CHAPTER IV

SELECTION OF EOS

Since introduction of the famous van der Waals equation of state, a century ago, many equations of state have been proposed for VLE. The range is from simple EOS with only two, usually adjustable, parameters to complex formulas of more than 50 parameters.

Cubic equations of state, the simple equations that can be transformed into cubic equation in Z, have received much attention during the last decade due to their simplicity and practical success. Although the many-constant equations have been utilized for precise representation of volumetric data, they are not generally prefered for phase equilibrium calculations and in process simulation studies [15], partly because they require excessive computer time and partly it is difficult to obtain generalized forms of these equations suitable for mixture calculations. In many situation, therefore, use of simple cubic equations of state represent a satisfactory compromise between accuracy and speed of computations. It is for these reasons that in this work, attention was given to cubic equations of state.

A large number of cubic equations of state have been developed and include those of Berthelot, Beattie and Brideman, Redlich and Kwong, and various modifications thereof. Only the

current common used Redlich-Kwong type of equations will be discussed as the earlier equations have essentially been replaced by these formulations.

Since the time of Redlich-Kwong, about 40 years ago, more than 50 modifications have been proposed for quantitative predictions of VLE, still remaining relatively uncomplicated. The practicing engineer, obviously confused on finding so many equations of state, wants to use the best available method and probably chooses an EOS from literature. However, since each published equation is reputed to produce the best results, the engineer will tend to select a new method without checking its limitations and properties. The purpose of this study is to evaluate the most relevant equations of state for natural gas systems, especially at high pressure. The most general form of the cubic equation of state may be written as [11].

$$P = \frac{RT}{(V - b)} - \frac{a(V - k_3 b)}{(V - b)(V^2 + k_1 bV + k_2 b^2)} \qquad (4.1)$$

where k_1, k_2 and k_3 may be just constants or may be functions of temperature and of the acentric factor of the component. By specializing for k_1, k_2, k_3, all cubic equations available in the literature may be written under the form of Equation (4.1). In table 4.1 are a number of examples.

Table 4.1 Some Cubic Equations of State.

NAME		EQUATION	k_1	k_2	k_3
Van der Waals	(1873)	$P = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$	0	0	1
SOAVE	(1972)	$P = \dfrac{RT}{V-b} - \dfrac{a(T)}{V(V+b)}$	1	0	1
PR	(1976)	$P = \dfrac{RT}{V-b} - \dfrac{a(T)}{V(V+b)+b(V-b)}$	2	-1	1
Harmens and Knapp	(1980)	$P = \dfrac{RT}{V-b} - \dfrac{a(T)}{V^2+Vcb-(c-1)b^2}$	3	-2	1
Schmidt and Wenzel	(1980)	$P = \dfrac{RT}{V-b} - \dfrac{a(T)}{V^2+ubV+wb^2}$	1+3w	-3w	1
Fuller	(1976)	$P = \dfrac{RT}{V-b} - \dfrac{a(T)}{V(V+cb)}$	c	0	1

4.1 CRITERIA OF SELECTION

In order to choose the most appropriate EOS to predict multicomponent VLE, one must consider the capability of predicting the physical properties of pure substances. It has been common practice in recent years to compare the simple equations of state by noting how well they predict saturated liquid volumes and vapour pressures through the equality of liquid and gas fugacities [14,15]. But in this study, two more properties at the critical point were studied, Z and Σ, and the following four basic counts were considered

1. Prediction of compressibity factor at the critical point
2. Prediction of vapor pressure
3. Prediction of saturated liquid volume
4. Z-Chart sum

4.1.1 Prediction of Compressibility Factor at the Critical Point

Since the critical isotherm shows a point of inflection at the critical pressure and volume, the following conditions must hold :

$$\left(\frac{\partial P}{\partial V}\right)_{Tc} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{Tc} = 0 \qquad (4.2)$$

For an equation with only two parameters, i.e van der Waals, Soave, PR, the simultaneous solution yields a fixed value of calculated critical compressibility factor, $\zeta = Pc/RTc)V_{c,calc.}$, which is characteristic for the equation.

