CHAPTER III

CALCULATION PROCEDURE

The most reliable procedure for the determination of parameters involves a fit to experimental data over a range of liquid compositions. The solution of model parameters required mathematical method such as Newton-Raphson which may be solved rather easily with computer software.

3.1 Back calculation method

The values for a set of parameters $\{\theta_j\}$ were obtained through regression by a weighted least squares technique that minimized the objective function

$$S = \sum_{i=1}^{n} \left(\frac{H_{cal}^{E} - H_{\exp}^{E}}{H_{\exp}^{E}} \right)_i^2 \qquad (3.1)$$

and

$$S = \sum_{i=1}^{n} \left(\frac{G_{cal}^{E} - G_{\exp}^{E}}{G_{\exp}^{E}} \right)_i^2 \qquad (3.2)$$

where n is the number of experimental observations and use subscripts exp and cal to denote experimental and calculated values, respectively.

3.2 Newton Raphson method

Newton Raphson method is readily extended to the solution of simultaneous equations. The general formula for iteration is

$$f(X_n) + \left[\frac{d\,f(X)}{dX} \right]_{X=X_n} \Delta X_n = 0 \qquad (3.3)$$

where

$$\Delta X_n \equiv X_{n+1} - X_n \qquad \text{or} \qquad X_{n+1} = X_n + \Delta X_n$$

Equation (3.3), written for successive iterations (n = 0, 1, 2, ...), procedures successive values of ΔX_n and successive values of $f(X_n)$. The process starts with an initial value X_0 and continues until either of ΔX_n or $f(X_n)$ approaches zero to within a preset tolerance.

3.3 Computer program

In this section are presented the input data and algorithm of the program. There are two subroutines for obtaining parameters from the excess enthalpy data.

3.3.1 Input data

The information which are required in the calculation procedure are listed as follows:

1. Constant variable: gas constant
2. Selected binary systems: benzene + cyclohexane, etc.
3. Experimental data:
   - vapor-liquid equilibrium (VLE) data involving pressure (*P*), temperature (*T*), number of experimental data points (*n*), and composition of liquid (*x*).
   - heat of mixing (H^E) data involving temperature (*T*), excess enthalpy (H^E_{exp}), and composition of liquid (*x*).
4. Specific data: molar liquid volume (v_i^L) which using in the Wilson model and volume parameter (r_i) and surface area parameter (q_i) for the UNIQUAC equations.

5. Initial estimate parameters: A, B, and the tolerance used in this investigation is 0.0001.

3.3.2 Algorithm of the program

A simplified algorithm of the calculation procedure is listed below. Figure 3.1 illustrates the flow chart involving calculation based on VLE data.

1. Input all the data mentioned in section 3.4.1 except H^E data.
2. Calculate parameters and pressures in subroutine by using Newton Raphson method. Figure 3.2 and 3.3 illustrate the flow chart of subroutine Func WilsonP, Func UNIQP, respectively.
   - If selection is Wilson, go to subroutine Func WilsonG.
   - If selection is UNIQUAC, go to subroutine Func UNIQG.
3. Write optimum parameters from step 2.
4. Calculate the activity coefficients.
5. Calculate the pressures according to

$$P_{cal} = \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat} \tag{3.7}$$

   where P_i^{sat} is the vapor pressure of pure component i.

6. Calculate the percentage average absolute deviation (%AAD) which is defined by the expression:

$$\%AAD = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{P_{cal} - P_{exp}}{P_{exp}} \right|_i$$

