A Thermodynamic Model for Predicting Wax Formation in Crude Oils

Most crude oils contain high molecular weight components, which at low temperatures may precipitate as a wax phase. This may cause plugging of pipes and numerous other problems. This paper presents a solid-liquid equilibrium based model for the description of wax formation. The model for the Gibbs energy contains a contribution based on Flory's theory of multicomponent polymer solutions and a contribution from a metastable subcooled state which oil mixtures may attain. The latter is formulated in terms of the surface tension of the wax phase. Experimental wax appearance points (temperatures), WAP's, are reported for 17 different stabilized North Sea crude oils. The values predicted by the new model are in very good agreement with the experimental WAP's.

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Introduction

The majority of crude oils contains heavy hydrocarbons, which at low temperatures may precipitate as a wax phase. Wax precipitation may cause plugging of pipes and process equipment. This is particularly troublesome when oil mixtures are transported across arctic regions or cold oceans. When designing pipelines and process equipment it is of great importance to be able to calculate the wax appearance point (WAP, the temperature at which the first small amount of wax is formed) and the amount of wax formed at given conditions.

Description of the Wax

The first compounds to freeze out from a crude oil when the temperature decreases are paraffins (P) and naphthenes (N). The wax phase formed will often consist of orthorhombic crystals. This is the case when the temperature is decreased slowly and the wax phase formed consists solely of molecules of type P and N. A fast temperature decrease will introduce crystal imperfections and the same is the case for special flow patterns.

Another reason for formation of imperfections in the crystal lattice is the incorporation into the lattice of heavy aromatics from the crude oil. These heavy aromatic compounds are mainly alkylphenyls. The aliphatic parts of the aromatic compounds are easily incorporated into the orthorhombic structure of the crystal lattice whereas, due to sterical hindrance, the aromatic parts cause lattice imperfections. These lattice imperfections are of great importance, and they must be taken into consideration when modeling the wax formation in hydrocarbon mixtures.

The presence of molecular groups which sterically hinder the formation of a regular crystal lattice results in a wax phase composed of many small, independent crystal lattices. The structure of the wax phase may thus vary between two extremes: an ideal crystalline structure and a structure consisting of many small, independent crystal cell units. The chemical potentials of the constituents of the wax phase will to some extent depend on which of these mesomorphic states is favored by the physical conditions under which the wax formation took place.

Experimental Data

The wax appearance points have been measured on 17 stabilized North Sea crude oils (i.e., the liquid phases obtained when flashing reservoir oils to atmospheric conditions). The measurements were carried out using a LABORLUX 12 microscope (polarized light) with temperature control. The samples were first heated to 70°C to remove all visible wax crystals. Then the temperature was slowly decreased (about 8–10°C per hour), until the first wax crystals appeared. The measurements were repeatable to within about 2°C.

The compositions of two of the 17 oils are shown in Tables 1 and 2. The molar compositions of the remaining 15 oils are included in the supplementary material. The measured WAP's are shown in Table 3.

Table 1. Analytical Data for Mixture No. 1

Wax appearance point: 35°C, measured at 1 atm			
Component	Wt. %	Mol. Wt. g/mol	Density (15°C, 1 atm) g/cm³
$\leq C_4$	0.031	29	0.416
C_5	0.855	71	0.632
C_6	0.737	82	0.695
C_7	2.371	91	0.751
C_8	2.825	103	0.778
C_9	2.539	116	0.793
C_{10+}	90.642	306	0.869
C_{10}	2.479	132	0.798
C_{11}	1.916	147	0.803
C_{12}	2.352	163	0.817
C_{13}	2.091	175	0.836
C_{14}	3.677	190	0.843
C_{15}	3.722	205	0.849
C_{16}	2.034	215	0.853
C_{17}	4.135	237	0.844
C_{18}	3.772	251	0.846
C_{19}	3.407	262	0.857
C_{20+}	61.057	426	0.885
C_{20}	2.781	268	0.868
C_{21}	3.292	284	0.862
C_{22}	3.140	299	0.863
C_{23}	3.445	315	0.863
C_{24}	3.254	330	0.865
C_{25}	2.975	342	0.867
C_{26}	3.038	352	0.869
C_{27}	2.085	371	0.873
C_{28}	2.740	385	0.877
C_{29}	3.178	399	0.881
C_{30+}	31.129	578	0.905

