



## CHAPTER 3

### PROPOSED MODIFICATION AND PROCEDURE

#### 3.1 Formulation of the Modified Hard-Sphere Equation of State

Semiempirical equations of state generally express pressure as the sum of two terms, a repulsion pressure  $P_R$  and an attraction pressure  $P_A$  as follows :

$$P = P_R + P_A \quad (3.1)$$

The equations of van der Waals , Redlich and Kwong , and Soave are examples and all have the repulsion pressure expressed by the van der Waals hard sphere equation, that is

$$P_R = \frac{RT}{(V-b)} \quad (3.2)$$

For hard sphere equation of state by Ishikawa et al.(8), the repulsion pressure is modified as :

$$P_R = \frac{RT (2V+b)}{V (2V-b)} \quad (3.3)$$

However, the attraction pressure can be expressed as

$$P_A = \frac{a}{f(V)} \quad (3.4)$$

where  $f(V)$  is a function of the molar volume  $V$  and the constant  $b$  which is related to the size of the hard spheres. The parameter  $a$  can be regarded as a measure of the intermolecular attraction force. Applying Equation (3.1) at the critical point where the first and second derivatives of pressure with respect to volume vanish one can obtain expressions for  $a$  and  $b$  at the critical point in term of the critical properties. While  $b$  is usually treated as temperature independent,  $a$  is constant only in van der Waals equation. For the Redlich-Kwong equation and the Soave-Redlich-Kwong equation, dimensionless scaling factors are used to describe the temperature dependence of the energy parameter.

Table 3.1 Repulsion and Attraction Pressure of Equation of State

	P Repulsive	P Attractive
Van der Waals	$\frac{RT}{V-b}$	$\frac{a}{V^2}$
Redlich-Kwong	$\frac{RT}{V-b}$	$\frac{a}{T^{0.5} V(V+b)}$
Soave-Redlich-Kwong	$\frac{RT}{V-b}$	$\frac{a}{V(V+b)}$
Peng-Robinson	$\frac{RT}{V-b}$	$\frac{a}{V(V+b)+b(V-b)}$
Carnahan-Starling	$\frac{RT(1+y+y^2-y^3)}{V(1-y)^3}$	$\frac{a}{T^{0.5} V(V+b)}$
De Santis et al.	$\frac{RT(1+y+y^2-y^3)}{V(1-y)^3}$	$\frac{a}{V(V+b)}$
Ishikawa, Chung & Lu	$\frac{RT(2V+b)}{V(2V-b)}$	$\frac{a}{T^{0.5} V(V+b)}$
This work	$\frac{RT(2V+b)}{V(2V-b)}$	$\frac{a}{V(V+b)}$

The modified hard sphere equation used in this work combines the hard sphere repulsive term of Ishikawa et al. (8) and the empirical attractive term as follows :

$$P = \frac{RT(2V+b)}{V(2V-b)} - \frac{a}{V(V+b)} \quad (3.5)$$

To obtain the parameters in this equation, the following conditions that at the critical point are used

$$[\partial P / \partial V]_{T_c} = [\partial^2 P / \partial V^2]_{T_c} = 0 \quad (3.6)$$

which leads to

$$a = \Omega_a RT_c^2 / P_c \quad (3.7)$$

$$b = \Omega_b RT_c / P_c \quad (3.8)$$

Equation (3.5) can be used to represent fluid properties in both gas and liquid states. In this work, the constants  $\Omega_a$  and  $\Omega_b$  were considered as temperature-dependent characteristic parameters for individual fluids and were evaluated from saturated liquid properties. The references from which the saturated properties were obtained are reported in Table 3.2. The calculated  $\Omega_a$  and  $\Omega_b$  values were further correlated by means of Equations (3.9) and (3.10) :

$$\Omega_a = \sum_{i=0}^2 a_i Tr^{-i} \quad (3.9)$$

and

$$\Omega_b = \sum_{i=0}^2 b_i Tr^{-i} \quad (3.10)$$

Equation (3.5) can be rewritten as

$$2Z^3 + (B-2)Z^2 + (2A-3B-B^2)Z - (B^2 - AB) = 0 \quad (3.11)$$

where

$$A = aP/R^2 T^2 \quad (3.12)$$

$$B = bP/RT \quad (3.13)$$

Equation (3.11) yields one or three roots depending upon the number of phases in the system. In the two phases region, the largest root is for the compressibility factor of the vapor while the smallest positive root corresponds to that of the liquid.

