



PETROLEUM SCIENCE AND TECHNOLOGY  
Vol. 21, Nos. 3 & 4, pp. 409–424, 2003

## A Systematic Method to Predict Cloud Point Temperature and Solid Precipitation

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### ABSTRACT

Solid precipitations (or depositions) in crude oil operations are undesirable because they may eventually plug the process equipment and/or pipelines; as such, accurate prediction of cloud point temperature is essential in the design and operation of many oil production facilities. Determining the cloud point temperature of a mixture requires a robust solution of a multiphase, multicomponent phase equilibrium problem. Solution of the phase equilibrium problem rests on the relations set by the Gibbs criterion for stable equilibrium and the principle of mass conservation. Mathematically, two solution methods are used to characterize the equilibrium properties of a mixture at given temperature and pressure: the equal-fugacity

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(iteration-function formulation) and the Gibbs free energy minimization approach. In addition, an accurate solution model capable of predicting multiphase formation is required. In this study, we implement the iteration function method enhanced with a solid-liquid-vapor phase-check procedure to calculate cloud point temperatures and the amount of solid precipitations. The Peng-Robinson equation of state with a modified  $\alpha$  function, as suggested by Gasem et al. (2001), was utilized to model vapor-liquid equilibria while regular solution theory was used to describe solid-liquid equilibria. We also present a systematic method to characterize the heavy components of oil. The results of this study are in excellent agreement with experimental cloud point temperature and solid precipitation data for four North Sea oils reported by Pedersen et al. (1991).

## INTRODUCTION

Wax deposition problems have long been recognized in the oil industry. This deposition occurs when crude oil is exposed to cold temperatures such as those commonly encountered in the arctic regions or cold oceans. Wax deposition problems have caused significant losses due to reduced production, well shut-in, failure of equipment, and additional horsepower requirements.

Cloud point temperature is defined as the temperature at which a small amount of solid precipitates. When the temperature of a crude oil being processed or transported is lower than the cloud point temperature, the heavy hydrocarbons contained in the oil may precipitate as a solid waxy material. Therefore, to avoid wax deposition in crude oil operations, reliable predictions of cloud point temperatures and amounts of solid precipitation are required.

Naturally occurring oil and gas mixtures consist of many components. Pedersen et al. (1989) classified the components of an oil mixture into three groups: the defined components, the true boiling point (TBP) fractions, and the TBP residue. The defined components encompasses non-hydrocarbons and hydrocarbons up to hexane ( $C_6$ ), where their critical temperature ( $T_c$ ), critical pressure ( $P_c$ ), and the acentric factor ( $\omega$ ) are well defined. The TBP fractions cover the fractions of  $C_7$  up to  $C_{30}$ , where each fraction contains different components and information may only be available for density and the average molecular weight of each fraction. The TBP residue consists of components that are too heavy to be separated and usually left as one fraction. Measurements for density, mole fractions, and average molecular weight of this fraction are typically available.



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Often considering the TBP residue as one component, the equilibrium phase behavior predictions using equations of state (EOS) will be inaccurate (Chorn and Mansoori, 1989). Therefore, a representative characterization of the TBP residue is essential for predicting cloud point temperature and solid precipitation. The characterization procedure involves two steps: First, the TBP residue is broken into a number of pseudocomponents, where their mole fractions and density distributions can be determined. Next, the TBP fractions and pseudocomponents are assigned critical property and acentric factor values. Several correlations are available for estimating  $T_c$  and  $P_c$  and  $\omega$  of pseudocomponents (see, e.g., Cavett, 1964; Gasem et al., 1993; Kesler and Lee, 1976). In this study, a model recently suggested by Gao et al. (2001) is used to estimate the pseudocomponents'  $T_c$ ,  $P_c$ , and  $\omega$  directly without the need for normal boiling point temperatures.

Once a suitable distribution function for the TBP fractions is identified, the TBP residue is broken into several pseudocomponents by extrapolation. This technique has been used by several researchers. For example, Won (1986) and Pedersen et al. (1989) used an exponential distribution function with two adjustable parameters. In this study, the same function is used. However, we have devised a new algorithm to determine the adjustable parameters for matching the average molecular weight and mole fraction of the pseudocomponents with those of the TBP residue.

