

CHAPTER 4

Modified Regular Solution Model

The asphaltene precipitation modeling in this thesis is based on a previously developed regular solution approach. In this chapter, the approach is presented along with the previously developed methodology to characterize heavy oils. Modifications to the characterizations for blends and live oils are presented in the relevant chapters later on.

4.1 Modified Regular Solution Model

The modified regular solution model (Alboudwarej et al., 2003; Akbarzadeh et al., 2005; Yarranton et al., 2007) includes a Flory-Huggins entropic contribution from the difference in molecular sizes as well as an enthalpy contribution from regular solution or Scatchard-Hildebrand solubility theory. A liquid-liquid equilibrium is assumed and the equilibrium ratio, K_i^{hl} , for any given component is given by:

$$K_i^{hl} = \frac{x_i^h}{x_i^l} = \exp \left\{ \frac{v_i^h}{v_m^h} - \frac{v_i^l}{v_m^l} + \ln \left(\frac{v_i^l}{v_m^l} \right) - \ln \left(\frac{v_i^h}{v_m^h} \right) + \frac{v_i^l}{RT} (\delta_i^l - \delta_m^l)^2 - \frac{v_i^h}{RT} (\delta_i^h - \delta_m^h)^2 \right\} \quad (4.1)$$

where x_i^h and x_i^l are the heavy and light liquid phase mole fractions, R is the universal gas constant, T is absolute temperature, v_i and δ_i are the molar volume and solubility parameter of component i in either the light liquid phase (l) or the heavy liquid phase (h), and v_m and δ_m are the molar volume and solubility parameter of either the light liquid phase or the heavy liquid phase. The terms containing only molar volumes are the

entropic contribution and the terms containing solubility parameters are the enthalpic contribution.

Once the equilibrium ratios are known, the phase equilibrium is determined using standard techniques (Rijkers and Heidemann, 1986; Alboudwarej et al., 2003). Briefly, the phase equilibrium calculations are performed as follows:

- 1) The fluid mixture is appropriately divided into pure and pseudo components. The properties (molar volume and solubility parameter) of each component are determined. Both the fluid composition and the properties of each component are inputs to the calculation.
- 2) The equilibrium ratios or the K values of each component are initiated using the fluid composition.
- 3) The amounts of heavy and light liquid phases are calculated using the Rachford-Rice method.
- 4) The composition of the heavy and light liquid phases is updated and normalized.
- 5) Convergence is checked using the bisection method.
- 6) The K values for each component are updated using the new composition.
- 7) Return to Step No. 3 until the desired convergence is achieved.

In the phase equilibrium calculation, it was assumed that only asphaltenes and resins partition to the heavy phase; that is, the equilibrium is between an asphaltene-rich phase including asphaltenes and resins (the heavy liquid phase) and a solvent-rich phase including all components (the light liquid phase). This assumption is thermodynamically incorrect but is a reasonable approximation for heavy liquid phases with high asphaltene content and it provides a more stable flash calculation with much faster convergence. Asphaltene-rich phases have been found to contain approximately 95 wt% asphaltenes and resins (George, 2009).

To use this model, the mole fraction, molar volume, and solubility parameter of each component in the mixture must be specified. For a complex fluid like a crude oil, the fluid must be divided into pure components and pseudo-components to adequately represent the fluid without using an extremely large set of components.

4.2 Characterization

Characterization is the division of the fluid into components and pseudo-components and the assignment of properties to each component. For the regular solution model, the required properties are molar mass and density (to determine molar volumes) and the solubility parameter. In this thesis, characterizations are required for three types of fluid mixtures:

- 1) asphaltenes in solvents
- 2) solvent diluted heavy oils or crude oil blends
- 3) live oils

Characterization methodologies for the first two fluid mixtures have been developed previously (Alboudwarej et al., 2003; Akbarzadeh et al., 2005) and are presented here. A new methodology is required for live oils and is presented in Chapter 6.

