Thermodynamics of Wax Precipitation under the Influence of Magnetic Fields

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A thermodynamic framework is developed for calculating wax precipitation in multi-component (nonferromagnetic) hydrocarbon mixtures under the influence of a static magnetic field. A mathematical expression was derived for calculating the compositional derivatives of the magnetic susceptibilities using an equation of state. These susceptibilities are required for calculating magneto-chemical fugacities. The model was used to predict the effect of a static magnetic field on crystallization temperature and amount of precipitated wax for three normal-paraffin mixtures and one synthetic gas-condensate. Calculated results indicate that static magnetic fields increase the probability of formation of paraffin crystals, in accordance to the experimental evidence. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2887–2897, 2006

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Introduction

The thermodynamic description of wax precipitation in petroleum fluids has improved significantly over the past 10 years. The multisolid character of wax, its co-existence with vapor and liquid phases in equilibrium, and other related phenomena in multi-component retrograde gases and heavy oils can all now be described by a simple thermodynamic model based on an equation-of-state.[1-4] As industry seeks for improved control of depositions, a number of field-level tools, such as magnetic fluid conditioners (MFC′s) have been developed and applied for mitigating the extent of wax deposition in many producing facilities by different technologists. While the conditioning of oil by an external magnetic field has become a frequent correction alternative for pipeline blockage caused by wax deposition in many producing assets, no thermodynamic description has been reported to date for explaining the effect of magnetism on the wax equilibria in these systems.

From a general viewpoint, fundamental models have been developed to describe the effects of external fields on the phase properties of physicochemical systems.[5-7] Nonetheless, there seems to be a discrepancy among the different formulations proposed, owed essentially to the definition of the work done by the external field, and to the mathematical way of expressing the effect of the field in terms of a proper combination of extensive and intensive variables.[8] Experimental studies on the ability to improve the separation efficiency in some separation processes by an external magnetic (or electric) field have been carried out by several investigators.[9-12] They have shown that the properties of many systems could be altered by those fields.[13] For the case of reservoir fluids, Ivakhnenko and Potter [14] measured magnetic susceptibilities of crude oils and formation waters from samples of various parts of the world. They suggested that these fluids might be classified in the future, according to the magnetic susceptibilities presented.

Kul'skii and Duskin[15], as quoted by Sokolovic et al.[16], found experimentally that a magnetic field increases the probability of formation of a crystalline nucleus in static systems, thus affecting the crystallization rate. Sokolovic et al. applied a pulsed electromagnetic field to 11 crude oils with different pour

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points, density, molecular weight, and a total content of organic solids (paraffins and asphaltenes). In all cases, they found a pulsed field frequency where the minimum viscosity of the oils was obtained. They concluded that, in certain cases, no measurable effects are found when a static magnetic field was applied. Away from such characteristic frequency, the viscosity may increase (or decrease) without a clear tendency. These somewhat unpredictable changes were interpreted as possible effects of the magnetic field on the molecules and crystal orientation: crystal population, size, nature, and form. According to these authors, the field affects the interparticule interactions. If the field affects the crystallization kinetics, it then affects the number of crystals (paraffinic or not), their nature and form, causing shear stress either increase or decrease.

In recent laboratory tests, Marques et al.[17] found that pure paraffins in hydrocarbon solutions show susceptibility to magnetic treatments, opposing to the idea that the interaction between crude oils and a magnetic field does not depend on the paraffinic crystals, but rather on the presence of polar compounds in the fluid, such as asphaltenes. Although they observed viscosity reductions in the crude oils studied, they did not find sensible changes in WAT (Wax Appearance Temperature). However, they concluded that the influence of magnetic fields on paraffin crystallization is not understood clearly, owing to the range of compounds, their complex chemical nature and compositions.

The objective of this work is two-fold. First, we develop a thermodynamic formulation of phase equilibria in multicomponent (nonferromagnetic) hydrocarbon mixtures under the influence of a static magnetic field, including an expression to calculate the compositional variation of the magnetic susceptibility of the mixture. Second, we apply the proposed model to explore the effect of a static magnetic field on calculated WAT′s and amounts of precipitated wax for three normal-paraffin mixtures, and one synthetic gas-condensate whose measured WAT′s and dew point temperatures (without the effect of magnetic fields) are available. The results from the model are finally presented and discussed.

Matter in a magnetic field

The relation between the magnetic field strength ($\vec{H}$) and the magnetic flux density ($\vec{B}$), is well-known in magnetism theory as[18]

$$\vec{B} = \hat{\mu}_0\vec{H} \tag{1}$$

where $\hat{\mu}_0$ is the vacuum permeability. For an arbitrary medium, isotropic or anisotropic, the following expression is defined

$$\vec{B} \equiv \hat{\mu}_0\vec{H} + \vec{J} \tag{2}$$

where $\vec{J}$ is called the intrinsic induction (also called: *magnetic polarization*), which is negligible *in vacuum*.

Another physical quantity, called the magnetization, $\vec{M}$, is given by

$$\vec{M} \equiv \frac{\vec{B}}{\hat{\mu}_0} - \vec{H} = \frac{\vec{J}}{\hat{\mu}_0} \tag{3}$$

where

$$\vec{m} = \vec{M}V \tag{4}$$

is called the magnetic moment of the polarized matter that occupies the volume V. If nonferromagnetic substances are considered, Eq. 1 may be replaced by

$$\vec{B} = \hat{\mu}_m\vec{H} \tag{5}$$

where $\hat{\mu}_m$ is the permeability of the medium. $\hat{\mu}_m$ generally depends on temperature, pressure and composition of the medium. A dimensionless relation for $\hat{\mu}_m$ is given by

$$\hat{\mu}_r \equiv \frac{\hat{\mu}_m}{\hat{\mu}_0} \tag{6}$$

where $\hat{\mu}_r$ is the relative permeability.

From Eqs. 2–6, the following expression is obtained

$$\vec{J} = \bar{\lambda}_{(m)}\vec{H} \tag{7}$$

where

$$\bar{\lambda}_{(m)} \equiv \hat{\mu}_0(\hat{\mu}_r - 1) \equiv \hat{\mu}_0 k_{(m)} \tag{8}$$

and $k_{(m)}$ is the volumetric susceptibility, commonly defined as

$$k_{(m)} \equiv \frac{\vec{M}}{\vec{H}} \tag{9}$$

Given that $\vec{M}$ and $\vec{H}$ have the same units, $k_{(m)}$ is dimensionless.