Here, the cloud point temperatures and solid precipitations are determined using the split approach, where the liquid–vapor equilibria is modeled using the Peng–Robinson (Peng and Robinson, 1976) cubic equation of state, while liquid–solid equilibria is described using regular solution theory. Flash calculations using the conventional iteration function method (IFM) enhanced with the solid–liquid–vapor phase-check procedure are performed. The phase-check procedure is used to determine the number of phases present at the operating conditions of interest. Data for four oils collected from the North Sea, as described by Pedersen et al. (1991), are used in this study. Those oils are categorized as aromatic oil (Oil 1), paraffinic oil (Oil 2 and Oil 8), and waxy oil (Oil 5).

### MOLE FRACTION DISTRIBUTION OF HEAVY COMPONENTS

We have used the following exponential distribution function to represent the TBP fraction:

$$z_j = \exp(A + B \times MW_j) \quad (1)$$



where  $A$  and  $B$  are adjustable parameters, and  $z_j$  and  $MW_j$  are the mole fraction and molecular weight of component  $j$ , respectively. For pseudocomponents, the molecular weight is related to the carbon number as:

$$MW_j = -4 + 14CN_j \quad (2)$$

where  $CN_j$  is the carbon number of component  $j$ . To ensure that the distribution of pseudocomponents is reflecting the actual condition of the TBP residue, two constraints are imposed. The first constraint requires that the total mole fraction of pseudocomponents should be the same as the mole fraction of TBP residue expressed as:

$$\sum_{j=1}^n \exp(A + B \times MW_j) = z_{\text{residue}} \quad (3)$$

Note that in Eq. (3), the summation begins from the first pseudocomponent, not the first component in the mixture. The second constraint states that the average molecular weight of the pseudocomponents should be the same as the molecular weight of the TBP residue, or:

$$\frac{\sum_{j=1}^n z_j MW_j}{\sum_{j=1}^n z_j} = MW_{\text{residue}} \quad (4)$$

The molecular weight of each pseudocomponent is estimated using Eq. (2). The following two residual functions

$$f(A, B) = \sum_{j=1}^n \exp(A + B \times MW_j) - z_{\text{residue}} \quad (5)$$

$$g(A, B) = \frac{\sum_{j=1}^n MW_j \exp(A + B \times MW_j)}{\sum_{j=1}^n \exp(A + B \times MW_j)} - MW_{\text{residue}} \quad (6)$$

are solved simultaneously to determine the parameters  $A$  and  $B$  that match the mole fraction and molecular weight of the TBP residue. These residual functions are derived by rearranging Eq. (3) and substituting Eq. (1) into Eq. (4).

### CRITICAL PROPERTIES AND ACENTRIC FACTOR ESTIMATES

Accurate estimations of critical properties and acentric factor are important in determining the solid precipitation when an equation of state is used. Pedersen et al. (1984) applied Cavett's (1964) and Kesler



Table 1. The ABC model parameters.

	Critical temperature $T_c$ (K)	Critical pressure, $P_c$ (MPa)	Acentric factor, $\omega$
$Y_\infty$	981.8	0	5.492
$Y_0$	370.1	4.244	0.1515
$\alpha$	1.276	1	0.6851
$\beta$	0.1435	0.3757	0.06859
$\gamma$	0.6667	0.5684	0.6667

and Lee (1976) correlations, and Avaulee et al. (1997, 2001) developed correlations based on group characteristics for estimating those properties. The asymptotic behavior correlation (ABC) as suggested by Gasem and coworkers (1993) and updated recently by Gao et al. (2001) is used in this study to calculate the critical properties and acentric factor of heavy  $n$ -paraffins. The ABC model is expressed as:

$$Y = [Y_\infty^\alpha - (Y_\infty^\alpha - Y_0^\alpha) \exp(-\alpha\beta(CN^\gamma - CN_0^\gamma))]^{1/\alpha} \quad (7)$$

where  $Y$  is the selected property,  $CN_0$  is the initial property values ( $CN_0=3$ ),  $Y_\infty$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  are constants. The ABC model constants for estimating  $T_c$ ,  $P_c$ , and  $\omega$  are given in Table 1. The ABC model is capable of representing experimental  $T_c$ ,  $P_c$ , and  $\omega$  measurements of  $n$ -paraffins to  $n$ -C<sub>20</sub> with average absolute percent deviations (%AAD) of 0.2, 0.8, and 0.4%, respectively.

## THERMODYNAMIC MODELS

For multicomponent systems where most of the components are not normal fluids, accurate phase behavior can be obtained by implementing the split approach. This approach utilizes different thermodynamic models to describe the liquid–vapor and solid–liquid behavior at equilibrium.