For an example, the van der Waals equation which is defined by

$$P = \frac{RT}{(v-b)} - \frac{a}{v^2} \tag{4.3}$$

Then if the subscript c denotes the critical point,

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \tag{4.4}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0 \tag{4.5}$$

from (4.4) $RT_c = 2a(V_c-b)^2/V_c^3$ \hfill (4.6)

from (4.5) $RT_c = 3a(V_c-b)^3/V_c^4$ \hfill (4.7)

When Eqs (4.6) and (4.7) are combined, the result is

$$V_c = 3b \tag{4.8}$$

Substituting this value of V_c in Eq.(4.5) gives

$$T_c = \frac{8a}{27Rb} \tag{4.9}$$

and $$P_c = \frac{a}{27b^2} \tag{4.10}$$

At the critical point, free from constants a and b, the calculated critical compressibility is obtained such that

$$\jmath = \frac{P_cV_c}{RT_c} = \frac{a}{27b^2}\frac{(3b)}{(8a/27Rb)R} = \frac{3}{8} \tag{4.11}$$

This equation is important because of the conclusion reached that the critical compressibility is equal to 0.375 regardless of the substance under consideration. With reference to Table 4.2, it is shown that this physical critical compressibility factor , Z_c , varies appreciably from this value and is by no means the same for all substances.

In Table 4.3 and Figure 4.1 presented the calculated critical compressibility factor ( ) from several cubic equations of state.

<u>Table 4.2</u> Experimental critical compressibility factor (Z_c). [1]

	Z_c
methane	0.29
ethane	0.285
Propane	0.276
n-Butane	0.274
i-Butane	0.283
n-Pentane	0.269
i-Pentane	0.268
n-Hexane	0.264
n-Heptane	0.259
n-Octane	0.256
n-Nonane	0.250
n-Decane	0.247
Nitrogen	0.291
Carbon dioxide	0.276

Table 4.3 Calculated critical compressibility factor (ξ) from several
cubic EOS [16-25]

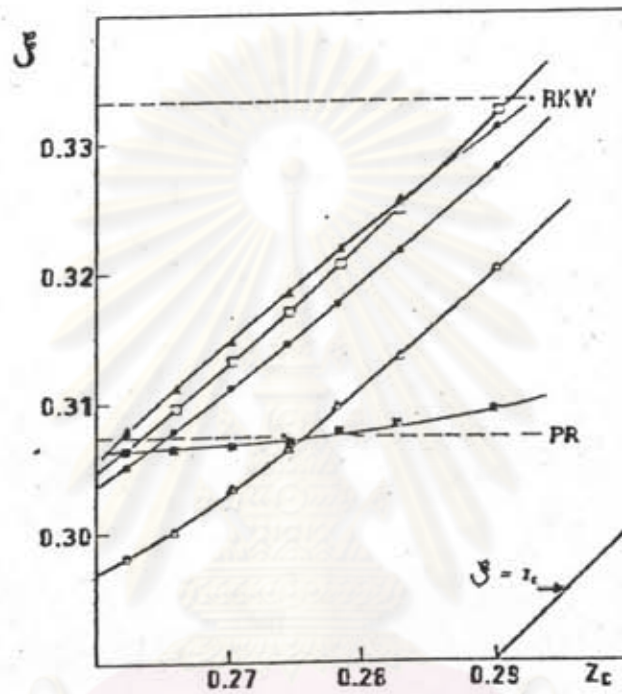| EOS	ξ
Van der Waals (1873)	0.3750
RK (1949)	0.3333
Soave (1972)	0.3333
Leiva (1980)	0.3333
PR (1976)	0.3074
Fuller (1976)	$\xi(\beta)$
Harmens (1977)	0.2862
Martin (1979)	0.25-0.375
Harmens and Knapp (1980)	$\xi(\omega)$
Schmidt and Wenzel (1980)	$\xi(\omega)$
Ishikawa Chung LU (1980)	0.3152
Stein (1982)	ξ
Petel and Teja (1982)	ξ

Fig. 4.1 Calculated critical compressibility factor in cubic equation
of state.
□ Schmidt and Wenzel (1980), △ Harmens and Knapp (1980),
■ Rauzy (1982), ● Patel and Teja (1982).