In addition, the molar susceptibility is defined as

$$\delta_{(j)} = k_{(j)}\nu \tag{10}$$

The units for $\delta_{(j)}$ are *cm^3/mol.* In Eq. 10, ν is the molar volume of the system. All nonpermanent magnetized material has nonzero values of k. Energetic considerations prevent k to take values lower than -1, whereas any greater value is possible.[19] Based on values of k, materials may be classified into three groups: *diamagnetic*, with $-1 < k < 0$, which become magnetized in a direction opposite to the local magnetic field and are repelled from regions where the magnetic field is strong; *paramagnetic*, with $k > 0$, which are attracted to strong magnetic fields. Materials with $|k| \leq 0.01$ are considered as *nonmagnetic*. This includes most common materials and almost all living tissues. Hydrocarbons (i.e., normal paraffins) belong to this group, and are *diamagnetic*. Finally, *ferromagnetic* materials (or magnetics) have values of $k \geq 0.01$. These materials respond strongly to an applied magnetic field.[20]

Thermodynamics of mixtures in the presence of a magnetic field

When a homogeneous (closed) system with variable volume is subjected to a reversible process of compression (or expansion) against an external pressure P, the work done over the system is given by the common expression[21]

$$dW = -PdV \tag{11}$$

If, in addition to the above work, the system is magnetized in a reversible way, then, according to Haase,[22] the total work done over the system may be expressed as

$$dW = -PdV + \vec{H}d(\vec{J}V) \tag{12}$$

Note that, in Eq. 12, both terms of the righthand side are the result of a multiplication of an intensive property and a differential extensive property. Therefore, Eq. 12 may be expressed as

$$dW = \sum_i L_i dl_i \tag{13}$$

Subscript i extends over every kind of work depending on the internal coordinates of the system. l_i and L_i are called work coordinates (extensive quantities) and conjugated work coefficients (intensive quantity), respectively. The internal state of the system is given empirically by the variables l_i and L_i when the temperature and composition of the system are known. Forces depending on the variation of external coordinates of the system (for example, gravitational, centrifugal, acceleration) or on the presence of irreversible processes (for example, friction forces) should not be interpreted as work coefficients L_i.[22]

For a reversible change in a closed-system′s internal state, we have, from the first law of thermodynamics and Eq. 13, that

$$dU = TdS + \sum_i L_i dl_i \quad \text{or} \quad TdS = dU - \sum_i L_i dl_i \tag{14}$$

Equation 14 expresses the entropy (S) dependence on internal energy (U) and on the work coordinates at (l_i), keeping constant the amount of each substance, n_j. Differentiating Eq. 14

$$T\left(\frac{\partial S}{\partial U}\right)_{l_i,n_j} = 1, \quad T\left(\frac{\partial S}{\partial l_i}\right)_{U,l_{j\neq i},n_j} = -L_i \tag{15}$$

Since entropy also depends on the amount of a substance, analogous to the work coefficients and coordinates, the chemical potentials can, therefore, be defined as

$$\tilde{\mu}_i \equiv -T\left(\frac{\partial S}{\partial n_i}\right)_{U,l_j,n_j\neq k} \tag{16}$$

Therefore, from Eqs. 15-16, a generalized form of the Gibbs equation is obtained for the derivative of the entropy in a region of variable amount and composition

$$TdS = dU - \sum_i L_i dl_i - \sum_{i=1}^{NC} \tilde{\mu}_i dn_i \tag{17}$$

From Legendre transforms[23] it is possible to define other extensive thermodynamic potentials as

$$E \equiv U - \sum_i L_i l_i; \quad A \equiv U - TS; \quad G \equiv A - \sum_i L_i l_i \tag{18}$$

where E, A and G are enthalpy ("H" was replaced by E in order to avoid later confusion with the notation for the magnetic field strength), Helmholtz and Gibbs free energies, respectively.

Differentiating Eq. 18 and using Eq. 7, the corresponding fundamental equations are obtained

$$dU = TdS + \sum_i L_i dl_i + \sum_{i=1}^{NC} \tilde{\mu}_i dn_i \tag{19}$$

$$dE \equiv TdS - \sum_i l_i dL_i + \sum_{i=1}^{NC} \tilde{\mu}_i dn_i \tag{20}$$

$$dA \equiv -SdT + \sum_i L_i dl_i + \sum_{i=1}^{NC} \tilde{\mu}_i dn_i \tag{21}$$

$$dG \equiv -SdT - \sum_i l_i dL_i + \sum_{i=1}^{NC} \tilde{\mu}_i dn_i \tag{22}$$

whose characteristic functions are $U(S, l_i, n_j)$, $E(S, L_j, n_j)$, $A(T, l_i, n_j)$ and $G(T, L_j, n_j)$, respectively.

Equation 22 is central in this work. For a system subjected to a pressure-volume work and in the presence of a static magnetic field, Eq. 22 reduces to,

$$dG \equiv -SdT + VdP - (\vec{J}V)d\vec{H} + \sum_{i=1}^{NC} \tilde{\mu}_i dn_i \tag{23}$$

Phase Equilibrium

T, P, n_j, and $\vec{H}$ are the independent variables of interest in this work. From Eq. 23, the following Maxwell relation can be obtained

$$-\left(\frac{\partial(\vec{J}V)}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} = \left(\frac{\partial \tilde{\mu}_i}{\partial \vec{H}}\right)_{T,P,n_j} \tag{24}$$

or

$$-\left(\frac{\partial(\vec{J}V)}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} = -\vec{J}\left(\frac{\partial V}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} - V\left(\frac{\partial \vec{J}}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} \tag{25}$$

Using Eq. 7

$$\left(\frac{\partial \vec{J}}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} = \vec{H}\left(\frac{\partial \bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} \tag{26}$$

We define

$$\bar{\nu}_i \equiv \left(\frac{\partial V}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} \quad \text{and} \quad V = n_T \nu \tag{27}$$

Substituting Eqs. 25-27 into Eq. 24, we get

$$\left(\frac{\partial \tilde{\mu}_i}{\partial \vec{H}}\right)_{T,P,n_j} = -\left[\nu n_T \left(\frac{\partial \bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} + \bar{\nu}_i \bar{\lambda}_{(m)}\right]\vec{H} \tag{28}$$

$$\int_{\mu_i}^{\tilde{\mu}_i} d\tilde{\mu}_i = -\int_{\vec{H}=0}^{\vec{H}} \left[\nu n_T \left(\frac{\partial \bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} + \bar{\nu}_i \bar{\lambda}_{(m)}\right]\vec{H} d\vec{H} \tag{29}$$