### Vapor–Liquid Model

The vapor–liquid equilibrium constant can be calculated as:

$$K_j^{VL} = \frac{\hat{\phi}_j^L}{\hat{\phi}_j^V} \quad (8)$$



where  $K_j^{VL}$  is the vapor–liquid equilibrium constant of component  $j$ ,  $\hat{\phi}_j$  is the fugacity coefficient of component  $j$  in the mixture, and the superscripts  $L$  and  $V$  denote the liquid and vapor phases, respectively. In this study, the Peng–Robinson equation of state with modified temperature dependence ( $\alpha$  function), as proposed by Gasem et al. (2001), is applied. The  $\alpha$  function takes the form:

$$\alpha = \exp\left[(A + BT_r)(1 - T_r^{C+D\omega+E\omega^2})\right] \quad (9)$$

where  $T_r$  is the reduced temperature ( $=T/T_c$ ), and  $A$  to  $E$  are model parameters. Values of these parameters are:  $A=2.00$ ,  $B=0.836$ ,  $C=0.134$ ,  $D=0.508$  and  $E=-0.0467$ . This new  $\alpha$  function improves the vapor pressure predictions especially for heavier hydrocarbons (AAD of 1% for the 28 pure fluids considered).

### SOLID–LIQUID MODEL

The solid–liquid equilibrium constants of component  $j$  can be written as:

$$K_j^{SL} = \frac{s_j}{x_j} = \frac{\gamma_j^L}{\gamma_j^S} \exp\left[\frac{\Delta H_j^f}{RT} \left(1 - \frac{T}{T_j^f}\right) - \frac{1}{RT} \int_T^{T_j^f} (C_{pj}^L - C_{pj}^S) dT + \frac{1}{R} \int_T^{T_j^f} \frac{C_{pj}^L - C_{pj}^S}{T} dT\right] \quad (10)$$

where for component  $j$ ,  $K^{SL}$  is the solid–liquid equilibrium constant,  $s$  and  $x$  are the mole fractions of the solid and liquid phase, respectively,  $\gamma$  is the activity coefficient,  $\Delta H^f$  is the heat of fusion,  $C_p$  is the heat capacity, and  $T^f$  is the fusion temperature.  $R$  is the universal gas constant,  $T$  is the temperature, and superscripts  $L$  and  $S$  denote the liquid and solid phases, respectively. By substituting the correlation for the liquid–solid heat capacity change, as given by Pedersen and Skovborg (1991),

$$\Delta C_{pj} = MW_j(a_1 + a_2 \cdot T)$$

Eq. (10) can be written as:

$$K_j^{SL} = \frac{\gamma_j^L}{\gamma_j^S} \exp\left[\frac{\Delta H_j^f}{RT} \left(1 - \frac{T}{T_j^f}\right) + \frac{a_1 MW_j}{R} \left(\frac{T_j^f}{T} - 1 - \ln \frac{T_j^f}{T}\right) - \frac{a_2 MW_j}{2R} \left(\frac{(T_j^f)^2}{T} + T - 2T_j^f\right)\right] \quad (11)$$



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where  $a_1 = 0.3033$  cal/(g.K) and  $a_2 = -4.635 \times 10^{-4}$  cal/(g.K). For the pseudocomponents,  $T_j^f$  and  $\Delta H_j^f$  are calculated from correlations given by Won (1986) and Pedersen and Skovborg (1991) as:

$$T_j^f = 374.5 + 0.02617MW_j - \frac{20172}{MW_j} \quad (12)$$

$$\Delta H_j^f = a_3 \times MW_j \times T_j^f \quad (13)$$

where  $a_3 = 0.07341$  (cal/g). In Eq. (11),  $\gamma_j^L$  and  $\gamma_j^S$  are calculated using a modified regular solution theory as suggested by Won (1986):

$$\ln \gamma_j = \frac{v_j(\bar{\delta} - \delta_j)^2}{RT} \quad (14)$$

where  $\bar{\delta} = \sum_j \Lambda_j \delta_j$  and  $\delta_j$  are the average solubility and the solubility parameter of component  $j$ , respectively,  $v_j$  is the molar volume of component  $j$ , and  $\Lambda_j$  is the volume fraction of component  $j$ .  $\Lambda_j$  for the liquid and solid phases are defined, respectively, as:

$$\Lambda_j^L = \frac{x_j v_j}{\sum_i x_i v_i} \quad (15)$$

$$\Lambda_j^S = \frac{s_j v_j}{\sum_i s_i v_i} \quad (16)$$

The following correlations for the solubility parameters in (cal/cm<sup>3</sup>)<sup>0.5</sup> were introduced by Pedersen and Skovborg (1991) to account for the paraffinic and naphthenic contributions of C<sub>7+</sub>:

$$\delta_j^L = 7.41 + 0.594(\ln CN - \ln 7) \quad (17)$$

$$\delta_j^S = 8.50 + 5.763(\ln CN - \ln 7) \quad (18)$$

Won (1986) used the following expression for the liquid and solid molar volume in cm<sup>3</sup>/mol:

$$v_j = v_j^L = v_j^S = \frac{MW_j}{d_{j,25}^L} \quad (19)$$

where  $d_{j,25}^L$  is the liquid phase density (in g/cm<sup>3</sup>) of component  $j$  at 25°C and is expressed by Eq. (20) below:

$$d_{j,25}^L = 0.8155 + 0.6272 \times 10^{-4} \times MW_j - \frac{13.06}{MW_j} \quad (20)$$

**SOLID-LIQUID-VAPOR PHASE CHECK**

The broad volatility and melting point range of hydrocarbons found in petroleum lead to various formation of vapor, liquid, and solid phases in response to changes in pressure, temperature, or composition. The Rachford-Rice (Rachford and Rice, 1952) iteration function can be extended for three-phase equilibrium system and expressed as:

$$F_1(\alpha_S, \alpha_V) = \sum_j \frac{z_j(K_j^{SL} - 1)}{1 + \alpha_S(K_j^{SL} - 1) + \alpha_V(K_j^{VL} - 1)} = 0 \quad (21)$$

$$F_2(\alpha_S, \alpha_V) = \sum_j \frac{z_j(K_j^{VL} - 1)}{1 + \alpha_S(K_j^{SL} - 1) + \alpha_V(K_j^{VL} - 1)} = 0 \quad (22)$$

where  $\alpha_S$  and  $\alpha_V$  are the solid fraction and vapor fraction, respectively.

For a given  $T$ ,  $P$  and the estimate values for  $K^{SL}$  and  $K^{VL}$ , one to three phases may exist in equilibrium. To avoid false solutions and convergence problems when performing equilibrium calculations with an inappropriate number of phases, we have implemented the solid-liquid-vapor phase-check procedure as proposed by Sofyan (2001). By incorporating the phase-check procedure, the calculation with the higher number of phases is only performed if the phase check on the lower number of phases fails. The phase-check procedure for the existence of a single phase and of two phases is summarized as follows:

**A Single Phase Exists**

(i) only vapor phase:

$$\sum_j z_j \frac{K_j^{SL}}{K_j^{VL}} < 1 \quad \text{and} \quad \sum_j \frac{z_j}{K_j^{VL}} < 1 \quad (23)$$

(ii) only liquid phase:

$$\sum_j z_j K_j^{VL} < 1 \quad \text{and} \quad \sum_j z_j K_j^{SL} < 1 \quad (24)$$

(iii) only solid phase:

$$\sum_j \frac{z_j}{K_j^{SL}} < 1 \quad \text{and} \quad \sum_j z_j \frac{K_j^{VL}}{K_j^{SL}} < 1 \quad (25)$$



**Two Phases Exist**

(i) vapor and liquid phase:

$$\sum_j \frac{z_j}{K_j^{VL}} > 1, \quad \sum_j z_j K_j^{VL} > 1 \quad (26)$$

and  $F_1(0, \alpha_V) < 0$  at the root of  $F_2(0, \alpha_V) = 0$ 

(ii) solid and liquid phase:

$$\sum_j z_j K_j^{SL} > 1, \quad \sum_j \frac{z_j}{K_j^{SL}} > 1 \quad (27)$$

and  $F_2(\alpha_S, 0) < 0$  at the root of  $F_1(\alpha_S, 0) = 0$ 

(iii) solid and vapor phase:

$$\sum_j z_j \frac{K_j^{SL}}{K_j^{VL}} > 1, \quad \sum_j z_j \frac{K_j^{VL}}{K_j^{SL}} > 1 \quad (28)$$

and  $F_2(\alpha_S, 1 - \alpha_S) > 0$  or  $F_1(1 - \alpha_V, \alpha_V) > 0$  at the root of  $F_1(\alpha_S, 1 - \alpha_S) - F_2(\alpha_S, 1 - \alpha_S) = 0$ 