Table 2. Analytical Data for Mixture No. 2

Wax appearance point: 41°C, measured at 1 atm			
Component	Wt. %	Mol. Wt. g/mol	Density (15°C, 1 atm) g/cm³
$\leq C_4$	0.035	38	0.465
C_5	4.061	65	0.605
C_6	2.357	81	0.677
C_7	4.321	97	0.734
C_8	4.570	106	0.756
C_9	4.050	119	0.775
C_{10+}	80.370	317	0.881
C_{10}	2.468	134	0.788
C_{11}	2.558	148	0.791
C_{12}	3.051	162	0.801
C_{13}	2.898	177	0.818
C_{14}	2.541	188	0.830
C_{15}	3.028	201	0.836
C_{16}	2.592	215	0.841
C_{17}	2.609	234	0.839
C_{18}	2.604	250	0.843
C_{19}	2.428	264	0.852
C_{20+}	53.831	489	0.913

Table 3. Calculated and Measured WAP's (K) for 17 Crude Oils

Mix No.	T_{exp}	$T80$ $+\sigma$	$T80$ $-\sigma$	$T20$ $+\sigma$	$T10$ $+\sigma$	$\Delta T80$	T_{Won}
1*	308	304	319	304	305	−4	355
2	314	298	313	299	301	−1	361
3*	289	290	309	286	281	+1	330
4*	298	297	311	297	300	−1	356
5*	292	294	304	293	290	+2	343
6*	291	292	306	289	286	+1	342
7*	287	289	304	283	277	+2	324
8	312	294	308	292	291	−4	343
9	310	294	308	293	291	−2	345
10	312	297	312	296	294	0	346
11*	288	290	304	290	294	+2	358
12*	307	297	311	297	297	+4	354
13*	296	297	312	298	299	+1	358
14*	296	292	307	293	295	−4	361
15*	301	297	311	297	297	−4	357
16*	290	295	310	296	298	+5	364
17*	291	297	312	298	299	+6	358

T_{exp} Measured WAP
$T80$ WAP's calculated using max 80 PN and 80 A components to represent mixture
$T20$ WAP's calculated after grouping into 20 PN and 20 A components
$T10$ WAP's calculated after grouping into 10 PN and 10 A components
$+\sigma$ Contribution to excess Gibbs energy from surface tension of wax phase included
$-\sigma$ Contribution to excess Gibbs energy from surface tension of wax phase not included
$\Delta T80$ Difference between T_{exp} and underlined temperature in $T80$ columns
T_{Won} WAP's calculated using method of Won
* Crude oils used for estimating parameters of Eqs. 12–14

The Model of Won

At equilibrium between a liquid phase (oil, L) and a solid phase (wax, S) the isofugacity criterion ($f_a^S = f_a^L$) applies and the following equation is fulfilled for component a:

$$\ln \frac{a_a^S}{a_a^L} = \frac{\Delta H_a^f}{RT}(1 - T/T_a^f) + \frac{\Delta C_{p,a}}{R}(T_a^f/T - 1) - \frac{\Delta C_{p,a}}{R}\ln (T_a^f/T) \quad (1)$$

In this equation a_a^S is the activity of the component in the solid phase, a_a^L is the activity in the liquid phase, ΔH_a^f is the enthalpy of melting, T_a^f is the melting point temperature, and R is the gas constant. $\Delta C_{p,a}$ is the difference between the molar heat capacities of the substance in the subcooled liquid state and in the solid state. The last two terms in Eq. 1 are close to zero and will be neglected in the following. Equation 1 can be rewritten in terms of the equilibrium ratio, K_a^{SL} (i.e., the ratio of the mole fractions of component a in the solid and liquid phases, respectively):

$$K_a^{SL} = \frac{s_a}{x_a} = \frac{\gamma_a^L}{\gamma_a^S}\exp\left[\frac{\Delta H_a^f}{RT}(1 - T/T_a^f)\right] = \frac{\gamma_a^L}{\gamma_a^S}\exp\left[\frac{-\Delta g}{RT}\right] \quad (2)$$