If $\bar{\lambda}_{(m)}$ is assumed independent of the field, integrating Eq. 29

$$\tilde{\mu}_i = \mu_i - \frac{1}{2}\left[\nu n_T \left(\frac{\partial \bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} + \bar{\nu}_i \bar{\lambda}_{(m)}\right]\vec{H}^2 \tag{30}$$

Defining $\tilde{\mu}_i$ in terms of component fugacities, f_i

$$\tilde{\mu}_i(T, P, n_i, \vec{H}) \equiv RT \ln \tilde{f}_i(T, P, n_i, \vec{H}) + \mu_i^0(T) \tag{31}$$

By using the traditional definition

$$\mu_i(T, P, n_i) \equiv RT \ln f_i(T, P, n_i) + \mu_i^0(T) \tag{32}$$

Equation 30 can then be cast to

$$\tilde{f}_i = f_i \exp\left(-\frac{1}{2RT}\left[\nu n_T \left(\frac{\partial \bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,\vec{H},n_{j\neq i}} + \bar{\nu}_i \bar{\lambda}_{(m)}\right]\vec{H}^2\right); \quad i = 1 \cdots NC \tag{33}$$

In using Eq. 33, the term $n_T(\partial \bar{\lambda}_{(m)}/\partial n_i)_{T,P,\vec{H},n_{j\neq i}}$ has to be calculated. Here, the following expression is proposed, which is derived in detail in the Appendix

$$n_T\left(\frac{\partial \bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,H,n_{j\neq i}} = \left(\frac{1}{\nu}\right)\left[\sum_{j=1}^{NC} \bar{\lambda}_{(j)} x_j \left(n_T \frac{\partial \bar{\nu}_j}{\partial n_i}\right)_{T,P,\vec{H},n_{s\neq i}} + \bar{\nu}_i(\bar{\lambda}_{(i)} - \bar{\lambda}_{(m)})\right] \tag{34}$$

Therefore, Eq. 33 is finally cast to

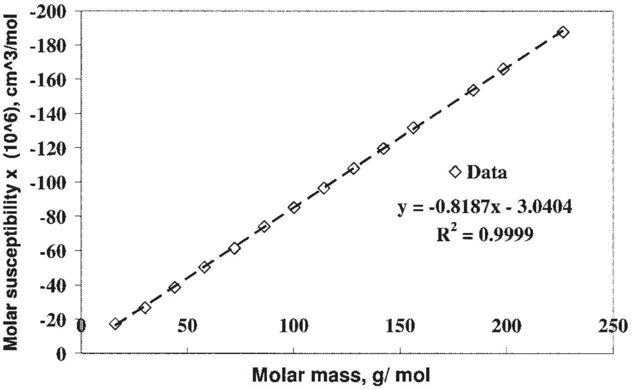

Figure 1. N-paraffin molar susceptibilities as a function of molar mass[25] at T = 25°C.

$$\tilde{f}_i = f_i \exp\left(-\frac{1}{2RT}\left[\sum_{j=1}^{NC} \bar{\lambda}_{(j)} x_j \left(n_T \frac{\partial \bar{\nu}_j}{\partial n_i}\right)_{T,P,\vec{H},n_{s\neq i}} + \bar{\nu}_i \bar{\lambda}_{(i)}\right]\vec{H}^2\right) \tag{35}$$

Equation 35 describes the fugacity of a component in a mixture under the influence of a static magnetic field. To the best of our knowledge, no previous derivation for this equation had been reported in the literature.

For a pure-component, Eq. 35 reduces to the following form

$$\tilde{f}_{pure\,i} = f_{pure\,i} \exp\left(-\frac{1}{2RT}\bar{\lambda}_{(i)} \nu_{pure\,i} \vec{H}^2\right) \tag{36}$$

Equation 35 is suitable for any multicomponent fluid or solid phase under the assumptions considered in this work. Equation 35 is suitable to a solid solution, and Eq. 36 is suitable for a pure phase.

Correlations for pure-component properties

Here $\vec{B}$, $\vec{H}$, $\vec{M}$ are assumed collinear, thus, the vectorial notation will be omitted, hereafter. This is a reasonable assumption for organic diamagnetic substances (such as n-paraffins) in the fluid state. Even though $\vec{M}$ may change somewhat with crystal orientation,[24] it will be demonstrated later that crystal-anisotropy effects were negligible on the thermodynamic predictions in this work.

Thus, for a hydrocarbon crystal

$$\tilde{f}_{pure\,i}^S = f_{pure\,i}^S \exp\left(-\frac{1}{2RT}\bar{\lambda}_{(i)} \nu_{pure\,i}^S \vec{H}^2\right) \tag{37}$$

where $\nu_{pure\,i}^S$ is the n-paraffin molar volume of the pure component i in the crystal state at given T and P.

The susceptibilities of hydrocarbon reservoir fluids will then depend on composition (chemical nature and traces of other components, such as metals, if present). This fact may limit our present understanding of the effects of magnetic fields on oil mixtures in a rigorous manner.[17]

Figure 1 shows the variation of molar susceptibilities, δ of homologous series of paraffins, as a function of the paraffin molar mass. This variation fits almost perfectly to a straight line. Data were taken from Lide,[25] where all the tabulated values correspond to room-temperature and atmospheric pressure, and the most stable state. Ambient temperature was taken as 298.15 K. At this temperature, most normal alkanes in the $nC5 - nC17$ range are liquids, but the heavier ones are solids.[26]

From Figure 1, the following correlations were derived

$$k_{(j)} = \frac{4\pi \times 10^{-6}}{1000\nu^{S}_{pure\,j}}(-0.8187MW_j - 3.0404) \tag{38}$$

or

$$k_{(j)} = \frac{4\pi \times 10^{-6}}{1000\nu^{L}_{pure\,i}}(-0.8187MW_j - 3.0404) \tag{39}$$

where $\nu^S_{pure\,i}$ and $\nu^L_{pure\,i}$ for n-paraffins are calculated from the correlations reported by Nichita et al.[3]

$$\nu^S_{pure\,j} = \frac{MW_j}{836.93317 + 0.01446MW_j - \dfrac{1.56856 \times 10^4}{MW_j}} \tag{40}$$

$$\nu^L_{pure\,i} = \frac{RTc_i}{Pc_i}(0.309816 - 0.00632518\nu_{c_i}^{1/3})^{[1+(1-T_r)^{2/7}]} \tag{41}$$

For some n-paraffins, Eqs. 38 and 40 or 39 and 41 are used depending on the value of melting point. Equation 41 is only evaluated at 298.15 K. In fact, magnetic susceptibilities of diamagnetic substances (that is, n-paraffins) are independent of temperature.[5] Changes in the magnetic susceptibility of a diamagnetic substance (that is, water [24]) in its different physical states is small.