If three phases are present, the iteration functions, Eqs. (21) and (22), are solved simultaneously for  $\alpha_S$  and  $\alpha_V$ . The new mole fraction of component  $j$  in the liquid, solid, and vapor phases can be calculated as:

$$x_j = \frac{z_j}{1 + \alpha_S(K_j^{SL} - 1) + \alpha_V(K_j^{VL} - 1)} \quad (29)$$

$$s_j = K_j^{SL} x_j; \quad y_j = K_j^{VL} x_j \quad (30)$$

**CLOUD POINT TEMPERATURE ALGORITHM**

The algorithm for calculation may be summarized as follows:

1. Perform characterization procedure.
2. For the given feed composition, generate initial-guess values for  $K_j^{VL}$  and  $K_j^{SL}$ .
3. Perform a phase-check procedure by satisfying the condition given by Eqs. (23) to (28).
4. If a one-phase or two-phase system is identified, calculate the mole fraction distributions for the liquid, solid, and vapor phases using Eqs. (29) and (30).



5. If a three-phase system is identified, solve Eqs. (21) and (22) simultaneously for  $\alpha_S$  and  $\alpha_V$ , and calculate the mole fraction distributions for the liquid, solid, and vapor phases using Eqs. (29) and (30).
6. Use the thermodynamic models to update values of  $K_j^{VL}$  and  $K_j^{SL}$  using Eqs. (8) to (20).
7. Compare the new value of  $K_j^{VL}$  and  $K_j^{SL}$  to the old ones. If they do not satisfy the convergence criteria, go back to Step 3.
8. Observe the amount of solid phase fraction generated. If it is not within the specified tolerance, increase the temperature and use the new values of  $K_j^{VL}$  and  $K_j^{SL}$  and go back to Step 3. Otherwise, cloud point temperature is determined; stop the process.

The solid weight percent is calculated as:

$$\text{Sol. Wgt\%} = 100 \frac{\alpha_S \sum_j s_j MW_j}{\sum_j z_j MW_j} \quad (31)$$

## RESULTS AND DISCUSSION

Figure 1 presents the mole fraction distribution using the characterization technique developed in this study as applied to the data given by Pedersen et al. (1989). As shown in this figure, the new procedure produces results that are in excellent agreement with those of Pedersen and coworkers.

Won (1986) provided a detailed description of a representative case study. The required physical properties for a forty-component system were given, except for the acentric factor. We have considered this to be a suitable case study for validating the present algorithm. Figure 2 presents our results for this case study, where we used acentric factor estimates from the Kesler and Lee (1976) correlation and the initial guesses  $K_j^{VL} = P_{cj}/P \exp[5.42(1 - T_{cj}/T)]$  and  $K_j^{SL} = \exp[\Delta H_j^f/RT(1 - T/T_j^f)]$ . As indicated by the figure, our predictions are in excellent agreement with comparable work by Won (1986).

The effect of  $\Delta C_p$  and  $\delta$  on the amount of solid precipitation is shown in Fig. 3. The triangles are the results obtained when  $\Delta C_p$  effect is neglected. The diamonds represent the results obtained using  $\delta^S$  and  $\delta^L$  as given by Won (1986), which are close in value to those of normal paraffins. As shown in this figure,  $\Delta C_p$  impacts the predictions for solid precipitation because it effects the solubility of the heavier hydrocarbons



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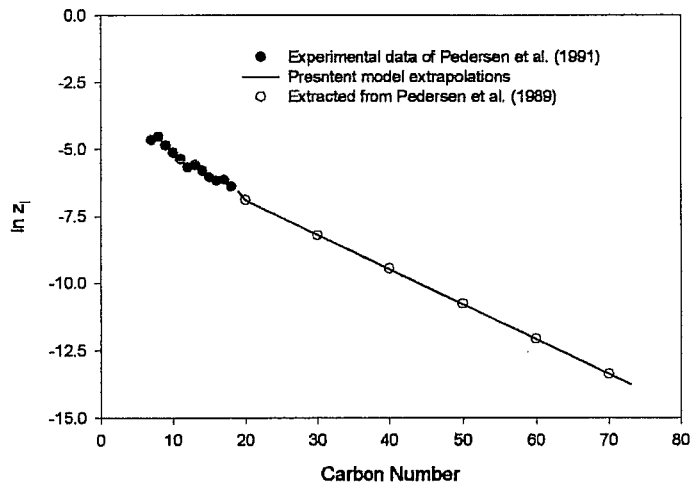


Figure 1. The pseudocomponents distribution obtained from the present exponential function compared with the work of Pedersen et al. (1989).