In this equation γ_a^S and γ_a^L are the activity coefficients of component a in the solid and the liquid phases, respectively; x_a and s_a are the corresponding mole fractions. Δg is the change in Gibbs energy in going from the liquid to the solid state.

Won (1986) has proposed a method for modeling wax formation using a modified regular solution theory for γ_a^L and γ_a^S. The resulting activity coefficients for the components forming the wax phase turn out to be close to unity. Hence, the values of the K factors in Eq. 2 depend almost solely on the values of the pure-component properties, T_a^f and ΔH_a^f. The WAP is calculated to be a few degrees (5–10 K) lower for all mixtures than the melting temperature of the heaviest component used to represent the mixture. This means that the calculated WAP is almost independent of the contents and molecular structures of the lighter constituents of the mixture. In addition the calculated WAP depends to a large degree on the details of the C_{7+} characterization (number of groups used to represent the total C_{7+} fraction), which is unsatisfactory. The results of using Won's model to predict the WAP's of the 17 oil mixtures of this work are shown in Table 3. The WAP's are much too high. To improve the results one must either reduce the activity coefficients or the melting enthalpies drastically. The former alternative was chosen in this work.

Development of a New Model

C_{7+} characterization

The C_{7+} fractions of the oil mixtures are characterized using the method proposed by Pedersen et al. (1985). A logarithmic dependence of the mole fractions against carbon number is assumed. The heaviest component considered is C_{80}.

The PNA (paraffin, naphthene, aromatic) distributions of each of the carbon number fractions are estimated using the correlations proposed by Riazi et al. (1980). For each carbon number fraction, two subfractions are considered. One contains the paraffins and the naphthenes (PN subfraction) and the other contains the aromatics (A subfraction). The final number of fractions considered may be as large as 160. The results of the characterization are shown in the supplementary material for mixtures 1 and 2.

Won (1986) has proposed a correlation for estimating the melting point temperature of the components. The parameters used in Won's correlation are found by correlating the melting temperatures of n-paraffins against carbon number. In crude oils the content of n-paraffins decreases with increasing carbon number. Since hydrocarbon branching tends to lower the melting point temperatures, it was found necessary to modify slightly the correlation of Won. The result is the following (temperature in K):

$$T_a^f = 402.4 - 0.01896 \cdot MW_a - \frac{27109}{MW_a} \tag{3}$$

MW_a is the molecular weight of component a. Equation 3 is used for both the PN and the A subfractions, since the melting point temperatures for these are found to be very close, as shown in Figure 1. The enthalpy of melting is estimated using the correlation suggested by Won:

$$\Delta H_a^f = 0.1426 \cdot MW_a \cdot T_a^f \tag{4}$$

Liquid phase activity coefficients

The liquid phase activity coefficients are modeled using a generalized polymer solution theory (Flory, 1953). The following general thermodynamic relation is used:

$$\Delta G_M = \Delta H_M - T \cdot \Delta S_M \tag{5}$$

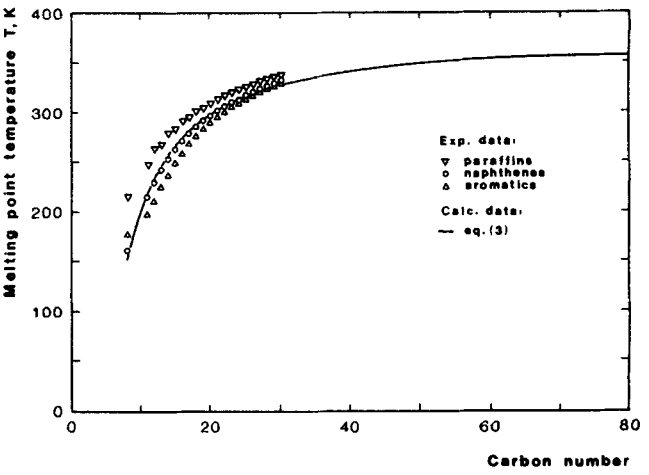

Figure 1. Melting point temperatures vs. carbon numbers.

where ΔG_M, ΔH_M, and ΔS_M are the changes of mixing in, respectively, the Gibbs energy, the enthalpy, and the entropy.