Table 3.2 Literature Sources of the Saturation Properties Used in the Investigation.

COMPOUND	Saturated Liquid Volume	Vapor Pressure
Methane	Vennix et al.(27), Goodwin (28), and Goodwin et al.(29)	Goodwin (28)
Ethane	Sage et al.(30), Pal et al.(31), and Maass et al.(32)	Sage et al.(30), Maass et al.(32), and Porter (33)
Propane	Reamer et al.(34), Deschner et al.(35), Sage et al.(36), and Stearns et al.(37)	Reamer et al.(34), Deschner et al.(35), Sage et al.(36), and Stearns et al.(37)
n-Butane	Das et al.(38), Olds et al.(39) and Sage et al.(40)	Das et al.(38), Olds et al.(39) and Sage et al.(40)
i-Butane	Das et al.(41), Sage et al.(42) ,and Waxman et al.(43)	Das et al.(41), Sage et al.(42) ,and Waxman et al.(43)
n-Pentane	Sage et al.(44), and Das et al.(45)	Sage et al.(44), and Das et al.(45)
i-Pentane	Isaac et al.(46), and Das et al.(47)	Isaac et al.(46), and Das et al.(47)
n-Hexane	Stewart et al.(48), and Kay (49)	Stewart et al.(48), Huisman et al.(50)
Ethylene	Maass et al.(32), and Calado et al.(51)	Maass et al. (32)
Propylene	Maass et al.(32), Vaughan et al.(52) and Farrington et al.(53)	Maass et al.(32), Vaughan et al.(52) and Farrington et al.(53)

### 3.2 Evaluation of $\Omega_a$ and $\Omega_b$

The modified hard sphere equation of state, Equation (3.5), is rearranged as follows :

$$Z = \frac{(2+h)}{(2-h)} - \frac{A}{B} \frac{h}{(1+h)} \quad (3.16)$$

$$h = \frac{BP}{Z} \quad (3.17)$$

$$A = \frac{\Omega_a T_c^2}{T^2 P_c} = \frac{a}{R^2 T^2} \quad (3.18)$$

$$B = \frac{\Omega_b T_c}{T P_c} = \frac{b}{RT} \quad (3.19)$$

Equation (3.16) is rewritten as follows:

$$(A+B)h^3 - (2A-3B-B^2P)h^2 - (B^2P-2B)h - 2B^2P = 0 \quad (3.20)$$

at equilibrium

$$f_{1v} = f_{1l} \quad (3.21)$$

or in terms of fugacity coefficient

$$\phi_{1v} = \phi_{1l} \quad (3.22)$$

The quantity  $\phi_{11}$  for a pure component may be evaluated from the following equation :

$$\ln \phi_1 = Z_1 - 1 - \ln Z_1 - 2 \ln(2-h_1) - \frac{A}{B} \ln(1+h_1) \quad (3.23)$$

similarly

$$\ln \phi_v = Z_v - 1 - \ln Z_v - 2 \ln(2-h_v) - \frac{A}{B} \ln(1+h_v) \quad (3.24)$$

It may be readily shown that combining Equation (3.23) with Equations (3.16), (3.17) and (3.22) gives :

$$\ln Z_1 \phi_v + 1 - Z_1 + 2 \ln(2-h_1) + \frac{[(2+h_1)-Z_1(2-h_1)](1+h_1)}{h_1(2-h_1)} \ln(1+h_1) = 0 \quad (3.25)$$

These equations were employed in the evaluation of  $\Omega_a$  and  $\Omega_b$  in this investigation. The calculation procedure may be briefly outlined as follows :

- [1] For a given value of  $Z_1$ , and an assumed value of  $\phi_v$  calculate  $h_1$  by means of Equation (3.25).
- [2] Calculate B from Equation (3.17) and A from Equation (3.16).
- [3] Substitute A and B values obtained from step 2 into Equations (3.20) and (3.16) and solve simultaneously for another set of roots of  $Z_v$  and  $h_v$ . (As there are three

roots of  $h$  in Equation (3.20), the largest root is  $h_1$  and the smallest one is  $h_v$ . In this investigation, the roots were located by means of the Newton's rule which is quadratically convergent).