7. Write values of pressure over the whole composition range, average absolute deviation (%AAD).

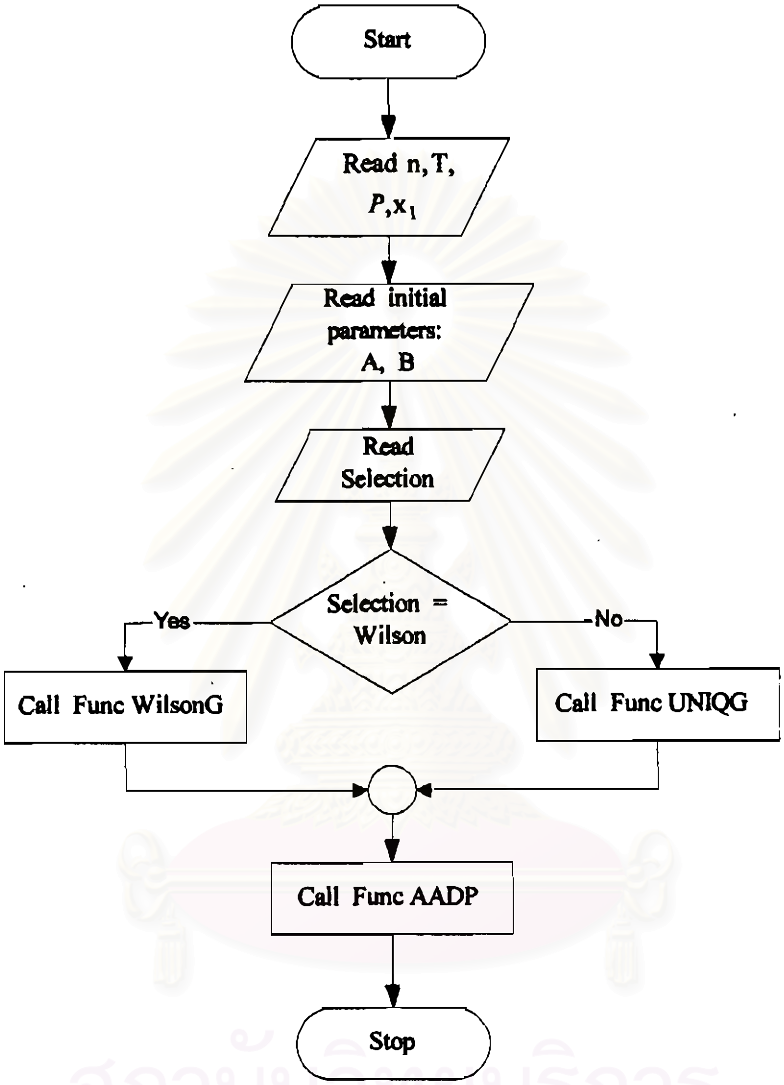

Figure 3.1 A simplified flow chart of the calculation procedure based on VLE data.

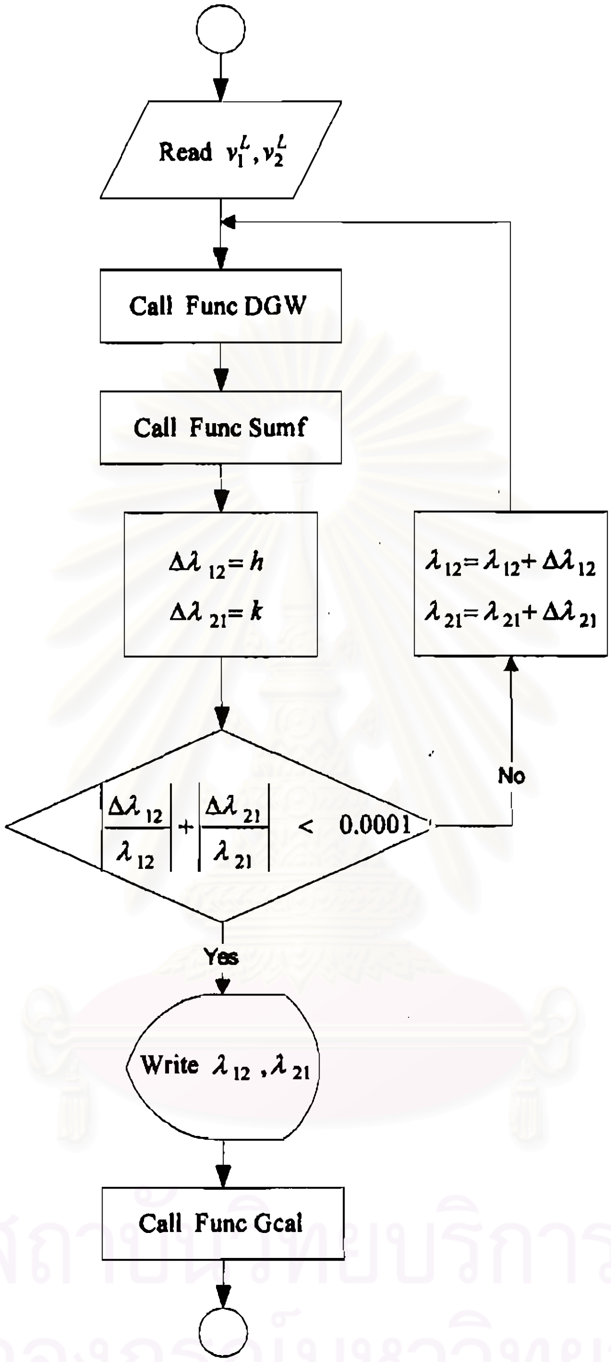

Figure 3.2 A schematic diagram of subroutine Func WilsonG.

