phase is as a pure component/pseudo-component that does not mix with other solid phases (components). The validity of the mentioned assumption has been experimentally proven and accepted widely.

Figure 6, shows a typical vapor-liquid-solid solution model for wax precipitation.

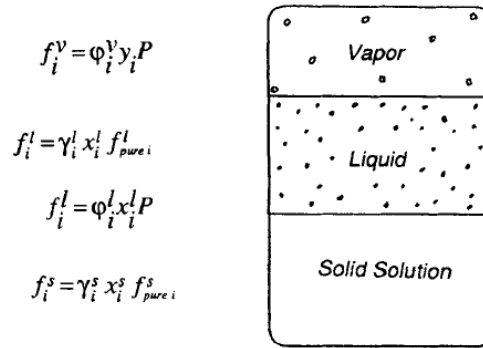


Figure 6, typical three phase solution model for wax precipitation by previous authors.

The activity coefficient approach seemed to overestimate the cloud point temperature. It has been reasoned that since activity coefficient has been chosen to be near unity for wax forming components, the K_i^{sl} -factor only depends on the ratio of $\left(\frac{f_i^l}{f_i^s}\right)_{pure i}$. Many other authors attempted to compensate this overestimation and several new approaches were introduced. However, the main limitation for those approaches were their incomprehensiveness which required them to have fitting parameters to repeat the experimental data.

Firoozabadi model

An innovative method has been proposed that accurately matches the experimental data. In this method, the pseudo components that are responsible for wax precipitation will be determined through the following stability expression.

$$f_i(P, T, z) - f_{pure i}^s(P, T) \geq 0, \quad (i = 1, 2, \dots, N)$$

Where $f_i(P, T, z)$ is the fugacity of component i with feed composition z . The mixture components that fulfill the preceding expression will precipitate, while those that do not, will only be present in the liquid and vapor states. The Peng-Robinson EOS in the form described by Robinson et al. is used for calculating fugacities for components in the fluid phases.

After determining N_s (number of responsible pseudo components in wax precipitation), there are some equations that need to be solved to obtain desired parameters.

EOS and material balance equations

The first step is to characterize the plus fraction. Assigning critical properties and acentric factors to all pseudo components using available correlations.

Then, a system of equations need to be solved simultaneously to give unknown parameters. For liquid-multisolid equilibria, the unknowns are N_s solid-to-feed molar fractions, $\frac{S_i}{F}$, and $(N - 1)$ compositions in the liquid phase, x_i . For vapor-liquid-multisolid systems, the unknowns are $2(N-1)$ compositions for the vapor and liquid phases, y_i x_i^l , respectively, N_s solid-to-feed molar phase fractions, (S_i/F) , and the fraction of feed that exists as vapor, $\frac{V}{F}$.

The equations are as follow:

(1) N vapor-liquid isofugacity equations

$$f_i^v(P, T, y_1, y_2, \dots, y_{N-1}) - f_i^l(P, T, x_1, x_2, \dots, x_{N-1}) = 0, \quad [i = 1, \dots, N]$$

(2) N_s Liquid-solid isofugacity equations

$$f_i^l(P, T, x_1, x_2, \dots, x_{N-1}) - f_{purei}^s(P, T) = 0, \quad [i = (N - N_s) + 1, \dots, N]$$

(3) $N - 1$ material-balance equations

(a) For the non-precipitating components:

$$z_i - x_i^l \left[1 - \sum_j^{N_s} \frac{S_j}{F} - \frac{V}{F} \right] - K_i^{vl} x_i^l \left(\frac{V}{F} \right) = 0 \quad [i = 1, \dots, (N - N_s)].$$

(b) For the precipitating components, where all solid phases are pure:

$$z_i - x_i^l \left[1 - \sum_j^{N_s} \frac{S_j}{F} - \frac{V}{F} \right] - \frac{S_i}{F} - K_i^{vl} x_i^l \left(\frac{V}{F} \right) = 0$$

$$[i = (N - N_s) + 1, \dots, N - 1] \quad (N_s > 1)$$

It is important to note that activity coefficient approach has not been used in this study. And an equation of state which has the best accuracy is applied. Also, all the proposed equations for ΔH_i & T_i^f are based on the fact that they want to be as closely related as possible to all the species of a certain carbon number (Naphthenes, Aromatics and n-Alkanes).