- [4] Calculate  $\phi_v$  from Equation (3.24) .
- [5] Obtain new  $h_1$  value from Equation (3.25) and compare it with that obtained in step 1. If disagreeable, repeat the steps 1-5 using the new value of  $\phi_v$  obtained from step 4.

An iteration loop is thus built up until the change of  $h_1$  value is less than the specified tolerance. The final set of A and B values are used to obtain  $\Omega_a$  and  $\Omega_b$  values from Equations (3.18) and (3.19) , respectively . The tolerance used in this investigation is 0.00005 . A schematic diagram outling the evaluation is given in Figure 3.1 .

### 3.3 Determination of the Temperature Dependence of the Parameters

Based on the modified hard sphere equation of state (Eq.3.5) and the procedure in Figure 3.1 with the use of saturated liquid density data, the temperature-dependent parameter  $\Omega_a$  and  $\Omega_b$  were evaluated for pure component light hydrocarbons. The calculated  $\Omega_a$  and  $\Omega_b$  values were further correlated by means of Equations (3.9) and (3.10). The values of coefficients  $a_0$  ,  $a_1$  ,  $a_2$  ,  $b_0$  ,  $b_1$  ,  $b_2$  were determined using the method of least-squares. The details of the computer program is shown in Appendix A.

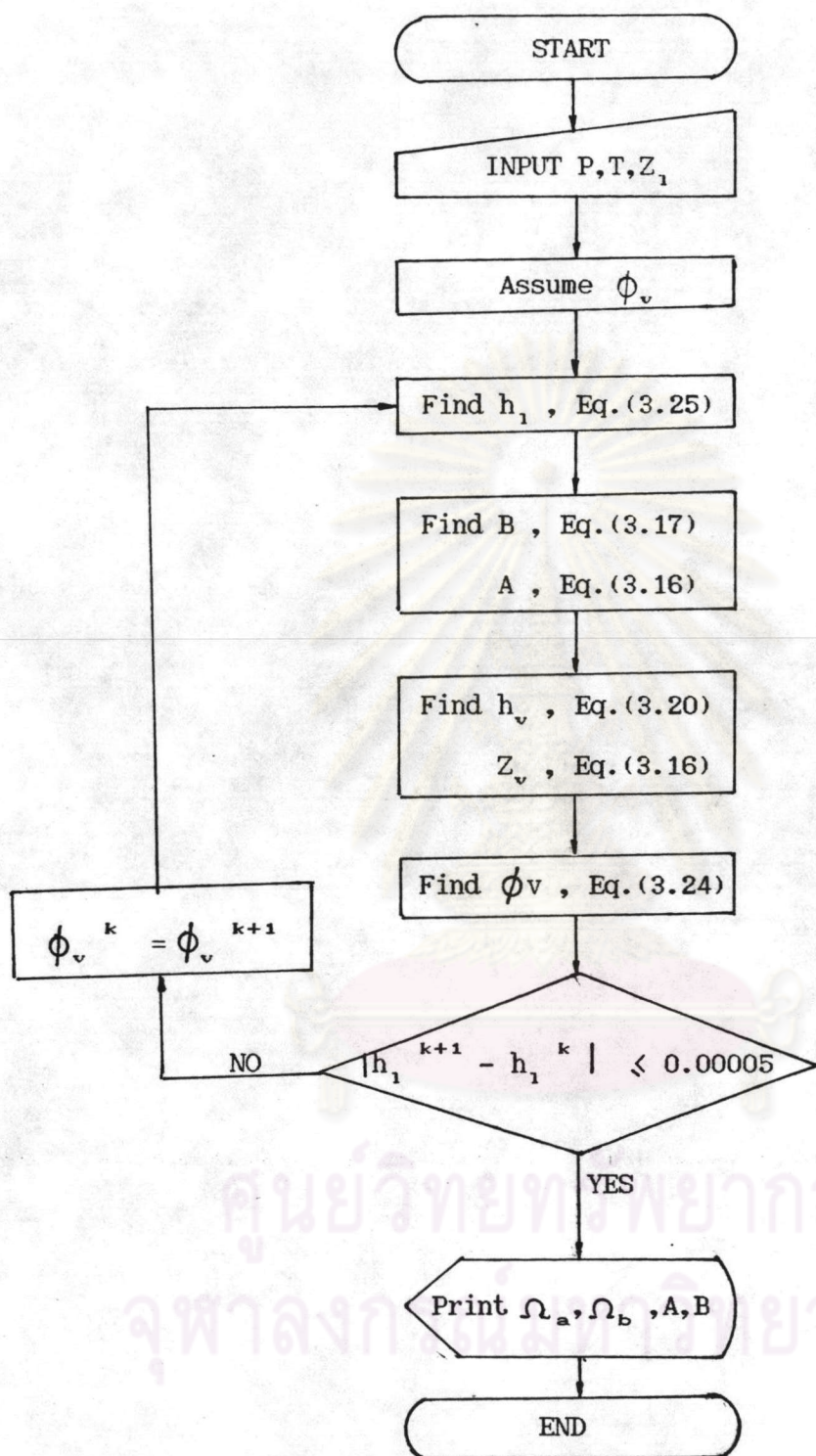


Figure 3.1 Diagram for Evaluation of  $\Omega_a$  and  $\Omega_b$  .



### 3.4 Representation of Pure Component Properties

The properties selected in this work for testing the capability of Equation 3.5 together with the  $\Omega_a$  and  $\Omega_b$  values represented by Equations 3.9 and 3.10 for representing pure component properties include three saturated properties (vapor pressure, liquid and vapor volumes). The ten compounds selected for the calculation are listed in Table 3.3. The new modified hard sphere equation of state is tested by comparing calculated results with experimental