4.2.1 Asphaltenes in Pure Solvents

The mass fractions of the pure solvents and the asphaltenes are controlled variables in the experiments and therefore are known. The molar mass and density of pure solvents are either known or calculated using well-established Hankinson-Brost-Thomson (HBT) technique (Reid et al., 1989; Perry and Green, 1997). The HBT technique accounts for the effects of both temperature and pressure. Solubility parameters at 25°C were obtained from Barton (1991) and Hansen (2007). The effect of temperature on the solubility of *n*-

alkanes was required for some studies and was accounted for using an expression developed for *n*-alkanes by Akbarzadeh et al. (2005):

$$\delta = \delta_{25^{\circ}\text{C}} - 0.0232(T - 298.15) \quad (4.2)$$

Note, the slope of $-0.0232 \text{ MPa}^{0.5}/\text{K}$ is consistent with the order of magnitude of the derivative of the solubility parameter ($d\delta/dT \approx -0.03 \text{ MPa}^{0.5}/\text{K}$) found for hydrocarbons in general (Barton, 1991). Pressure effects on density and solubility parameter are discussed in Chapter 6. Properties at 25°C for the solvents used in this thesis are summarized in Table 4.1.

Table 4.1: Properties of pure components at 25°C and 1 atm.

Component	Molar Mass (g/mol)	Density (kg/m ³)	Solubility Parameter (MPa ^{0.5})
<i>n</i> -heptane	100	678	15.2
<i>n</i> -hexadecane	226	771	16.3
toluene	92	864	18.3

Asphaltenes are more challenging to characterize because they are a mixture of many thousands of chemical species and they are known to self-associate (Yarranton, 2005). Here, they are treated as macromolecular nano-aggregates of monodispersed monomers. The asphaltene fraction was divided into 30 sub-fractions, each representing a different aggregate size range and the number of monomers in an aggregate or the aggregation number (r) is described by the relation:

$$r = \frac{M}{M_m} \quad (4.3)$$

where M is the molar mass of the particular asphaltene aggregate or the sub-fraction, and M_m is the monomer molar mass of the asphaltenes. The gamma distribution function (Whitson, 1983) was then used to describe the molar mass distribution of the aggregates according to Eq. (4.4) as:

$$f(M) = \frac{1}{M_m \Gamma(\beta)} \left[\frac{\beta}{(\bar{r} - 1)} \right]^\beta \times (r - 1)^{\beta-1} \exp \left[\frac{\beta(1-r)}{(\bar{r} - 1)} \right] \quad (4.4)$$

where \bar{r} is the average aggregation number of asphaltene fraction defined as the average molar mass of all self-associated asphaltene sub-fractions (\bar{M}) divided by the monomer molar mass, that is given by $\frac{\bar{M}}{M_m}$. β is a parameter that determines the shape of the distribution. The molar mass of an asphaltene monomer and the largest asphaltene aggregate were assumed to be 1800 and 30,000 g/mol, respectively. Note, the asphaltene monomer molar mass of 1800 g/mol is at the upper end of recent estimates of asphaltene monomers and may represent an already aggregated component (Groenzin and Mullins, 2007).

The molar mass of an asphaltene sub-fraction (M) is the associated molar mass (rM_m) of that pseudo-component as calculated from the gamma distribution. Its molar volume was determined from Eq. (4.5) (Alboudwarej et al., 2003):

$$v = 1.493M^{0.936} \quad (4.5)$$

where v is the molar volume (cm³/mol) of asphaltene sub-fraction. Its solubility parameter was determined from Eq. (4.6) (Yarranton and Masliyah, 1996; Akbarzadeh et al., 2005; Yarranton et al., 2007):

$$\delta_a = \left(\frac{1000A(T)M}{v} \right)^{1/2} \quad (4.6)$$

where, A is the heat of vaporization of asphaltene, $A(T) = 0.579 - 0.00075T$ (J/kg); T is the absolute temperature (K) and δ_a is the solubility parameter ($\text{MPa}^{0.5}$) of asphaltene sub-fraction. Both the molar volume and the solubility parameter of the asphaltenes were assumed to be independent of pressure.

All of the model parameters are fixed except for the average aggregation number, \bar{r} , and the shape factor, β , of the asphaltene molar mass distribution. For asphaltenes in a pure solvent, the average aggregation number can be determined from the average measured molar mass using vapor pressure osmometry (Yarranton et al., 2007). The value of β is chosen as 2.5.

In defining a value for β , it is important to note, at any given molar mass, there is a mixture of asphaltene components with different solubility parameters, molar volumes, and other properties (Speight, 1999). This multi-dimensional array of properties is not accounted for explicitly in the model but the effect has been projected onto a one-dimensional distribution of molar mass. The error in this simplification is rectified to some extent when the shape of the distribution is adjusted to fit the data; that is, all of the asphaltenes of a given solubility, irrespective of their other properties, are allocated to a given molar mass and density. At this time, there is insufficient compositional and physical property data to justify using multiple distributions of properties.