The correlation obtained from Figure 1 (including methane) indicates that each group contributes approximately with −11.4618 (= −0.8187 × 14) to the average diamagnetic susceptibility, and the constant (− 3.0404) represents the contribution of the two hydrogen atoms at the extremes of the n-paraffin. The linear tendency in Figure 1 is related with the additive contribution of the $- CH_2 -$ group (regardless of the physical state of a compound). Here the correlation obtained from Figure 1 is extrapolated to heavier n-paraffins. It is also due to the scarcity of experimental data of magnetic susceptibilities for n-paraffins of higher molecular weights.

Table 1. Compositions of Three *n*-Paraffin Synthetic Mixtures[28]

	Feed Composition (Mole Fraction)		
Component	M1	M2	M3
nC10	0.8000	0.8000	0.8000
nC18	—	0.0334	0.0249
nC19	—	0.0283	0.0236
nC20	0.0642	0.0241	0.0224
nC21	0.0439	0.0206	0.0213
nC22	0.0300	0.0177	0.0203
nC23	0.0205	0.0152	0.0193
nC24	0.0140	0.0130	0.0183
nC25	0.0096	0.0112	0.0174
nC26	0.0066	0.0096	0.0166
nC27	0.0045	0.0082	0.0159
nC28	0.0031	0.0072	—
nC29	0.0021	0.0061	—
nC30	0.0015	0.0052	—

Table 2. Effect of the Magnetic Flux Density ($\vec{B}$) Variation on Predictions of Crystallization Temperature at $P = 1$ bar

FIELD, $\vec{B}$	Crystallization Temperature, K		
(Tesla)	M1	M2	M3
0.00	280.11	290.73	290.63
0.25	280.16	290.79	290.68
0.50	280.33	290.96	290.83
0.75	280.61	291.24	291.07
1.00	280.99	291.64	291.41
1.50	282.10	292.77	292.39
2.00	283.66	294.36	293.76

For the illustrative purposes of this work, we use an EOS-based multisolid-wax thermodynamic model, which has been successfully applied to a number of oils and retrograde fluids involving wax precipitation.[1-4] However, other models could be used.[27, 30] In the model for wax precipitation used in this work, at a given set of pressure and temperature conditions, the number and identity of precipitating components from an oil is dictated by the following phase-stability condition

$$f_i(P, T, Z_i) - f^S_{pure\,i}(P, T) \geq 0 \quad (i = 1, 2, \cdots \mathrm{NC}) \tag{42}$$

where Z_i is the mole fraction of component, whose phase thermodynamic stability is being analyzed. The components which fulfill Eq. 42 will precipitate, while those which do not, will only be present in the fluid (gas or liquid) states. If a static magnetic field is present, Eq. 42 is then replaced by

$$\tilde{f}_i(p, T, Z_i) - \tilde{f}^S_{pure\,i}(P, T) \geq 0 \quad (i = 1, 2 \ldots \mathrm{NC}) \tag{43}$$

where $\tilde{f}_i$ and $\tilde{f}^S_{pure\,i}$ are obtained from Eqs. 35 and 37, respectively.

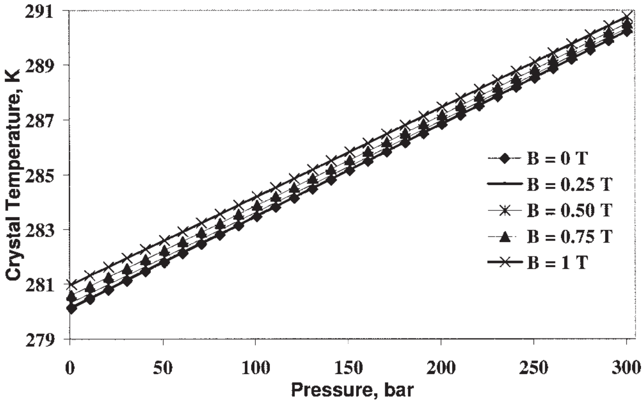

Figure 2. Effect of the magnetic flux density ($\vec{B}$) variation on predictions of crystallization temperature as a function of pressure for mixture M1.

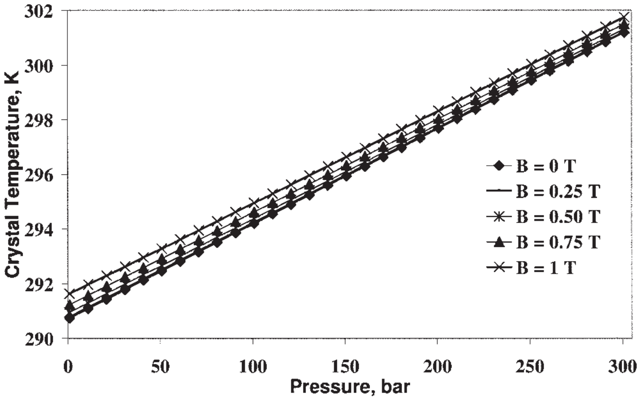

Figure 3. Effect of the magnetic flux density ($\vec{B}$) variation on predictions of crystallization temperature as a function of pressure for mixture M2.

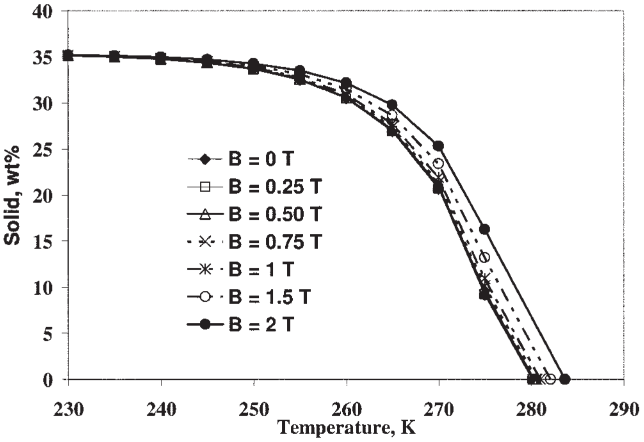

Figure 5. Effect of the magnetic flux density ($\vec{B}$) variation on predictions of the amount of n-paraffins precipitated for mixture M1 at P = 1 bar.