Based on physical considerations, Flory derived the following expression for the enthalpy of mixing:

$$\Delta H_M = kT \sum_j \sum_{i<j} n_i v_j \chi_{ij}, \quad \chi_{ii} = 0 \tag{6}$$

The summations in this and the following equations are, where nothing else is stated, over all components. k is Boltzmann's constant and n_i is the number of moles of component i. The volume fraction v_i is found from the following expression:

$$v_i = \frac{\zeta_i n_i}{\sum_j \zeta_j n_j} \tag{7}$$

ζ_i is the carbon number of component i.

χ_{ij} is a binary interaction parameter describing the interactions between molecules i and j. The coefficients are to be considered as a sum of the interactions between each segment (carbon atom) of molecule i with each segment of molecule j. Therefore the following relation applies:

$$\chi_{ji} = \chi_{ij}\left(\frac{\zeta_j}{\zeta_i}\right) \tag{8}$$

In his work on polymer solutions, Flory (1953) found that due to the large size of the molecules, the interaction coefficients may assume quite large values.

As a result of considerations based on statistical thermodynamics, it is found that the entropy of mixing can be expressed as follows:

$$\Delta S_M = -k \sum_i n_i \ln v_i - k \sum_i \sum_{j<i} \frac{\partial(\chi_{ij} T)}{\partial T} n_i v_j \tag{9}$$

The first term on the righthand side represents the configurational entropy, ΔS_M^*, that is, the contribution to the entropy from the volumetric mixing of the molecules. The last term on the righthand side of Eq. 9 represents contributions to ΔS_M from the

nonrandom coiling of the hydrocarbons (polymers) in the mixture. Contributions from this term are found to be negligible due to the lack of secondary molecular structures, and this term is therefore neglected in this work.

When Eqs. 6 and 9 are substituted into Eq. 5, the following expression is derived:

$$\Delta G_M = \Delta H_M - T\Delta S^*_M = kT\sum_j \sum_{i<j} n_i v_j \chi_{ij} + kT\sum_i n_i \ln v_i \quad (10)$$

By partial differentiation of the expression on the righthand side of Eq. 10 with respect to n_a and multiplication by Avogadro's number, an expression for the chemical potential of component a in the liquid phase is found:

$$\frac{\mu_a - \mu^o_a}{RT} = \ln v_a + 1 - v_a - \sum_{i\neq a}\frac{\zeta_a}{\zeta_i} v_i + \sum_{j\neq a} v_j \chi_{aj} \sum_{k\neq a} v_k - \sum_{j\neq a}\sum_{i<j}\left(\frac{\zeta_a}{\zeta_i}\right) v_i v_j \chi_{ij} \quad (11)$$

We use a group-contribution approach to model the interaction parameter, χ_{ij}. Group interaction parameters are required for three different types of interactions:

1. PN–PN
2. PN–A
3. A–A

The modeling of the liquid phase is based on interactions that depend on the chemical nature as well as on the size of the interacting molecules; see Eq. 8. Based on physical considerations, the three types of interactions are modeled using group-contributionlike principles. Each of the three types of interactions is described using a single parameter. For interactions between similar molecules the interaction parameter is proportional to the difference in "molecular size" whereas for unlike molecules (PN–A) it is proportional to the product of the "molecular sizes."

$$\chi_{ij} = C_1|\zeta_i - \zeta_j| \quad (12)$$

$$\chi_{ij} = C_2(\zeta_i \cdot \zeta_j) \quad (13)$$

$$\chi_{ij} = C_3|\zeta_i - \zeta_j| \quad (14)$$

C_1, C_2, and C_3 are constants and ζ_i is the number of carbon atoms in the ith component. The activity coefficients calculated using Eqs. 12–14 are very small ($\simeq 10^{-10}$), compared with those calculated using Won's model.