data for ten compounds. These saturated properties were also calculated by three other cubic equations of state, namely Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Ishikawa-Chung-Lu (ICL) for the purpose of comparison. The four equations of state used in this work are shown in Table 3.4.

Table 3.3 Physical Properties of Pure Component.

COMPOUND	Tc, K	Pc, atm.	MW	$\omega$	Ref.
Methane	190.77	45.65	16.0430	0.008	(27)
Ethane	305.40	48.20	30.0700	0.098	(61)
Propane	369.80	41.90	44.0970	0.152	(61)
n-Butane	425.16	37.47	58.1243	0.193	(38)
i-Butane	408.13	36.00	58.1243	0.176	(41)
n-Pentane	469.65	33.25	72.1514	0.251	(45)
i-Pentane	460.39	33.37	72.1514	0.227	(47)
n-Hexane	507.40	29.30	86.1780	0.296	(61)
Ethylene	282.40	49.70	28.0540	0.085	(61)
Propylene	365.00	45.60	42.0810	0.148	(61)

Table 3.4 Cubic Equations of State used in this study.

SOAVE-REDLICH-KWONG (SRK)	PENG-ROBINSON (PR)	ISHIKAWA, CHUNG & LU (ICL)	MODIFIED HARD-SPHERE (THIS WORK)
Standard form :			
$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}$	$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)}$	$P = \frac{RT}{V} \frac{(2V+b)}{(2V-b)} - \frac{a}{T^{0.5} V(V+b)}$	$P = \frac{RT}{V} \frac{(2V+b)}{(2V-b)} - \frac{a}{V(V+b)}$
Parameters :			
$a = 0.42747 R \frac{T_c}{P_c} \frac{T_c}{P_c}$	$a = 0.45724 R \frac{T_c}{P_c} \frac{T_c}{P_c}$	$a = \Omega_a R \frac{T_c}{P_c} \frac{T_c}{P_c}$	$a = \Omega_a R \frac{T_c}{P_c} \frac{T_c}{P_c}$
$b = 0.08664 R \frac{T_c}{P_c}$	$b = 0.07780 R \frac{T_c}{P_c}$	$b = \Omega_b R \frac{T_c}{P_c}$	$b = \Omega_b R \frac{T_c}{P_c}$
$\alpha = [1+m(1-Tr^{0.5})]^2$	$\alpha = [1+m(1-Tr^{0.5})]^2$	$\Omega_a = a_0 + a_1 Tr + a_2 Tr^2 + a_3 Tr^3$	$\Omega_a = a_0 + a_1 Tr + a_2 Tr^2$
$m = 0.48508 + 1.55171\omega - 0.15613\omega^2$	$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$	$\Omega_b = b_0 + b_1 Tr + b_2 Tr^2 + b_3 Tr^3$	$\Omega_b = b_0 + b_1 Tr + b_2 Tr^2$