4.2.2 Solvent Diluted Heavy Oils or Crude Oil Blends

The heavy oils or crude oil blends did not contain light components and based on simulated distillation data were equivalent to a C16+ residue; that is, they contained only

components with a normal boiling point equivalent or greater than nC_{16} (560 K). These dead oils were characterized into four pseudo components: saturates, aromatics, resins and asphaltenes.

Table 4.2 provides a summary of the average molar mass, density, and solubility parameter for saturates, aromatics, and resins at 25°C and 1 atm. Note that Akbarzadeh et al. (2005) demonstrated that using average properties for the saturates, aromatics, and resins introduced negligible error into the precipitation calculations, possibly because their mole fraction in the diluted oil was relatively small compared with the diluted solvent of the crude oil.

Table 4.2: Properties of saturates, aromatics, and resins at 25°C and 1 atm.

Components	Molar Mass (g/mol)	Density (kg/m ³)	Solubility Parameter (MPa ^{0.5})
saturates	460	880	16.4
aromatics	522	990	20.3
resins	1040	1044	19.3

The following curve fit equations were developed by Akbarzadeh et al. (2005) for the densities of the saturate and the aromatic fractions of an Athabasca bitumen sample as a function of absolute temperature in K:

$$\rho_{sat} = 1078.96 - 0.6379 T \quad (4.7)$$

$$\rho_{aro} = 1184.47 - 0.5942 T \quad (4.8)$$

where ρ_{sat} and ρ_{aro} are the densities of saturates and aromatics in kg/m^3 , respectively. The following correlations were developed by Akbarzadeh et al. (2005) to estimate the solubility parameters of saturates and aromatics at other temperatures:

$$\delta_{sat} = 22.381 - 0.0222 T \quad (4.9)$$

$$\delta_{aro} = 26.333 - 0.0204 T \quad (4.10)$$

where δ_{sat} and δ_{aro} are the solubility parameters of saturates and aromatics. The solubility parameter of saturates was updated based on a more extensive data set at 23°C than was previously available to obtain the following:

$$\delta_{sat} = 23.021 - 0.0222 T \quad (4.11)$$

In the above equations, the saturate and aromatic densities and solubility parameters were assumed to be independent of pressure. For live oils, a pressure dependence will be introduced for solubility parameter of saturates and aromatics in Chapter 6. The density of the resins was assumed to be independent of temperature and pressure.

The asphaltenes were characterized as was done for the mixtures of asphaltenes and pure solvents. However, the average molar mass of asphaltenes cannot be measured in a mixture like a crude oil. Therefore, the average aggregation number is used as a fitting parameter to match the asphaltene yield from a crude oil diluted with *n*-heptane. Thereafter, the average aggregation number (or average associated molar mass) is fixed. For most crude oils we have examined, a shape factor of 3.5 provides a good fit to the data; however, there are some exceptions and it is better to adjust the shape factor to fit the available data. A β of 3.5 was used for all solvent diluted heavy oil or crude oil blends cases in this thesis unless otherwise stated.

4.3 Example Application of Model

The application of the modified regular solution model is demonstrated using asphaltene precipitation data for a Lloydminster heavy oil (Akbarzadeh et al., 2005). The reported saturates, aromatics, resins, asphaltenes (SARA) and solids content of heavy oil are 23.1, 41.7, 19.5, 15.3 and 0.4 wt %, respectively. Asphaltene precipitation yield data were available for *n*-heptane-diluted and *n*-pentane-diluted heavy oil at 23°C and 1 atm.

The model inputs are the composition of heavy oil in terms of SARA fractions, the amount of solvent (*n*-heptane or *n*-pentane), and the average molar mass of asphaltenes. The only unknown parameter of the model is the average molar mass of the asphaltenes (\bar{M}). This parameter is determined by fitting the precipitation data for *n*-heptane diluted heavy oil. The precipitation of asphaltenes from the *n*-pentane diluted heavy oil is then predicted.