Results and discussion

Table 1 shows the composition of three n-paraffin synthetic mixtures (M1-M3), used for illustrative purposes. Further details on the characteristics of these dead-oils can be found elsewhere [3,28]. The results on the magnetic field effect for these synthetic oils and one additional synthetic gas-condensate fluid presented in this section are completely predictive (as no experimental data on the static magnetic-field effect on the wax equilibria in these mixtures is available).

Table 2 shows the effect of the magnetic flux density variation ($\vec{B}$) on WAT for the three mixtures modeled at 1 bar. Theoretically, the effect of the magnetic field on the crystallization temperature predictions in these oils is not negligible even at relatively low-fields. However, it is difficult to quantify experimentally this effect, especially at fields lower than 1 Tesla. It is interesting to notice that, as magnetic field increases, the tendency of n-paraffins crystallization also increases.

To illustrate the effects of magnetic field strength and pressure on predicted WAT for the above mixtures, Figures 2–4 show the effect of a magnetic flux density variation ($\vec{B}$) on the crystallization temperature for mixtures M1–M3 in a variable pressure range. The ability of the multisolid-wax thermodynamic model in reproducing the experimental data for these mixtures (without the effect of a magnetic field) is well discussed elsewhere.[3] It is easily seen that, as pressure increases, the effect of a constant magnetic field decreases. The insensitivity of the crystallization temperature (WAT) at relatively low-magnetic fields ($\vec{B} < \approx 1.0$ Tesla) found in this work, is in good agreement with the difficulties that Marques et al.[17] had to obtain experimentally changes in WAT for oils treated with a magnetic field.

Figures 5–7 show the effect of the magnetic flux density variation ($\vec{B}$) on the predicted (solid) wax amounts when temperature is reduced. Again, the model predicts that when magnetic field increases, the amount of paraffins precipitated also increases. This result further agrees with Kul'skii and Duskin's experimental observations aforementioned.[15]

For mixture M1, Figure 8 shows the effect of the magnetic flux density variation ($\vec{B}$) at high-pressures. The behavior of mixtures M2–M3 is similar to that of mixture M1. It is noticeable that for magnetic flux values normally used in experiments, the increase of the amount of precipitated material is

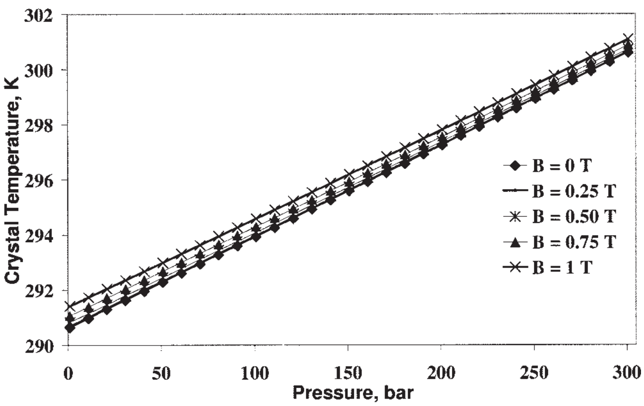

Figure 4. Effect of the magnetic flux density ($\vec{B}$) variation on predictions of crystallization temperature as a function of pressure for mixture M3.

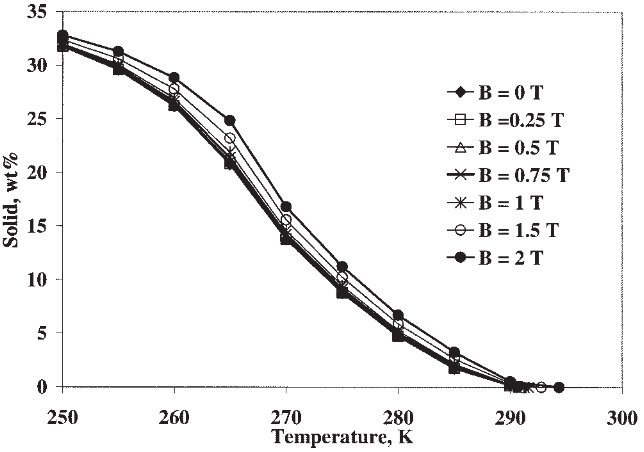

Figure 6. Effect of the magnetic flux density ($\vec{B}$) variation on predictions of the amount of n-paraffins precipitated for mixture M2 at P = 1 bar.

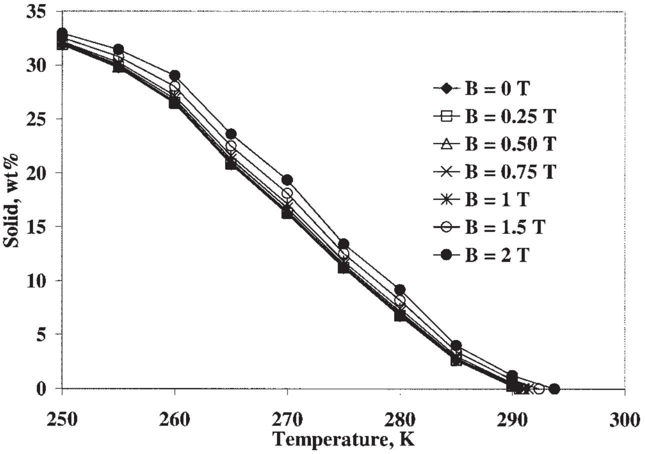

Figure 7. Effect of the magnetic flux density ($\vec{B}$) variation on predictions of the amount of n-paraffins precipitated for mixture M3 at P = 1 bar.

relatively low, and this is slightly lower as pressure increases. That is, at higher pressures the relative magnetic field effect decreases. Again the WAT increases with magnetic field and with pressure; nevertheless, the increase with pressure is bigger than that with a magnetic field.