4.1.2 Prediction of Pure Component Vapor Pressure

At the critical temperature, the constant critical
parameters can be obtained from Equations 4.9 and 4.10.

$$a(Tc) = \Omega_{ac} R^2 Tc^{2.5}/Pc \tag{4.12}$$

$$b(Tc) = \Omega_{bc} RTc/Pc \tag{4.13}$$

Table 4.6 are the numerical values of the critical omega, Ω_{ac} and
Ω_{bc}, from several cubic equations of state.

At temperature lower than the critical, the two omega
functions were fitted to physical properties, liquid density and
vapor pressure [28].As long as experimental data for vapor pressures
are available, it is possible to propose the omega functions which,
linked to the equation of state, represents these data with all the
precision desired [26].

$$a = \Omega_a(Tr)\frac{R^2 Tc^{2.5}}{Pc} \tag{4.14}$$

$$b = \Omega_b(Tr)\frac{RTc}{Pc} \tag{4.15}$$

Table 4.4, is the calculated pure-component vapor pressure from
several cubic equations of state.

Table 4.4 Comparison of Percentage Deviation for Vapor Pressure. [17]

Substance	Soave Equation	Peng-Robinson Equation	Fuller Equation	Haman-Lu Equation	Leiva Equation	T ($^{\circ}$K)	N
Methane	1.18	1.06	0.92	0.65	0.86	113.7 −188.71	27
Ethane	1.24	0.87	0.99	0.36	1.05	184.47−305	17
Propane	0.89	0.47	0.68	0.33	0.60	231.1 −369.5	26
Propylene	1.41	0.87	1.27	1.67	0.92	225.45−355.37	13
n-Butane	4.92	4.99	4.92	4.66	5.11	272.65−416.48	23
n-Pentane	1.37	0.74	1.09	0.53	0.43	309.0 −469.5	27
i-Pentane	1.25	0.72	1.00	0.53	0.58	301.03−4600	27
Neopentane	0.73	0.38	0.46	0.72	0.50	282.63−433.5	24
h-Hexane	1.09	1.33	0.60	1.59	2.30	273.15−505.37	22
n-Octane	1.98	3.38	1.98	1.50	2.86	298.15−560.0	30
n-Nonane	3.73	6.08	3.85	4.24	3.34	298.15−590.0	33
CO_2	0.41	0.82	0.22	1.40	1.08	216.58−304.00	32
Nitrogen	1.99	0.99	1.93	2.00	3.35	63.15−126.00	18
Water	6.89	3.93	5.60	6.83	3.12	322.04−644.22	18
Oxygen	1.04	1.06	0.84	0.55	1.46	90.21−149.82	12

Note : N = number of data points

Table 6.4   Optimum Values of K_{12} and Bubble Point Deviations Using Leiva EOS For N_2-Hydrocarbon Systems.