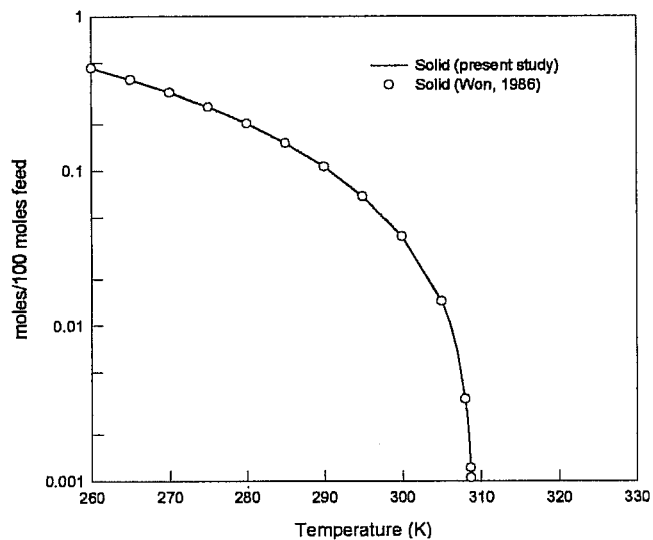


Figure 2. The amount of solid precipitation generated in the present study compared to those of Won (1986).

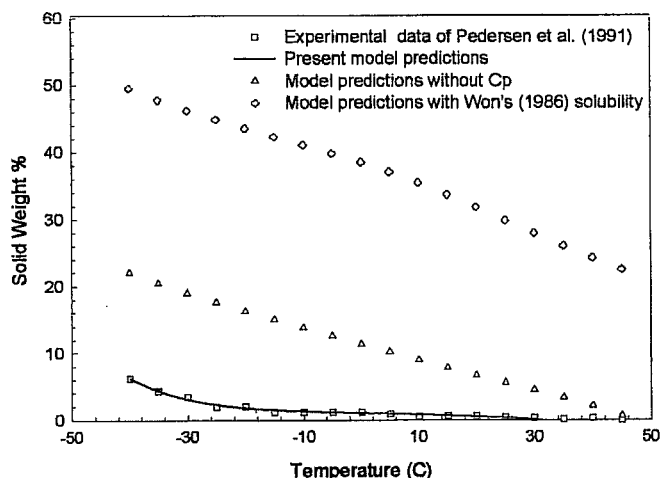


Figure 3. Model predictions for Oil 1 showing the effect of  $\Delta C_p$  and the solid solubility parameter suggested by Won (1986).

in the mixture (Pedersen et al., 1991). The results also indicate that  $\delta$  has a significant impact on predicting the solid precipitation.

An oil mixture consists of numerous components including paraffinic, naphthenic, and aromatic groups; therefore, substantially increasing the value of  $\delta^S$  for *n*-paraffins, as given by Won (1986), results in good agreement between measured and calculated solid (wax) precipitation estimates. The requirement for larger  $\delta^S$  values suggests that the non-ideality of the wax phase is much more pronounced than the solid solutions of *n*-paraffins.

As observed by Pedersen and Skovborg (1991), the measured  $\Delta H^f$  for twelve different oils are four to seven times greater than estimates generated by Eq. (13). This indicates the need for improved estimates for the multiplier of  $\Delta H^f$  (i.e., constant  $a_3$  in Eq. (13)), which would provide more accurate predictions of solid precipitation. In this study, the experimental solid-precipitation data of sixteen North Sea oils, as provided by Pedersen et al. (1991), are used to regress the optimum value of  $a_3$  for each oil. A fourth-degree polynomial correlation as a function of temperature provides accurate representation of the oils considered. The amount of solid precipitated using this correlation for Oil 2, Oil 5, and Oil 8 are given in Figs. 4 to 6, respectively. As shown in the figures, the experimental data are represented reasonably well. Also, an excellent agreement is obtained between experimental and