The specific steps to be followed are given below:

1. The heavy oil-solvent mixture is divided into five pseudo-components: solvent, saturates, aromatics, resins, and asphaltenes. The normalized fluid composition in terms of weight fractions is calculated based on the solvent-heavy oil dilution ratio and the amount of SARA fractions. In this case, *n*-heptane is the solvent.
2. Asphaltenes are further divided into 30 sub-fractions based on the gamma function as described in Eqs. 4.3 and 4.4. The parameters required to complete the specifications for the gamma function are the average molar mass of asphaltenes, \bar{M} , and the shape factor, β . Table 4.3 shows the calculated molar mass distribution for a given average molar mass of 3620 g/mol and shape factor of 3.5. Hence, the fluid is characterized into a total of 34 pseudo components. Note, the molar mass of each asphaltene sub-fraction is taken as the arithmetic average of the highest and lowest molar mass of that particular sub-fraction.

3. For a given pure solvent, the molar mass, density and solubility parameter are obtained from the literature. The HBT technique is used for calculating the molar volume or density of solvent at the given pressure and temperature conditions. The effect of temperature in the solubility parameter is accounted for using Eq. 4.2.
4. The properties of SAR fractions are taken from Table 4.2. The densities of saturates and aromatics at temperatures other than 25°C are calculated from Eqs. 4.7 and 4.8, respectively. The solubility parameters of saturates and aromatics at other temperatures are calculated from Eqs. 4.11 and 4.10, respectively. The properties of resins are assumed to be independent of temperature.
5. The molar volume or density of each asphaltene sub fraction is calculated from the molar masses in Table 4.3 using Eq. 4.5 and the solubility parameter is determined from Eq. 4.6.
6. Equilibrium calculations are then performed using Eq. 4.1 and standard techniques (Rijkers and Heidemann, 1986; Alboudwarej et al., 2003). A bisection method is used for model convergence.
7. The amount of asphaltenes precipitation is calculated at the desired pressure and temperature (25°C, 1 atm) conditions for a range of *n*-heptane mass fraction in the heavy oil-solvent mixture.
8. The calculated yield data for *n*-heptane diluted heavy oil is compared to the measured data. The measured data is fitted by changing the input average molar mass of asphaltenes. The fitting is carried out by comparing the average absolute deviation (AAD) in the yield (See Appendix A for the definition of AAD). The fitted molar mass for the current example is 3620 g/mol and the AAD is 0.31%.
9. The fitted average molar mass of asphaltenes is used as the input parameter for predicting the precipitation yield data for *n*-pentane diluted heavy oil. In other words, steps 1 through 7 are repeated with *n*-pentane as solvent and using the fitted average molar mass of the asphaltenes as the input. %AAD for the prediction is 0.66.
10. The predicted yield data is compared to the measured data (see Figure 4.1).