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### 3.5 Application of the Modified Hard-Sphere Equation of State to Mixtures : Vapor-Liquid Equilibrium

Extending a pure component equation of state to mixtures requires expressing its constants as function of composition. For vapor-liquid equilibrium computations this must be done in a manner which predicts the actual composition dependence of the mixture with sufficient accuracy to permit the differentiation of mixture properties with respect to either composition or moles of the individual components as this procedure is required to determine fugacities of individual components in the vapor and liquid mixtures.

From the equilibrium condition

$$f_{i,l}(P, T, x_1, \dots, x_n) = f_{i,v}(P, T, y_1, \dots, y_n) \quad (3.26)$$

one can obtain a system of equations numbering as many as the number of components.

Since estimating the fugacities requires applying the modified hard sphere equation of state, it is necessary to express the dependence of terms  $a$  and  $b$  on the composition by means of mixing rules of the pure compounds constants. The rules most often applied are

$$a_m = \sum_i \sum_j y_i y_j a_{i,j} \quad (3.27)$$

$$b_m = \sum_i y_i b_i \quad (3.28)$$

The same rule are used for liquid mixtures with  $x$  replacing  $y$  in these equations. The parameter  $a_{ij}$ , arises from interactions between two dissimilar molecules. In this study, the mixing rule for  $a_{ij}$  as proposed by Redlich and Kwong (1) was modified by the introduction of a binary interaction coefficient,  $c_{ij}$ , as suggested by Zudkevith and Joffe (18).

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - c_{ij}) \quad (3.29)$$

for hydrocarbons, Soave (2) suggested that  $c_{ij}$  was zero.

Once the mixing rules (Equations (3.27) to (3.29)) are chosen, from Equation (3.5) and the definition of the fugacity coefficient

$$RT \ln \phi_1 = \int_{\infty}^V \left[ \left( \frac{\partial P}{\partial n_1} \right)_{v, T, n_{j \neq 1}} - \frac{RT}{V} \right] dV - RT \ln Z \quad (3.30)$$

it is possible to obtain  $\hat{\phi}_1^v$  in a vapor mixture as

$$\begin{aligned} \ln \hat{\phi}_1^v &= \ln [f_1^v / y_1 P] \\ &= \frac{2bi}{2V - b_m} - 2 \ln \left( \frac{1 - b_m}{2V} \right) - \frac{2 \sum_{k=1}^m y_k a_{k1}}{RTb_m} \ln \left( \frac{V + b_m}{V} \right) \\ &\quad + \frac{ab_1}{RTb_m^2} \left[ \ln \left( \frac{V + b_m}{V} \right) - \frac{b_m}{V + b_m} \right] - \ln Z \end{aligned} \quad (3.31)$$

The same expression is applicable to the liquid fugacity coefficient ( $\hat{\phi}_1^l = \hat{f}_1^l / x_1 P$ ) by replacing  $y$  by Equation (3.31) with  $x$ .

At equilibrium

$$\hat{f}_1^v = \hat{f}_1^l \quad (3.32)$$

and

$$K_1 = y_1 / x_1 = \hat{\phi}_1^l / \hat{\phi}_1^v \quad (3.33)$$

Equations (3.27) to (3.33) are the working equations used in this study for the bubble point pressure calculations. Figure 3.2 shows a schematic diagram for the bubble point pressure calculations.