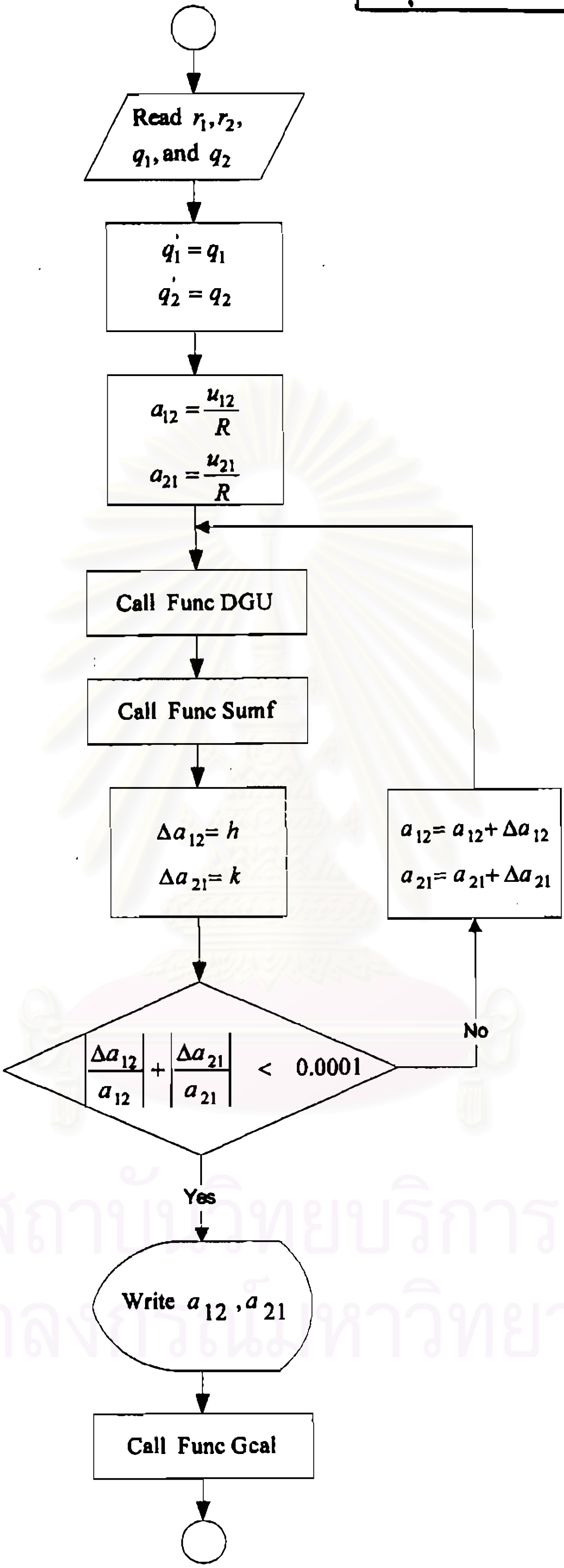

Figure 3.3 A schematic diagram of subroutine Func UNIQG.

In addition, a simplified flow chart of the calculation procedure based on heat of mixing data is shown in Figure 3.4.

1. Input all the data mentioned in section 3.4.1 except VLE data.
2. Calculate parameters and excess enthalpy in subroutine by using Newton Raphson method. Figure 3.5 and 3.6 illustrate the flow chart of subroutine Func Wilson, Func UNIQ, respectively.
   - If selection is Wilson, go to subroutine Func Wilson.
   - If selection is UNIQUAC, go to subroutine Func UNIQ.
3. Write optimum parameters from step 2.
4. Calculate the percentage average absolute deviation (%AAD) which is defined by the expression:

$$\%AAD = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{H_{cal}^{E} - H_{exp}^{E}}{H_{exp}^{E}}\right|_{i}$$

5. Write values of excess enthalpy over the whole composition range, average absolute deviation (%AAD).

The subroutines involving the calculation procedure based on two source data are discussed in Appendix D.