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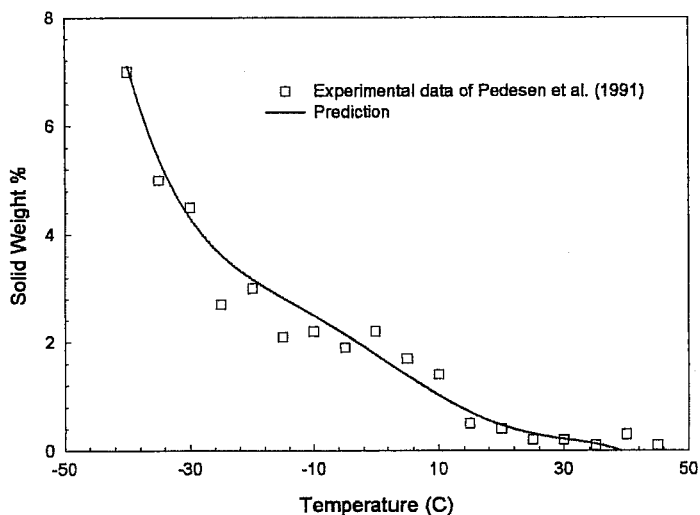


Figure 4. The amount of solid precipitation for Oil 2 when we apply:  $\Delta C_p$ , a solid solubility parameter higher than that of Won (1986), and better estimates for  $\Delta H^f$ .

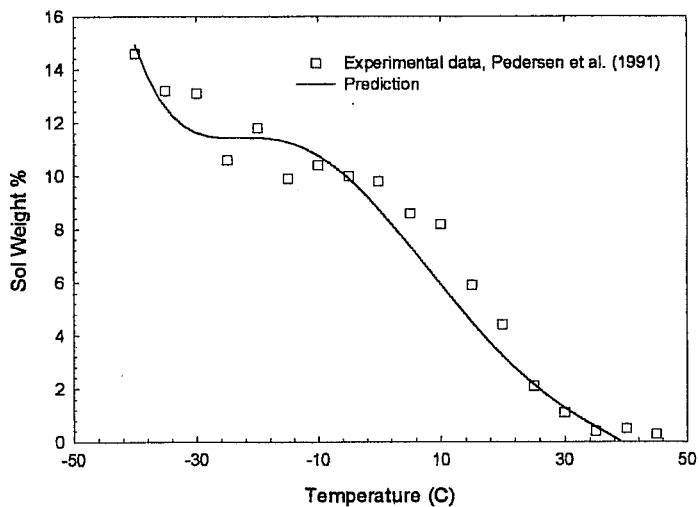


Figure 5. The amount of solid precipitation for Oil 5 when we apply:  $\Delta C_p$ , a solid solubility parameter higher than that of Won (1986), and better estimates for  $\Delta H^f$ .

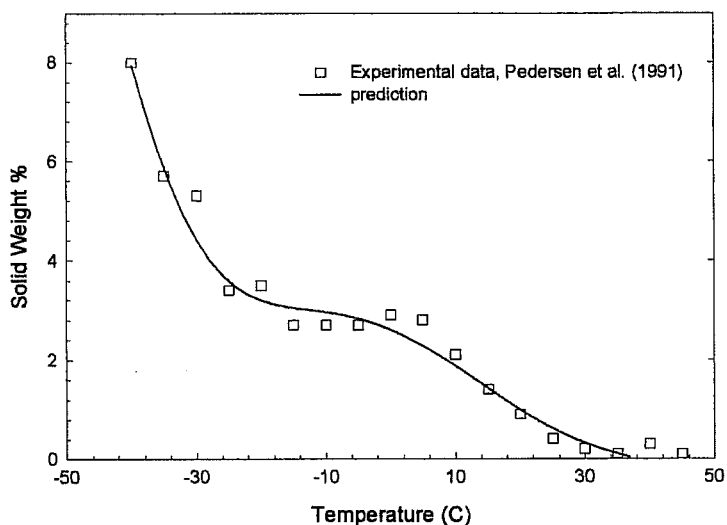


Figure 6. The amount of solid precipitation for Oil 8 when we apply:  $\Delta C_p$ , a solid solubility parameter higher than that of Won (1986), and better estimates for  $\Delta H^f$ .

Table 2. Experimental and calculated cloud point temperatures.

Oil No.	Cloud Point Temperature ( $^{\circ}\text{C}$ )		Deviation ( $^{\circ}\text{C}$ )
	Measured*	Calculated	
1	30.5	31	-0.5
2	38.5	39	-0.5
5	39.5	39	0.5
8	38	37	1

\*Pedersen et al. (1991).

calculated cloud point temperatures, as shown in Table 2 (deviations within  $0.5^{\circ}\text{C}$ ).