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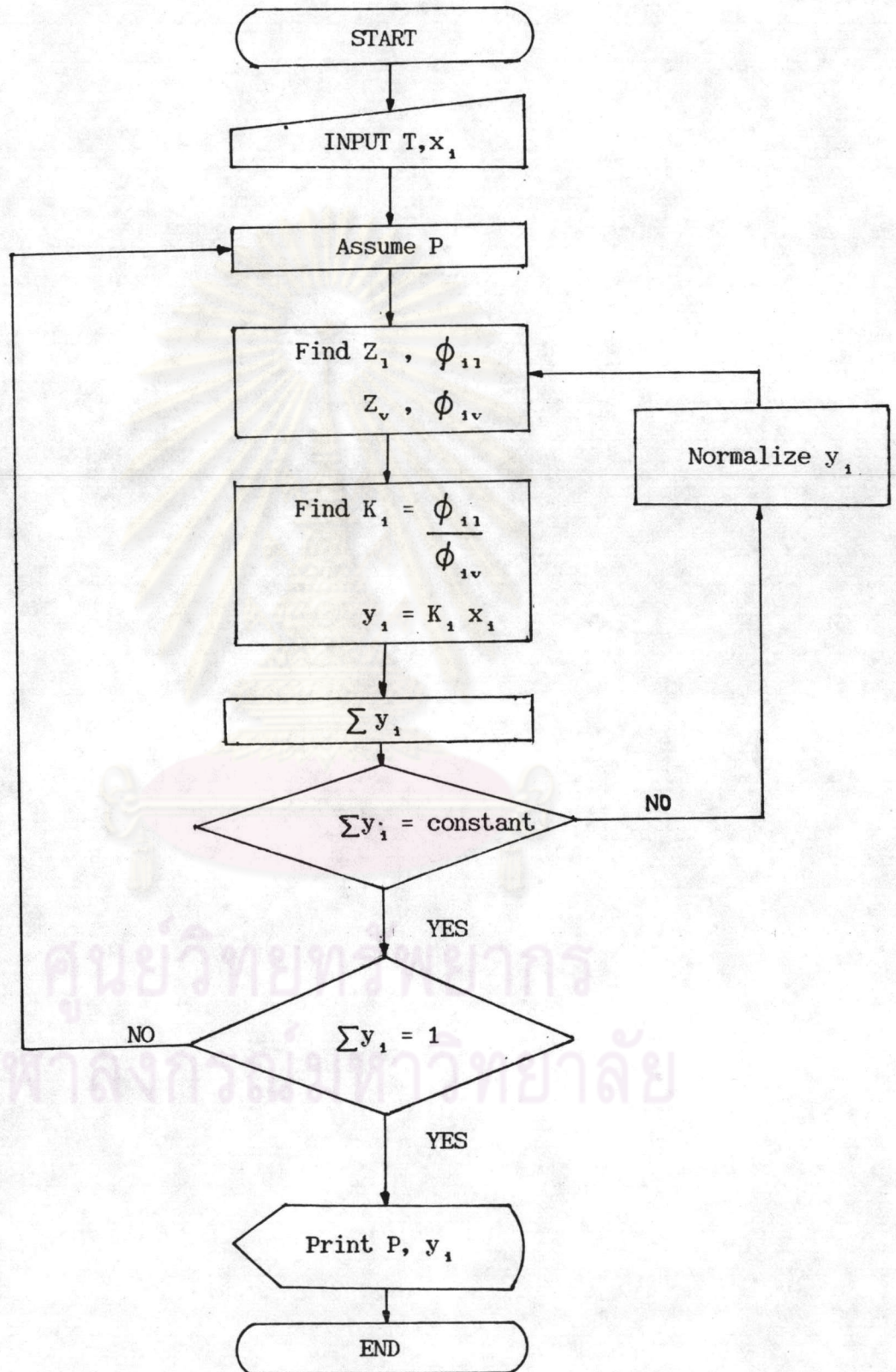


Figure 3.2 Diagram for Bubble Point Pressure Calculations.