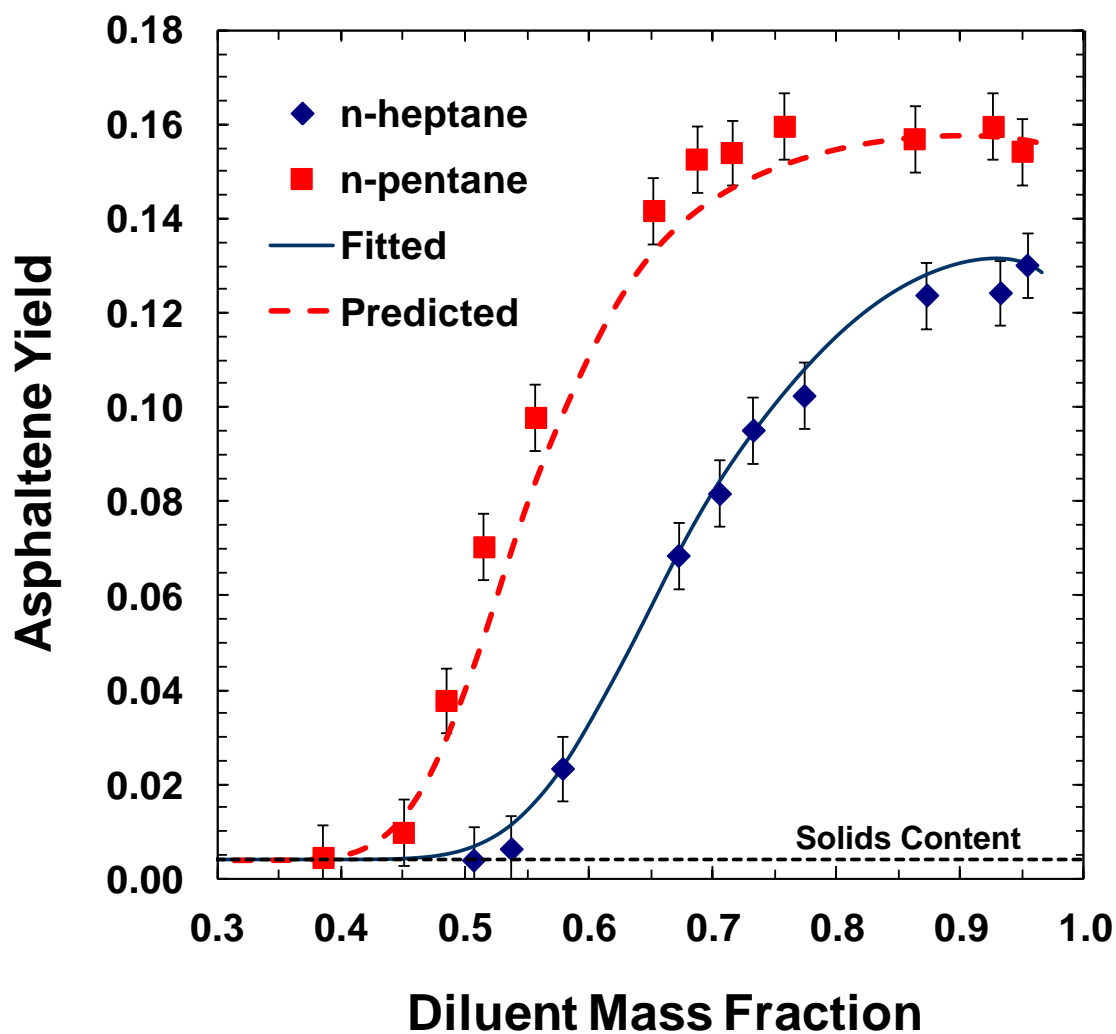


Figure 4.1: Measured and modeled asphaltene precipitation yields (in mass fraction) for Lloydminster heavy oil diluted with *n*-heptane and *n*-pentane. The data is from Akbarzadeh et al. (2005).

Table 4.3: Molar mass distribution of asphaltenes.

Asphaltene Subfraction	Molar Mass (g/mol)	f(M)	Mass Fraction	Mole Fraction
	1800	0	0	0
1	2469	3.08E-04	1.25E-01	1.82E-01
2	3201	4.70E-04	3.75E-01	4.21E-01
3	4088	2.86E-04	2.92E-01	2.57E-01
4	5006	1.11E-04	1.37E-01	9.89E-02
5	5934	3.46E-05	5.00E-02	3.04E-02
6	6866	9.39E-06	1.56E-02	8.16E-03
7	7801	2.33E-06	4.36E-03	2.01E-03
8	8738	5.42E-07	1.13E-03	4.65E-04
9	9675	1.20E-07	2.76E-04	1.03E-04
10	10613	2.57E-08	6.46E-05	2.19E-05
11	11551	5.34E-09	1.46E-05	4.54E-06
12	12489	1.08E-09	3.19E-06	9.20E-07
13	13428	2.16E-10	6.81E-07	1.83E-07
14	14367	4.22E-11	1.42E-07	3.56E-08
15	15306	8.13E-12	2.92E-08	6.86E-09
16	16245	1.55E-12	5.89E-09	1.31E-09
17	17185	2.92E-13	1.17E-09	2.46E-10
18	18124	5.45E-14	2.31E-10	4.58E-11
19	19064	1.01E-14	4.49E-11	8.47E-12
20	20003	1.85E-15	8.64E-12	1.56E-12
21	20943	3.38E-16	1.65E-12	2.84E-13
22	21882	6.13E-17	3.13E-13	5.14E-14
23	22822	1.11E-17	5.87E-14	9.27E-15
24	23762	1.98E-18	1.10E-14	1.66E-15
25	24701	3.54E-19	2.04E-15	2.97E-16
26	25641	6.30E-20	3.76E-16	5.28E-17
27	26581	1.12E-20	6.90E-17	9.34E-18
28	27521	1.97E-21	1.26E-17	1.65E-18
29	28460	3.47E-22	2.29E-18	2.90E-19
30	29400	6.08E-23	4.15E-19	5.08E-20