Modeling the solid phase

Wax formation is composed of two basic processes, nucleation and crystal growth. The formation of a nucleus is a necessary condition for the growth of a crystal. Lack of formation of nuclei causes subcooling. In crude oils, the subcooled state is relatively stable since heterogeneous nucleation very seldom occurs in hydrocarbon mixtures (Birdwell, 1964).

The reason for the subcooling is the contribution from the surface tension of the wax phase to the excess Gibbs energy. It stems from the curvature of the solid surface. In this work the geometry of the nuclei is assumed to be spherical. For a one-component system Mandelkern (1964) gives the following expression for calculation of the change in Gibbs energy connected with the phase transition from a liquid to a solid state for one crystal:

$$\Delta G = -4/3\pi r^3 \Delta G_v + 4\pi r^2 \sigma = 4\pi r^3 \rho \Delta g / MW_a \quad (15)$$

where ΔG_v is the bulk change of free energy per volume, r is the radius of the nucleus and, σ is the surface tension of the wax phase. As mentioned above, Eq. 15 applies to a one-component system. The same expression is used in this work; that is, it is assumed that the first wax crystal formed from a hydrocarbon mixture can be described using one pseudocomponent.

The surface tension, σ, is estimated using a correlation proposed by Pelofsky (1966):

$$\ln \sigma = \ln A + B/\eta \quad (16)$$

A and B are constants and η is the viscosity of the wax phase. For a wax $\eta \to \infty$, and Eq. 16 reduces to:

$$\sigma = A \quad (17)$$

Pedersen et al. (1988) have found that the constant A for paraffins equals 31.18 mN/m, and this value is used in the present work.

Formation of nuclei is a dynamic process in which nuclei of different sizes grow and disappear. The overall system always tends toward the minimum of the Gibbs energy. The behavior of the Gibbs function as given by Eq. 15 is outlined in Figure 2 as a function of the radius of the nucleus. The Gibbs energy function reaches its maximum at the critical radius, r^*, above which further crystal growth lowers the Gibbs energy. The driving force is the degree of subcooling, that is, the difference between the actual temperature and the temperature at which thermodynamic equilibrium exists. No experimental results giving quantitative data about subcooling of crude oils have been found. Based on data for linear polyethylenes (Mandelkern, 1964), the value of the critical radius, r^*, of the nuclei has been estimated to be 10^{-6} cm.

Apart from the contribution from subcooling, the wax phase is considered to be an ideal mixture of the constituent components, that is, γ^S is assumed to be equal to unity for all components.

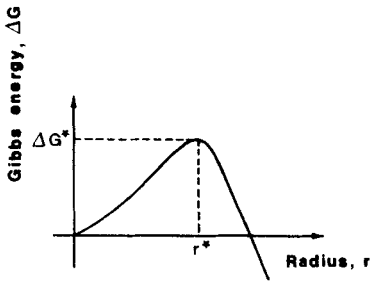

Figure 2. Change in Gibbs energy as a function of radius of nucleus.

Parameter estimation and grouping of components

The parameters C_1, C_2, and C_3 of Eqs. 12–14 were estimated using the liquid phase model and the phase model just described. Data for 10 different crude oils (marked * in Table 3) were used in the parameter estimation, which gave the following results:

$$C_1 = 3.05037 \cdot 10^{-2}$$
$$C_2 = -3.46841 \cdot 10^{-2}$$
$$C_3 = -1.19469 \cdot 10^{-1}$$

Including a total of up to 160 hydrocarbon fractions is impractical, and it is therefore desirable to be able to represent the mixture using a fewer number of fractions (or pseudocomponents). When grouping into pseudocomponents, the following mixing rule is used for calculating the interaction parameters of the pseudocomponents:

$$\bar{\chi}_{ij} = \frac{\sum_i \sum_j \chi_{ij} x_i x_j MW_i MW_j}{\sum_i \sum_j x_i x_j MW_i MW_j} \qquad (18)$$

MW_i is the molecular weight and x_i is the mole fraction of component i. The summations over i and j in Eq. 18 are over all the components from which the pseudocomponent is formed.