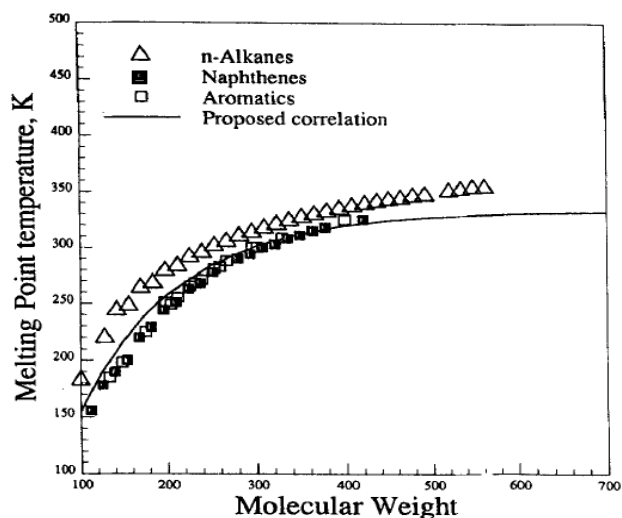


Figure 7, Melting-point temperature of hydrocarbons

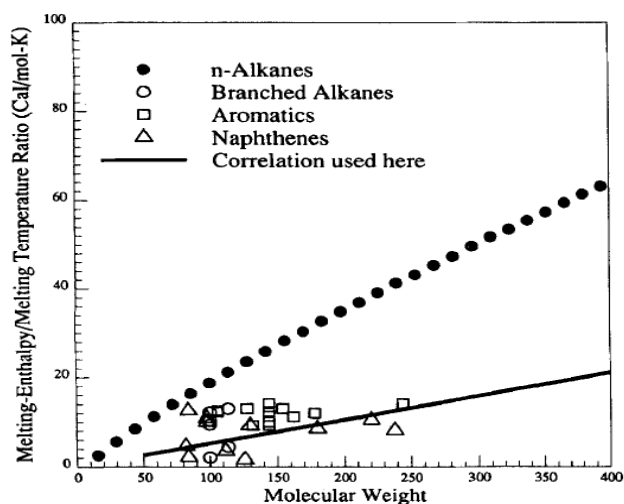


Figure 8, Entropies of fusion of hydrocarbons

Results

The wax fractions for four oil samples measured from the proposed modeling are compared with experimental data reported by Pederson et al.