### 3.6 Another Modification of Hard-Sphere Equation of State

Another modified hard sphere equation combines the hard sphere repulsive term of Ishikawa et al. (8) and the attractive term of Peng-Robinson (3) equation of state as follows :

$$P = \frac{RT}{V} \frac{(2V+b)}{(2V-b)} - \frac{a}{V^2 + 2bV - b^2} \quad (3.34)$$

To obtain the parameters in this equation, the following conditions that at the critical point are used

$$[\partial P / \partial V]_{T_c} = [\partial^2 P / \partial V^2]_{T_c} = 0 \quad (3.35)$$

which leads to

$$a = \Omega_a RT_c^2 / P_c \quad (3.36)$$

$$b = \Omega_b RT_c / P_c \quad (3.37)$$

The constants  $\Omega_a$  and  $\Omega_b$  were considered as temperature-dependent characteristic parameters for individual fluids and were evaluated from saturated liquid properties. The calculated  $\Omega_a$  and  $\Omega_b$  values were further correlated by means of Equations (3.38) and (3.39) :

$$\Omega_a = \sum_{i=0}^2 a_i Tr^{-i} \quad (3.38)$$

and

$$\Omega_b = \sum_{i=0}^2 b_i Tr^{-i} \quad (3.39)$$

Equation (3.34) can be rewritten as

$$2Z^4 + (3B-2)Z^3 + (2A-5B-4B^2)Z^2 - (B^2 - AB)Z + B^3 = 0 \quad (3.40)$$

where

$$A = aP/R^2 T^2 \quad (3.41)$$

$$B = bP/RT \quad (3.42)$$

:Evaluation of Parameters for Equation (3.34)

The Equation (3.34) is rearranged as follows :

$$Z = \frac{(2+h)}{(2-h)} - \frac{A}{B} \frac{h}{(1+2h-h^2)} \quad (3.43)$$

$$h = \frac{BP}{Z} \quad (3.44)$$

$$A = \frac{\Omega_a T_c^2}{T^2 P_c} = \frac{a}{R^2 T^2} \quad (3.45)$$

$$B = \frac{\Omega_b T_c}{T P_c} = \frac{b}{RT} \quad (3.46)$$

Equation (3.43) is rewritten as follows:

$$Bh^4 + (B^2P-A)h^3 + (2A-5B-4B^2P)h^2 + (3B^2P-2B)h + 2B^2P = 0 \quad (3.47)$$



at equilibrium

$$f_{1v} = f_{1l} \quad (3.48)$$

or in terms of fugacity coefficient

$$\phi_{1v} = \phi_{1l} \quad (3.49)$$

The quantity  $\phi_{1l}$  for a pure component may be evaluated from the following equation :

$$\ln \phi_{1l} = Z_{1l} - 1 - \ln Z_{1l} - 2 \ln(2-h_{1l}) - \frac{A}{2\sqrt{2} B} \frac{\ln(1+2.414h_{1l})}{(1-0.414h_{1l})} \quad (3.50)$$

similarly

$$\ln \phi_{1v} = Z_{1v} - 1 - \ln Z_{1v} - 2 \ln(2-h_{1v}) - \frac{A}{2\sqrt{2} B} \frac{\ln(1+2.414h_{1v})}{(1-0.414h_{1v})} \quad (3.51)$$

It may be readily shown that combining Equation (3.50) with Equations (3.43), (3.44) and (3.49) gives :

$$\ln Z_{1l} \phi_{1v} + 1 - Z_{1l} + 2 \ln(2-h_{1l}) + \frac{[(2+h_{1l}) - Z_{1l}(2-h_{1l})](1+2h_{1l}-h_{1l}^2)}{2 h_{1l} (2-h_{1l})} \frac{\ln(1+2.414h_{1l})}{(1-0.414h_{1l})} = 0 \quad (3.52)$$

These equations were employed in the evaluation of  $\Omega_a$  and  $\Omega_b$  for Equation (3.34). The calculation procedure similar to the proposed modified hard sphere equation of state, Equation (3.5).