Results

Flash calculations were carried out using a three-phase flash program. The Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972) was used for the gas-liquid equilibria, and the model presented in this work was used to represent the solid-liquid equilibria. In none of the 17 crude oils was a gas phase found at the conditions considered.

Flash calculations to determine the wax appearance points have been carried out for the 17 crude oils, and the results are listed in Table 3. The number of pseudocomponents used to represent the mixtures varied from 20 (10 PN and 10 A components) to 160 (80 PN and 80 A). It is seen from Table 3 that the results of using 40 and 160 pseudocomponents are comparable, whereas higher WAP's are in most cases found when the mixture is represented using only 20 pseudocomponents.

It is not obvious whether subcooling has influenced the measured wax appearance points, and two different kinds of calculations were therefore carried out. One included the contribution from the solid phase surface tension ($+\sigma$) as described earlier, while the other one did not include this contribution ($-\sigma$). For each mixture, the result showing the better agreement with the measured WAP has been underlined in Table 3.

It is seen from Table 3 that the agreement with the experimental results is very good. The measured WAP's match the result either in the $+\sigma$ column or in the $-\sigma$ column. Based on the results of Table 3 one may assume that in mixtures 2, 8, 9, 10, and 12 a nucleus capable of initiating further growth of the wax crystal was present.

Figure 3 shows a plot of calculated vs. measured WAP's. An excellent agreement is observed. The calculated results for 10 out of 17 WAP's are located within the ±2-K track, indicated by the two dotted lines.

In Figure 4 are shown examples of calculated wax precipitation curves. Calculated precipitation curves for the remaining crude oils are shown in the supplementary material. The solid curves indicate the total amount of precipitated wax and the dashed curves indicate the amount of precipitated paraffin plus naphthene (PN). The dotted lines at the lower part of the curves show the calculated results when no supercooling is assumed. The vertical lines at the end of the precipitation curves indicate the calculated WAP when subcooling is assumed. The measured WAP is indicated by ⋈ on the temperature axis. Up to 160 pseudocomponents were used in these calculations.

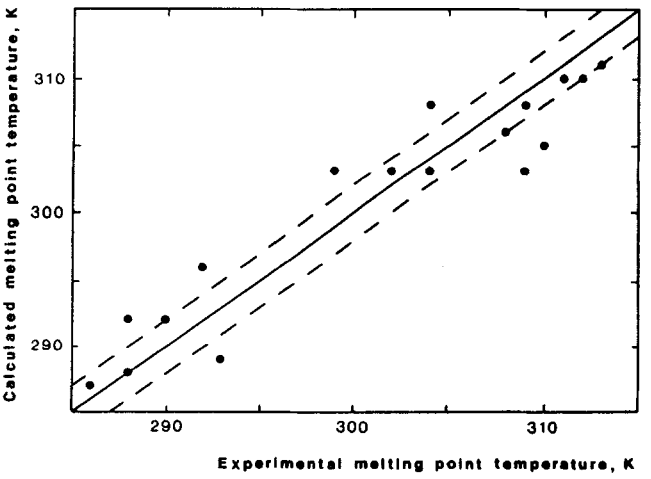

Figure 3. Calculated vs. measured WAP's.

In addition, results are shown of grouping into 40 pseudocomponents (indicated by ●). An excellent agreement is seen between results obtained with 40 and with 160 components. This shows that the new model is insensitive to the applied characterization procedure.