If Eq. 35 is examined, it can be seen that the first term in the exponential term is negative, and since even though the $(n_T(\partial \bar{\nu}_j/\partial n_i))_{T,P,\vec{H},n_{s\neq i}}$'s are positive, all the $\bar{\lambda}_{(j)}$' terms are negative. The second term is also negative (that is, all the $\bar{\nu}_j$'s are positive). Therefore, according to this model, a magnetic field always increases the fugacity of an n-paraffin in a mixture (diamagnetic mixtures with positive partial molar volumes). The same is true for the fugacity of the n-paraffin in the solid state (see Eq. 37). However, by taking a look to Eq. 43, it can be seen that the relative value of the fugacities defines the precipitation tendency.

The effect of the n-paraffin molecular anisotropy (in crystalline phase) on the predictions of WAT, and the amount of precipitated wax is also analyzed. Data published by Shao et al.[29] on anisotropy in orthorhombic and triclinic crystals were used. According to these authors, the largest branch of the paraffinic molecules tends to align perpendicular to the field, and, thus, the molecule tends to rotate such that the plane containing the carbon atoms is also perpendicular to the field. Actually, the anisotropic effect on thermodynamic predictions developed in this work was negligible. Therefore, it was not quantitatively reported here. On the contrary, the compositional effect on the mixture volumetric susceptibility proves here to be more important.

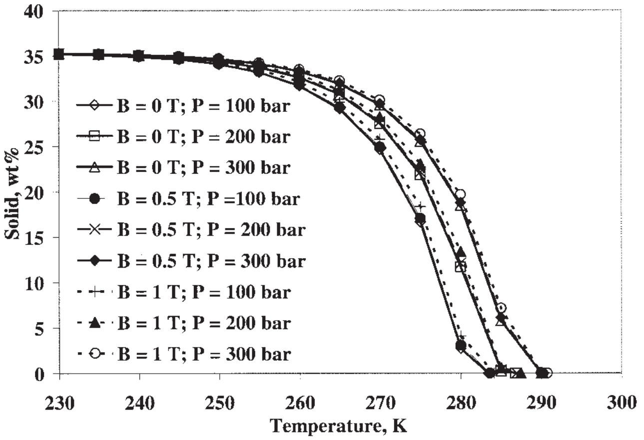

Figure 8. Effect of the magnetic flux density ($\vec{B}$) variation on predictions of the amount of n-paraffins precipitated for mixture M1 at P = 100, 200 and 300 bar.

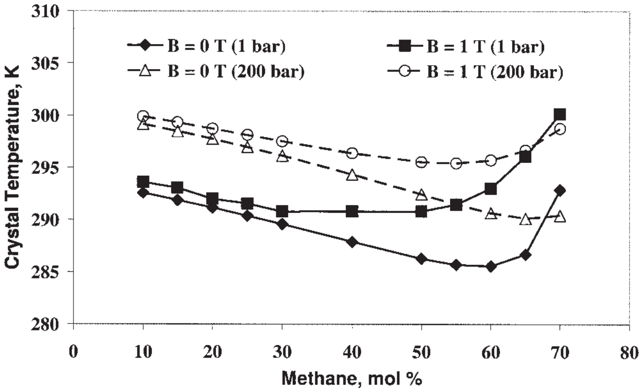

Figure 9. Effect of the amount of methane on the predictions of crystallization temperature for mixture M3 as a function of pressure and magnetic flux density.

The effect of methane content in a mixture was also analyzed. For instance, mixture M3 was artificially mixed with methane in several molar percentages. Figure 9 shows this effect on crystallization temperatures predicted at 1 and 200 bar, respectively. Results at 1 bar show the biggest influence. It is also noticeable that, in the absence of the magnetic field, there is a decrease in the crystallization temperature when methane is included in a mole percentage of up to 60, approximately. The WAT then starts to increase afterwards. At 200 bar, there is a similar, but less pronounced behavior. The magnetic field at both pressures increases the tendency to precipitate, showing the bigger effect at low-pressures, similar to the same effect seen for mixtures M1–M3. According to our model, as methane amount increases, the effect of the magnetic field increases. Increasing methane in the mixture normally increases the heavier paraffins′ solubility, decreasing in this way their tendencies to precipitate.[3] Nevertheless, the "crossing" of the calculated curves at 1 –and–200 bar is of interest (with and without a magnetic field), as it shows a reduction of the precipitation tendency with an increase in pressure, as it has in turn been reported in gas condensates for a certain range of pressure.[3] The minima represents transitions from oil to gas behavior

Ungerer et al.[30] measured the phase diagrams of four synthetic gas-condensate fluids in an experimental visual cell. We used their SHF4 synthetic gas-condensate to study the effect of the magnetic field on the measured multiphase (gas, liquid and solid) diagram. Normally, the models to predict wax precipitation have more difficulties with gas condensates that with heavier oils. Figure 10 shows the calculated (no magnetic field effects present) phase diagram compared to the experimental

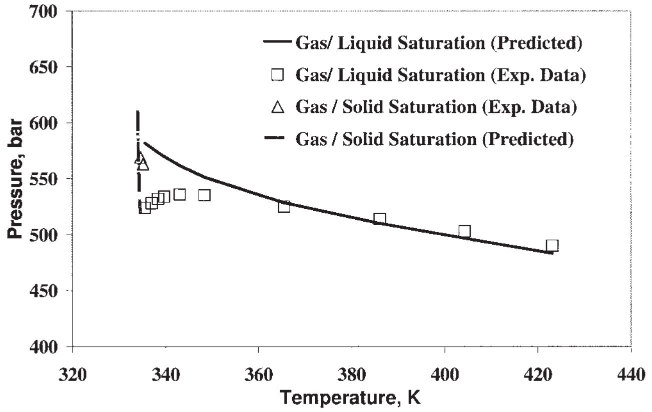

Figure 10. Phase diagram of mixture SHF4 (B = 0 T).

data. As previously shown by Nichita et al.[3], a good agreement is obtained, considering no magnetic field present and the uncertainty reported for the gas-liquid data points close to the gas-solid transitions.[3,30] Figure 11 shows the effect of magnetic field predicted by the model for the same model gas-condensate. Note that the gas-solid equilibrium is less sensitive to the external magnetic field than what the gas-liquid equilibrium is. As shown in Figures 9 and 11, even though the effect of the magnetic field on solid-liquid and solid-gas equilibria is somewhat weak, this is not necessarily true for the case of mixtures in which there are high methane concentrations.

While calculated results from the proposed model agreed favorably with experimental evidences, measurements on the wax equilibria under the effect of a static magnetic field in wide pressure and temperature conditions are clearly required.