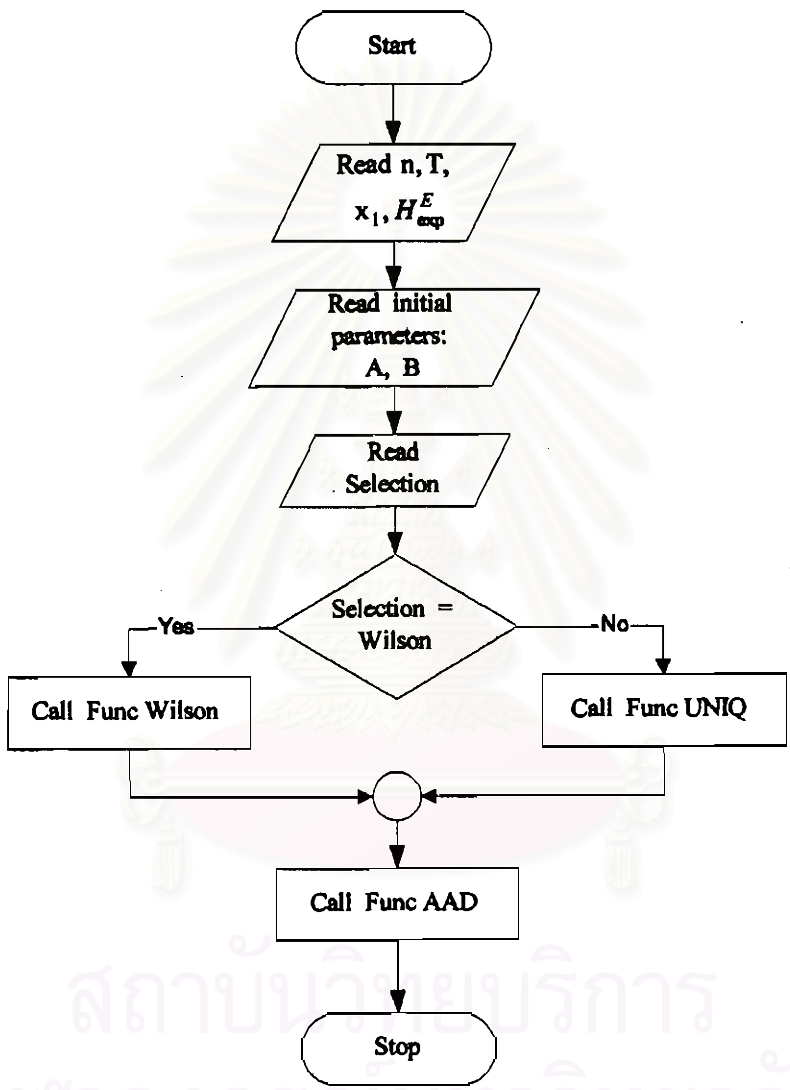

Figure 3.4 A simplified flow chart of the calculation procedure based on H^E data.