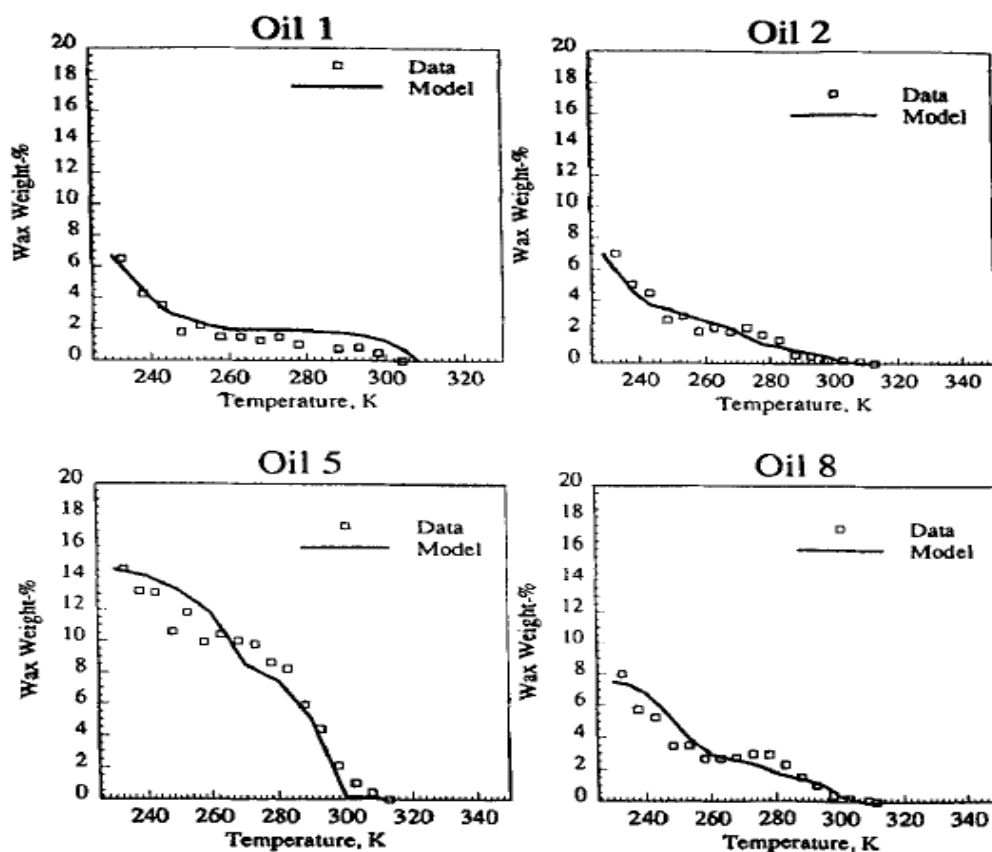


Figure 9, experimental and predicted wax-precipitation results for Oils 1, 2, 5 and 8

Table 2, Experimental and calculated cloud-point temperature

| Oil No. | Exp. K | Calc. K | Exp.-Calc. K |
|---------|--------|---------|--------------|
| 1 | 304.15 | 305.9 | -1.75 |
| 2 | 312.15 | 311.8 | 0.35 |
| 5 | 313.15 | 312.4 | 0.75 |
| 8 | 311.15 | 308.2 | 2.95 |
| 10 | 314.15 | 316.0 | -1.85 |
| 11 | 295.15 | 299.3 | -4.15 |
| 12 | 305.15 | 301.2 | 3.95 |
| 15 | 308.15 | 309.5 | -1.35 |

WinProp

WinProp models wax deposition using multiphase flash calculation. The fluid phases are described using EOS and the fugacities of the components in the solid phase are calculated using the following:

$$\ln f_S = \ln f_S^* + \frac{V_S}{R} \left[\frac{p - p_{tp}}{T} - \frac{p^* - p_{tp}}{T^*} \right] - \frac{\Delta H_{tp}}{R} \left[\frac{1}{T} - \frac{1}{T^*} \right] - \frac{\Delta C_p}{R} \left[\ln \left(\frac{T^*}{T} \right) - T_{tp} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right]$$

For details of this approach see [8]. Use the Asphaltene/Wax modeling module for modeling wax precipitation. There are two tabs in this module that give you a limited number of options. In Calculations tab, one may enter the pressure and temperature range for which the computations are desired. In the Ref. State tab, there are three options: (1) You can determine the number of components that are allowed to exist in the solid phase, (2) you can select a calculation ID which determines how the stability analysis are performed which will in turn influence the convergence of the model, and (3) you can select how the reference fugacities in the above model are calculated (correlation, input data, etc.) The results for Oil 1 are shown in Figure . The results suggest that while WinProp rather accurately predicts the WAT, it overestimates the solid weight percent at all temperatures. We tried all the options WinProp provides to improve the match; however, none of them resulted in a better match. One may consider using the regression module to improve the results.

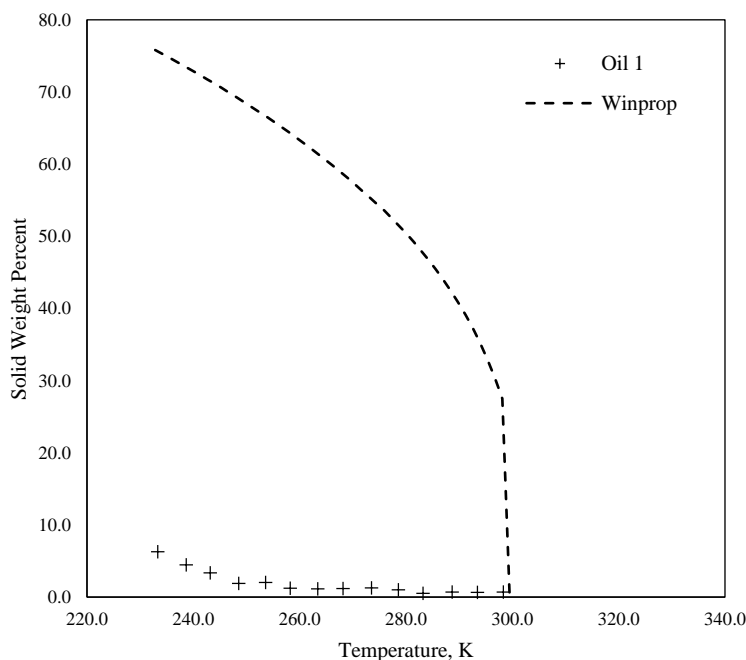


Figure 10—Wax precipitation match for Oil 1 using WinProp

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