Relevance to Flow Assurance and other Industrial Processes

Experimental reports on the effect of magnetic fields on diamagnetic substances are more limited than those related to paramagnetic and ferromagnetic substances. Studies on the effect of a magnetic field on crystallization processes in the chemical industries have been reported by several investigators. For instance, Liburkin et al.[31] found that a magnetic field affects the calcium sulfate (gypsum) structure in aqueous systems. According to them, the calcium sulfate particles formed under the influence of a magnetic field were bigger and more regularly oriented (more ordered). A similar report by Kronenberg [32] also shows a variation in the form of precipitated particles of calcium sulfate, forming disk-like structures, instead of tree-like in the absence of a field; that is a more ordered structure. Duffy[33] provided experimental information according to which the decrease of inorganic scale formation in magnetic-field-treated water was not due to the direct effect of the field on the fluid, but rather to the dilution of small amounts of iron from the pipe and the magnets. Results by Busch et al.[34], based on measurements of voltage produced by flowing fluids, support approximately the Duffy's hypothesis that electric currents may promote chemical reactions producing iron particles, and their corresponding effects on scale formation. The magnetic effect on the aging of the precipitated material has also been reported by Martynova et al.[35] They found that a magnetic treatment affects the solid structure to precipitate in subsequent stages.

As discussed earlier, experimental studies on the effect of magnetic fields are less common in organic (that is, petroleum) rather than inorganic substances. Recent flow-assurance related experiments by Marques et al.[17] and Rocha et al.[36] in magnetic flow loops, have allowed to figure out that magnetic fields directly interact with paraffins present in synthetic mixtures and reservoir fluids, affecting the morphology of the deposited crystals according to the reported scanning electron microscopy (SEM) images. According to Marques et al. and Rocha et al., magnetic fields change the crystals morphology, where less ordered structures replace those sheet- and slab-type normally found in the absence of magnetic fields. This is different to that found in inorganic scales by Liburkin et al.[31] and Kronenberg, [32] who reported more ordered structures.

Rocha et al. presented the hypothesis that, closer to the WAT, where "molecular aggregation" is predominant over individual molecules, the effect of a magnetic field may be increased by the coexistence of a great number of associated molecules that produce certain (deformed) molecular aggregates, similar to Baker and Judd's hypothesis for carbonate scale formation.[37] These authors found that even though the magnetic fields produce changes in crystals morphology, they do not alter the pour point, WAT, and density. Sokolovic et al.[16] found that, without magnetic fields, a clear correlation between the content of total compounds that could solidify (paraffins and asphaltenes), and the shear stress and pour point may exist. However, such a relation was not found when fluids were subjected to a magnetic field. This reflects the complexity of the interaction between magnetic fields and matter, particularly for systems with compositional complexities, such as petroleum.

Lorentz force has been widely used to reduce the natural convection in metals-related processes.[38] However, Lorentz force is not used in nonconductive substances, such as organic substances. Nowadays, there is a great interest in the effect of the magnetization force ($F_M = (1/2)\mu_0 k_{(j)} \nabla \vec{H}^2$) on systems formed by paramagnetic or diamagnetic material (or a combination of both). Magnetization force is a body force similar to gravitational, but with the advantage of its direction may be

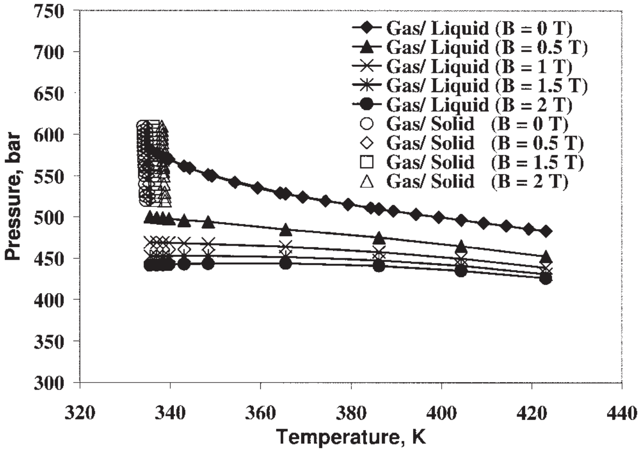

Figure 11. Effect of the magnetic flux density variation on phase diagram of mixture SHF4.

controlled. Most materials are diamagnetic and, thus, experience a repulsive force ($k_{(j)} < 0$), whereas paramagnetic materials are attracted ($k_{(j)} > 0$). One objective has been to study the effect of the change in the direction of the magnetization force on the damping of the convection. The control on the convection is fundamental in the solidification process of a material, where the convection due to thermal or concentration gradients dominates over molecular diffusion.[39]

The effect of absorbing or convection promotion on the crystal growth and protein quality has also been studied by several authors. For instance, Lin et al.[40] found an improvement in crystals quality when the crystallization process was carried out at microgravity conditions (F_M opposite to the gravity). Similar results have been reported by Lorbe et al.[41] Therefore, it is not surprising that the morphology and size of paraffinic crystals may suffer changes in the presence of a magnetic field. However, the exact mechanism is not currently known.

A magnetic field was also used to change air convection to promote combustion process taking advantage of the attractive force on paramagnetic oxygen.[42] Recently, Wang and Wakayama[39] study the effect of the change of direction of the magnetization force for diamagnetic nonconductive (or slightly conductive) fluids. They found that, if the magnetization force acts in an opposite direction to a thermal gradient (as it may occur in magnetic-conditioning devices used in petroleum wells), natural convection increases; but, if the force is applied in the same direction to a thermal gradient, convection is absorbed. The convection absorbing or promotion efficiency depends on Rayleigh number (*Ra*). If *Ra* increases, convection promotion efficiency decreases and absorbing efficiency increases. They also found that if a horizontal magnetization force is applied perpendicularly to a temperature gradient, convection is slightly promoted. This would be the case when a magnetic tool is placed in such a way that field lines were perpendicular to a thermal gradient, that is, the field lines are in the same direction to the flux. Note that in a vertical pipe the gravity does not take part directly on convection promotion toward the walls. The same is not right for horizontal pipes, where Wang and Wakayama found that a magnetization force opposite to the gravity absorbs convection, whereas if it is applied in the same direction (downward), convection is promoted. They found a slight dependence on *Ra*.