Conclusion

Based on the theory of multicomponent polymer solutions, a new thermodynamic model has been developed for describing wax formation in hydrocarbon mixtures. As is the case when linear polyethylenes crystallize, it appears that the oil mixtures may attain a metastable subcooled state. This phenomenon has been given a thermodynamic formulation in terms of the surface

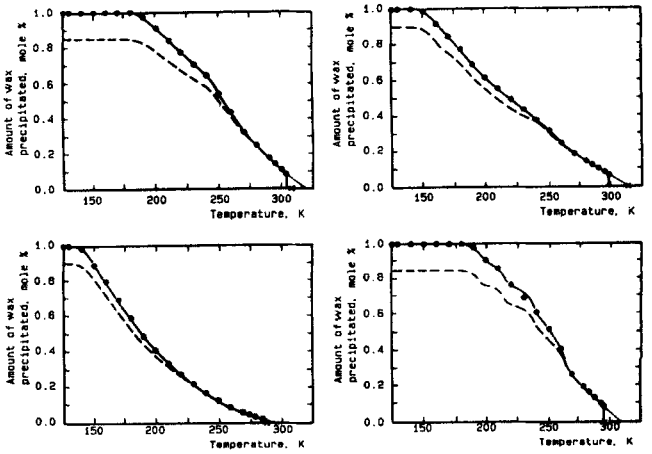

Figure 4. Calculated wax precipitation curves for mixture nos. 1–4.

tension of the wax phase. In order to obtain accurate results for the wax appearance points it is sufficient to use 40 pseudocomponents to represent the mixture.

The calculated wax appearance points (WAP) agree in most cases within ±4 K with the measured ones. Effectively, the predictions are less accurate than that, since it is not possible to tell from the experimental data whether subcooling is likely to take place or not.

While the measured WAP's are predicted within a few degrees K, due to lack of experimental data it has not been possible to check the validity of the precipitation curves presented in Figures 4.

Notation

A, B = constants for surface tension, Eq. 16
C_p = molar heat capacity
C_1, C_2, C_3 = constants, Eqs. 12–14
f = fugacity
g = molar Gibbs energy
G = Gibbs energy
H = enthalpy
k = Boltzmann's constant
K = equilibrium coefficient
MW = molecular weight
n = number of moles
r = radius of nucleus
r^* = critical radius of nucleus
R = gas constant
s = mole fraction in solid phase
S = entropy
S^* = configurational entropy
T = temperature, K
v = volume fraction
x = mole fraction in liquid phase

Greek letters

χ = interaction parameter
η = viscosity
γ = activity coefficient
μ = chemical potential
σ = surface tension
ζ = carbon number

Subscripts and superscripts

a = component index
f = fusion
i = component index
j = component index
L = liquid
M = mixing
S = solid
o = reference state

Literature Cited

Birdwell, B. F., "Effects of Various Additives on Crystal Habit and Other Properties of Petroleum Wax Solutions," Ph.D. diss., Pet. Eng., Uni. Texas, Austin (Jan., 1964).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, NY (1953).

Mandelkern, L., *Crystallization of Polymers*, 1st ed., McGraw-Hill, New York (1964).

Pedersen, K. S., T. Lund, and Aa. Fredenslund, "Surface Tension of Petroleum Mixtures," in press, *J. Can. Pet. Tech.* (1988).

Pedersen, K. S., P. Thomassen, and Aa. Fredenslund, "Thermodynamics of Petroleum Mixtures Containing Heavy Hydrocarbons. 3: Efficient Flash Calculation Procedures Using the SRK Equation of State," *Ind. Eng. Chem. Process Des. Dev.*, **24**, 948 (1985).

Pelofsky, A. H., "Surface Tension-Viscosity Relations for Liquids," *J. Chem. Eng. Data*, **2**, 394 (1966).

Riazi, M. R., and T. E. Daubert, "Simplify Property Predictions," *Hydrocarb. Proc.*, 115 (Mar., 1980).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Won, K. W., "Thermodynamics for Solid-Liquid Equilibria: Wax Phase Formation from Heavy Hydrocarbon Mixtures," *Fluid Ph. Equil.* **30**, 265 (1986).

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