The pronounced discrepancy in the calculated  $\Delta H^f$  by Pedersen and Skovborg (1991) is attributed to the fact that their correlation only considered  $\Delta H^f$  for the liquid-wax transition, which is fairly small as compared with  $\Delta H^f$  for the phase transitions taking place in the already formed wax. Due to the phase transitions, the wax consists of two or

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more solid phases. The model proposed by Lira-Galeana et al. (1996) provided a good representation of the multilayers of solid phase that formed wax. However, to match the solid precipitation data, Lira-Galeana et al. (1996) also developed a correlation for  $\Delta H^f$  to accurately represent the heat of fusion of paraffinic, naphthenic, and aromatic hydrocarbon groups. A general review addressing solid–solid and solid–liquid transition temperatures and enthalpies can be found in Dirand et al. (2002).

**CONCLUSIONS**

The present results indicate that the proposed algorithm for calculating cloud point temperatures and the amount of solid precipitation is effective. Specifically, the current implementation of the iteration function method enhanced with (a) a solid–liquid–vapor phase-check procedure, (b) a representative characterization procedure, and (c) a careful calibration of the solution models leads to precise representation of the cloud point temperatures and the amount of solid precipitation.

The accuracy of the predictions for cloud point temperature and the amount of solid precipitation is affected significantly by the characterization procedure and the thermodynamic model for describing the liquid–wax transitions. In particular, accurate predictions for the cloud point temperature and wax precipitation require accurate values for the pseudocomponents (a) heat of fusion, (b) solid solubility parameter, and (c) fusion heat capacity.

**REFERENCES**

- Avaulee, L., Neau, E., Jaubert, J. N. (1997). *Fluid Phase Equilibria* 141:87.
- Avaulee, L., Duchet-Suchaux, P., Durandea, M., Jaubert, J. N. (2001). *Journal of Petroleum Science and Engineering* 30:43.
- Cavett, R. H. (1964). 27th Midyear Meeting, API Division of Refining, San Francisco: CA, May 15.
- Chorn, L. G., Mansoori, G. A. (1989). *Advances in Thermodynamics, C<sub>7+</sub> Fraction Characterization*, L. G. Chorn and G. A. Mansoori eds. New York: Taylor & Francis.
- Dirand, M., Bouroukba, M., Chevallier, V., Petitjean, D., Behar, E., Ruffier-Meray, V. (2002). *J. Chem. Eng. Data* 47:115.
- Gasem, K. A. M., Gao, W., Robinson, Jr., R. L. (2001). *Fluid Phase Equilibria* 181:113.



- Gasem, K. A. M., Ross, C. H., Robinson, Jr., R. L. (1993). *Can. J. Chem. Eng.* 71:805.
- Gao, W., Robinson, Jr., R. L., Gasem, K. A. M. (2001). *Fluid Phase Equilibria* 179:207.
- Kesler, M. G., Lee, B. I. (1976). *Hydrocarbon Processing* 55:153.
- Lira-Galeana, C., Firoozabadi, A., Prausnitz, J. M. (1996). *AIChE J.* 42:239.
- Pedersen, K. S., Thomassen, P., Fredenslund, Aa. (1984). *Ind. Eng. Chem. Process Des. Dev.* 23:163.
- Pedersen, K. S., Fredenslund, Aa., Thomassen, P. (1989). Properties of Oils and Natural Gases. *Contribution in Petroleum Geology and Engineering*. Vol. 5. Chilingar, G. V., ed. Gulf Publishing Co.
- Pedersen, K. S., Skovborg, P. (1991). *Energy & Fuels* 5:924.
- Pedersen, W. B., Hansen, A. B., Larsen, E., Nielsen, A., Ronningsen, H. P. (1991). *Energy and Fuel* 5:908.
- Peng, D. Y., Robinson, D. B. (1976). *Ind. Eng. Chem. Fund.* 15:59.
- Sofyan, Y. (2001). Development of Multiphase Equilibrium Algorithms: Cloud Point Temperature and Solid Precipitation Predictions. PhD Thesis, Mechanical Engineering, Oklahoma State University at Stillwater.
- Rachford, H. H. Jr., Rice, J. D. (1952). *JPT* 4:19.
- Won, K. W. (1986). *Fluid Phase Equilibria* 30:265.