Note that a magnetic field repels diamagnetic substances, which tend to be located in regions where magnetic force is the less possible, that is, near the pipe center under a magnetic field transverse to the flux or out of the field influence. The paraffinic molecules (that is, wax) attempt to align its axis such that the axis with less magnetic susceptibility (more positive) be parallel to the magnetic field lines,[29] seeking, thus, to decrease the field rejection and, consequently, the magnetization energy. Baker and Judd [37] found that a magnetic tool is more effective if it operates on a fluid flowing orthogonally to the magnetic field orientation.

As is reported by Atrashenko and Voronina,[43] a magnetic field also influences the molecular diffusion process. The heaviest paraffinic molecules are more easily rejected compared to the lightest, since their susceptibilities are more negative. Therefore, anybody would be tempted to say that in the presence of magnetic fields the paraffinic deposits should be less hard.

Precipitation is a phenomena governed principally by thermodynamics, whereas deposition also involves crystal size and form effects, and hydrodynamic conditions. The effect of a magnetic field on both phenomena should be analyzed together, but not in the same way. Even though a magnetic loop is a good approach for studying paraffin precipitation, it does not represent exactly the different phenomena actually present in a deposition process, where the thermal gradient between the bulk of the fluid and the pipe wall, together with molecular diffusion, are usually considered as the principal driven forces in deposition process. Other more realistic experimental methodologies may be used to improve the comprehension of the effects of the changes in direction of the magnetic fields on paraffinic material crystallization and deposition kinetics, such as the so-called "cold disc wax deposition" (CoDWaD),[44] allowing to control the fluid temperature and the temperature of the "cold wall". A magnetic field affects both, precipitation and deposition. Obviously, the model here presented is only concerned with the precipitation phenomenon.

Conclusions

A thermodynamic description of phase equilibria for multicomponent (nonferromagnetic) hydrocarbon mixtures under the influence of a static magnetic field was developed. The model was used for predicting the effect of a magnetic field on both the crystallization temperatures (WAT) and the amounts of material precipitated for three n-paraffin multicomponent mixtures and one synthetic gas condensate. The results from the model agree well with the (few) experimental evidences available to date. For a more extensive testing of this model, much experimental work lies ahead. However, the experimental program for this purpose can be much aided by the EOS-based calculations presented here.

At magnetic fields lower than 1 Tesla (values usually used in experimental tests with petroleum reservoir fluids), their effects on crystallization temperatures (WAT) of oils and on the amounts of material precipitated are quantitatively small. In gas condensates the effect of magnetic fields is increased. In both cases the model predicts that magnetic field increases the probability of paraffinics crystals formation, according to experiments.

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Notation

A = Helmholtz energy
$\vec{B}$ = magnetic flux density, *Tesla*.
B = magnetic flux density magnitude, relation in PR-EOS
E = enthalpy
f = fugacity
$\tilde{f}$ = magneto-chemical fugacity
G = Gibbs free energy
$\vec{H}$ = magnetic field strength, *Amperes/meter*
$\vec{J}$ = intrinsic induction ("magnetic polarization")
k = volumetric susceptibility
l = work coordinate
L = work coefficient
$\vec{m}$ = magnetic moment
$\vec{M}$ = magnetization

MW = molar mass
NC = number of components
m = mixture property
P = pressure
S = entropy
T = temperature
U = internal energy
V = total volume
v = molar volume
W = work

Greek letters

$\underline{\delta}$ = molar susceptibility
$\bar{\lambda}$ = definition in Eq. 8
μ = chemical potential
$\tilde{\mu}$ = magneto-chemical potential
$\hat{\mu}$ = permeability

Subscripts

i,j,k = component indices
L = liquid
m = mixture
0 = pure component, vacuum
r = relative quantity
T = total

Superscripts

f = fusion
0 = pure component
S = solid
L = liquid

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Appendix

Derivation of $n_T(\partial\bar{\lambda}_{(m)}/\partial n_i)_{T,P,H,n_{j\neq i}}$

From Eqs. 4 and 9

$$k_{(m)} = \frac{m}{VH} \tag{A1}$$

where,

$$m = \sum_{j=1}^{NC} M_{(j)}V_j \tag{A2}$$

In Eq. A2, is the total volume occupied by component in a phase

$$V_j = n_j\bar{\nu}_j, \quad j = 1 \cdots NC \tag{A3}$$

Thus, Eq. A2 is

$$m = \sum_{j=1}^{NC} M_{(j)}n_j\bar{\nu}_j \tag{A4}$$

Substitution of Eq. A4 into Eq. A2

$$k_{(m)} = \frac{\sum_{j=1}^{NC} M_{(j)}n_j\bar{\nu}_j}{VH} = \sum_{j=1}^{NC}\left(\frac{M_{(j)}}{H}\right)\left(\frac{n_j}{n_T\nu}\right)\bar{\nu}_j \tag{A5}$$

Therefore

$$k_{(m)} = \frac{\sum_{j=1}^{NC} k_{(j)}x_j\bar{\nu}_j}{\nu} \tag{A6}$$

Equation A6 is the proposed equation to be derived. From Eq. 8 $\bar{\lambda}_{(m)} = \hat{\mu}_0 k_{(m)}$,

$$n_T\left(\frac{\partial\bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,H,n_{j\neq i}} = \hat{\mu}_0 n_T\left(\frac{\partial k_{(m)}}{\partial n_i}\right)_{T,P,H,n_{j\neq i}} \tag{A7}$$

Differentiating Eq. A6

$$n_T\left(\frac{\partial k_{(m)}}{\partial n_i}\right)_{T,P,H,n_{j\neq i}} = \left(\frac{1}{\nu}\right)\left[\sum_{j=1}^{NC} k_{(j)}x_j\left(n_T\frac{\partial\bar{\nu}_j}{\partial n_i}\right)_{T,P,n_{s\neq i}} + \bar{\nu}_i(k_{(i)} - k_{(m)})\right] \tag{A8}$$

Using Eq. A7

$$n_T\left(\frac{\partial\bar{\lambda}_{(m)}}{\partial n_i}\right)_{T,P,H,n_{j\neq i}} = \left(\frac{1}{\nu}\right)\left[\sum_{j=1}^{NC} \bar{\lambda}_{(j)}x_j\left(n_T\frac{\partial\bar{\nu}_j}{\partial n_i}\right)_{T,P,n_{s\neq i}} + \bar{\nu}_i(\bar{\lambda}_{(i)} - \bar{\lambda}_{(m)})\right] \tag{A9}$$

The partial derivatives can be obtained from a cubic EOS such as Peng-Robinson[45].

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