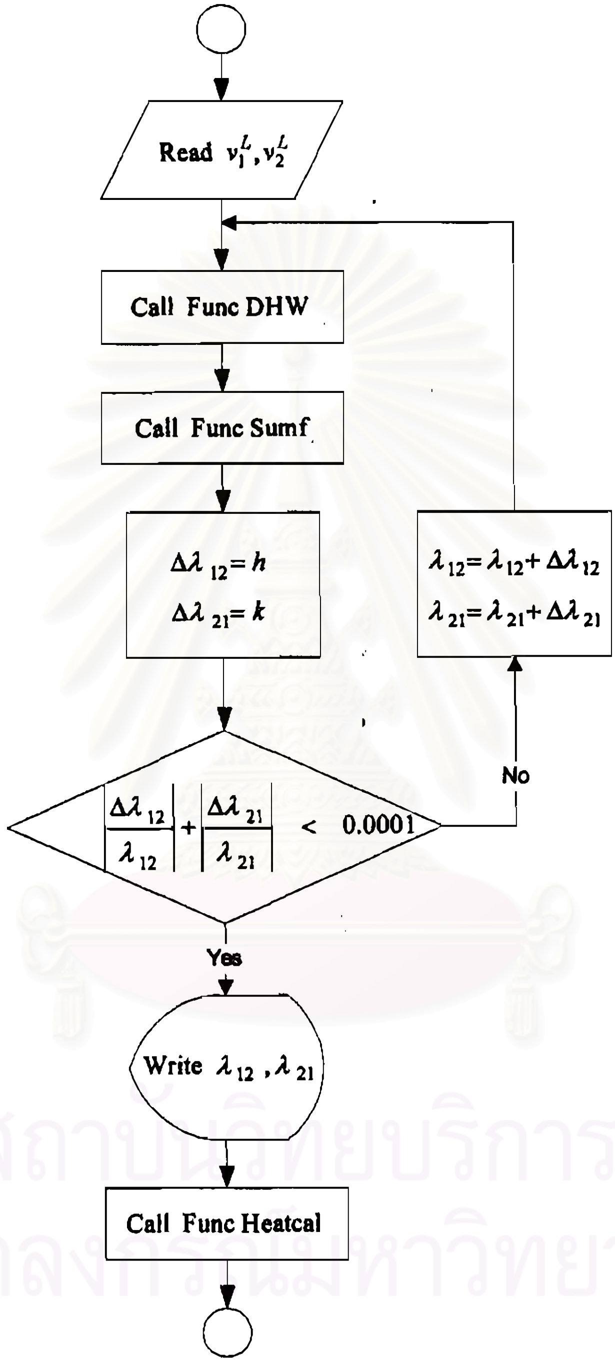

Figure 3.5 A schematic diagram of subroutine Func Wilson.

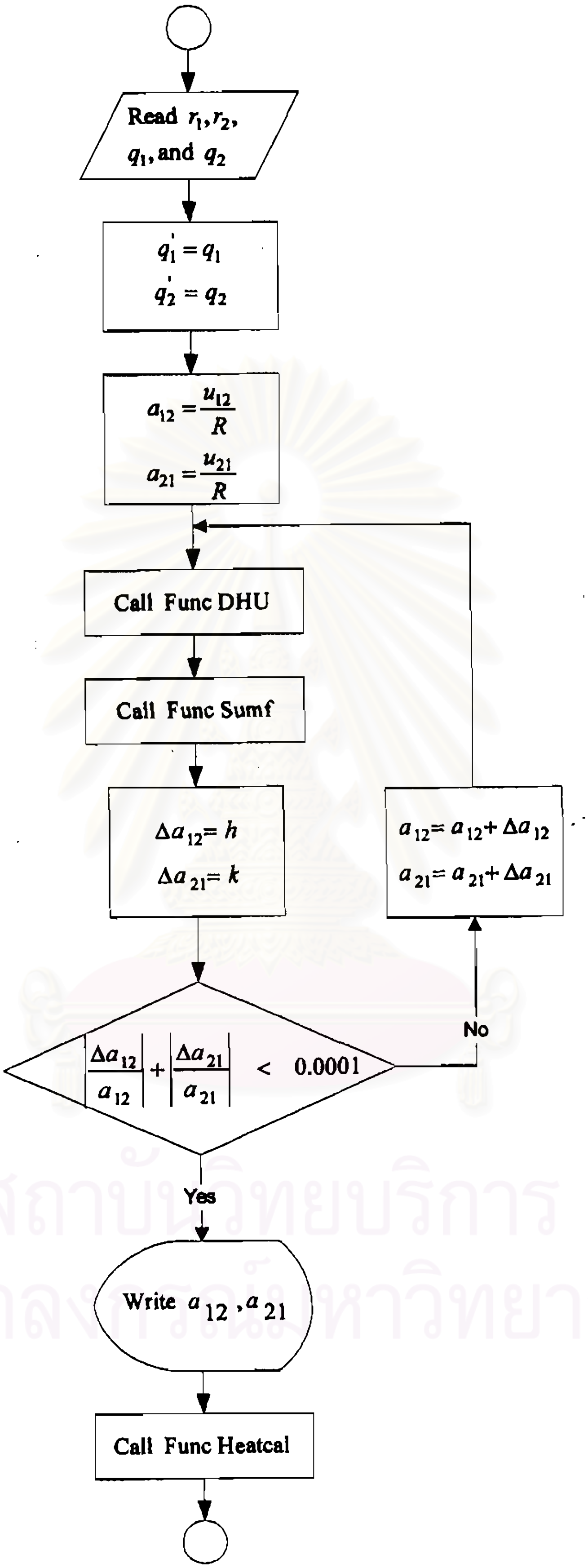

Figure 3.6 A schematic diagram of subroutine Func UNIQ.