CHAPTER III

PREDICTION THERMODYNAMIC MODELS FOR WAX PRECIPITATION

Wax formation can be thermodynamically described using the general solid-liquid equilibrium equation (Prausnitz *et al.*, 1986). For component *i*, solid-liquid equilibrium equation with neglecting the heat capacity term is

$$\ln \frac{s_i \gamma_i^S}{x_i \gamma_i^L} = \frac{\Delta h_{m,i}}{RT_{m,i}} \left(\frac{T_{m,i}}{T} - 1 \right) + \frac{\Delta h_{tr,i}}{RT_{tr,i}} \left(\frac{T_{tr,i}}{T} - 1 \right) \tag{3.1}$$

where x is the mole fraction in liquid phase, s is the mole fractions in solid phase, γ^L is the liquid phase activity coefficient, γ^S is the solid phase activity coefficient, Δh_m is the enthalpy of melting, Δh_{tr} is the enthalpy of solid transition, T_m is the melting temperature, T_{tr} is the solid transition temperature, T is the mixture temperature and R is the ideal gas constant.

For a given oil composition and temperature condition, the activity coefficients in both phases are evaluated using the iterative numerical solution procedure combined with mass balance constraints for each component. The calculation will yield equilibrium mole fractions in both phases as well as the total solid phase mass fraction (f_s). For binary system, the thermophysical properties for pure octacosane were obtained from Dirand and coworker (2002) and Yaws (1999) for nonparaffin solvents. For multicomponent systems, the *n*-alkane thermophysical properties can be obtained from Singh and coworker (2001). Component activity coefficient (γ) correlations for both phases are described in the following sections.

3.1 Liquid Phase Activity Coefficients

The liquid phase activity coefficient can be expressed as the products of two contributions: a combinatorial-free volume term ($\gamma^{comb-fv}$) accounting for the size and free volume effects and a residual term (γ^{res}) accounting for the energetic interaction.

$$\gamma_i = \gamma_i^{comb-fv} \cdot \gamma_i^{res} \qquad (3.2)$$

The combinatorial free-volume term described by Flory free-volume model (Kontogeorgis, 1994; Coutinho, 1995) is

$$\ln \gamma_i^{comb-fv} = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \qquad (3.3)$$

where x_i is the mole fraction of component i in the liquid phase. The composition fraction of component i, ϕ_i, is defined by

$$\phi_i = \frac{x_i \left(V_i^{1/3} - V_{wi}^{1/3}\right)^{3c}}{\sum_j x_j \left(V_j^{1/3} - V_{wj}^{1/3}\right)^{3c}} \qquad (3.4)$$

where V_i is the molar volume of component i (Elbro et al., 1991; Yaws, 1999) and V_{wi} is the van der Waals volume of component i. The calculations for molar volume and van der Waals volume are shown in Appendix A. The van der Waals volume is defined as the space occupied by a molecule, which is impenetrable to other molecules (Bondi, 1968). An external degree of freedom, c, for alkane systems has been empirically set set to be equal to 1.1 (Coutinho, 1995). Solutions consisting of only n-alkane components are known to behave athermally, such that γ^{res} equals unity.

For non-paraffin solvents, the residual term does not equal unity and is needed to take into account intermolecular interactions among components. The intermolecular interactions are resulted from dispersion forces. The residual term is calculated from the modified version of UNIFAC model (Larsen et al., 1987),

$$\ln \gamma_i^{res} = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \qquad (3.5)$$

where v_k^i is the number of k group in component i, Γ_k is the residual activity coefficient of group k at the mixture composition and Γ_k^i is the activity coefficient of group k in the pure component i. Γ_k and Γ_k^i are given by

$$\ln\Gamma_k = Q_k\left[1 - \ln(\sum_m^m \theta_m\psi_{mk}) - \sum^m\left(\frac{\theta_m\psi_{km}}{\sum_n(\theta_n\psi_{nm})}\right)\right] \tag{3.6}$$

where θ_k is the surface area fraction of group k and can be calculated by the following equation,

$$\theta_k = \frac{Q_kX_k}{\sum_{n=1}^n Q_nX_n} \quad ; \qquad X_k = \frac{\sum_{i=1}^i v_k^i x_i}{\sum_{i=1}^i \sum_{n=1}^n v_n^i x_i} \tag{3.7}$$

where Q_k is the surface parameter of group k. The interaction term, ψ_{mn}, is given by

$$\psi_{mn} = \exp(-a_{mn}/T) \tag{3.8.1}$$

, and $\quad a_{mn} = A_{mn} + B_{mn}(T - 298.15) + C_{mn}\left(T\ln\frac{298.15}{T} + T - 298.15\right) \tag{3.8.2}$

where a_{mn} is the interaction parameter between group m and group n (Larsen *et al.*, 1987). The interaction parameters (a_{mn}) describe the difference in the intermolecular interaction energy between the *m-n* pair (u_{mn}) and *n-n* pair (u_{nn}),

$$a_{mn} = u_{mn} - u_{nn} \tag{3.9.1}$$

$$a_{nm} = u_{mn} - u_{mm} \tag{3.9.2}$$

Note that, $a_{mn} \neq a_{nm}$. The example calculation of residual activity coefficient is shown in Appendix B.

3.2 Solid phase Activity Coefficients

In this study, the solid-phase nonideality is described by the local composition model, UNIQUAC (Coutinho, 1999; Abrams and Prausnitz, 1975).

$$\ln \gamma_i^S = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} - \frac{Z}{2} q_i \left(\ln \frac{\Phi_i}{\Theta_i} + 1 - \frac{\Phi_i}{\Theta_i} \right)$$

$$+ q_i \left(1 - \ln(\sum_{j=1}^{n} \Theta_j \tau_{ji}) - \sum_{j=1}^{n} \frac{\Theta_j \tau_{ij}}{\sum_{k=1}^{n} \Theta_k \tau_{kj}} \right) \qquad (3.10)$$

with

$$\tau_{ij} = \exp\left[-\frac{\lambda_{ji} - \lambda_{ii}}{RT} \right], \quad \lambda_{ii} = -\frac{2}{Z}(\Delta h_{sblm_i} - RT), \quad \Phi_i = \frac{s_i r_i}{\sum_{j=1}^{n} s_j r_j}$$

$$\text{and} \quad \Theta_i = \frac{s_i q_i}{\sum_{j=1}^{n} s_j q_j} \qquad (3.11)$$

where R is the gas constant, T is the equilibrium temperature, s_i is the mole fraction of component i in solid phase, Z is the coordination number (Z=6 for the orthorhombic phase) and $\lambda_{ij} = \lambda_{jj}$ where j is the shorter n-alkane in the pair ij. Δh_{sblm} is the enthalpy of sublimation of pure n-alkane and can be calculated from the following equation,

$$\Delta h_{sblm} = \Delta h_{vap} + \Delta h_{fus} + \Delta h_{tr} \qquad (3.12)$$

Heats of vaporization, Δh_{vap}, for pure n-alkane are calculated by using the correlation developed by Morgan and Kobayashi (1994). The structural parameters r and q are estimated with the assumption of 10 interaction methylene units representing the specificity of the interactions in the solid phase. The correlation used to calculate r_i and q_i are shown in Appendix C.