System	Experimental Data				K_{12}	AAD	
	Ref.	Temp.,K	Pressure,atm	N_p	Optimum	$\Delta P/_{P\%}$	ΔY_1
METHANE	[55]	113.71	3.41- 17.03	7	0.0481	0.64	0.0039
		122.04	2.76- 27.13	11	0.0447	0.76	0.0082
		127.60	3.49- 34.37	16	0.0386	1.59	0.0930
		138.47	6.83- 38.15	9	0.0344	1.49	0.0131
		149.83	12.19- 45.23	9	0.0329	1.66	0.0257
		160-94	17.03- 48.37	12	0.0202	1.66	0.0295
		172.60	25.24- 49.73	9	0.0348	1.28	0.0174
		177.60	30.66- 49.19	11	0.0208	1.57	0.0291
		183.16	39.24- 47.89	8	0.0322	0.78	0.0216
ETHANE	[56]	149.83	3.41- 87.81	12	0.0808	9.42	0.0054
		172.05	3.49- 89.19	13	0.0576	13.14	0.0304
		194.27	3.49- 91.42	14	0.0431	12.10	0.0464
	[57]	260.00	18.10- 93.80	8	0.0359	2.52	0.0351
		270.00	23.50- 81.42	20	0.0328	2.31	0.0220
		280.00	29.50- 82.25	15	0.0000	3.21	0.0495
PROPANE	[58]	173.16	13.60-136.05	6	0.1378	3.27	0.0042
		223.16	13.60-136.05	6	0.1271	4.88	0.0088
		248.16	13.60-136.05	6	0.0977	2.39	0.0182
		273.16	13.60-136.05	6	0.0807	3.34	0.0299
		298.16	13.60-136.05	6	0.0496	4.20	0.0539
		323.16	40.82-122.45	4	0.0000	6.82	0.0867
		333.16	40.82-108.84	4	0.0000	9.13	0.1013
		343.16	40.82- 81.63	4	0.0000	3.70	0.0773
		353.16	40.82-68.03	3	0.0007	7.41	0.0427

4.1.3 Prediction of Saturated Liquid Volume

Equation (4.1) expresses P in terms of V and T. In practice this is inconvenient since our usual independent variables are T and P. In term of the compressibility factor, Equation (4.1) has the following form :

$$Z^3 - Z^2 + AZ + B = 0 \qquad (4.16)$$

where A and B are arbitrary constants. This is a cubic for Z as a function of T and P. After solving for Z, the desired V follows from

$$Z = Pv/RT \qquad (4.17)$$

In Table 4.5 presented the accuracy of the calculated saturated liquid volume from a number of cubic equations of state.

Equation 4.16 can be solved analytically or by numerical iterative methods. The possible forms of the f(z), eq (4.16), are presented in Fig.4.2. When eq. (4.16) has three real roots (form III), the largest represents the vapor phase and the smallest represent the liquid phase. Evidently, the problem arises when the vapor compressibity factor Z^v is to be predicted from curves IV or V. In these cases, Z^L incorrect value is obtained for the vapor composition. The similar situation appears for the liquid phase with case I or II. These cases occured at high pressures especially in the neighborhood of the critical point.

Table 4.5 Comparison of Percentage Deviation for Saturated Liquid Volume.[17]

Substance	Soave Equation	Peng-Robinson Equation	Fuller Equation	Haman-Lu Equation	Leiva Equation	T (°K)	N
Methane	10.92	7.61	1.34	1.94	1.02	113.7 –188.71	27
Ethane	14.70	7.76	2.01	1.44	2.46	184.47–305	17
Propane	20.86	11.06	3.31	0.96	2.98	231.1 –369.5	26
Propylene	11.71	5.82	2.92	1.14	0.94	225.45–355.37	13
n-Butane	20.74	10.82	2.32	0.67	3.60	272.65–416.48	23
n-Pentane	24.54	13.57	2.16	0.86	2.88	309.0 –469.5	27
i-Pentane	22.64	12.22	1.84	1.28	3.45	301.03–460.0	27
Neopentane	19.96	10.63	2.30	2.16	4.01	282.63–433.5	24
n-Hexane	21.50	9.98	3.09	2.59	2.87	273.15–505.37	22
n-Octane	21.20	8.30	4.26	3.74	5.59	298.15–560.00	30
n-Nonane	19.88	7.44	4.32	3.32	5.81	298.15–590.00	33
CO_2	17.96	7.97	2.34	1.57	2.41	216.58–304.00	32
Nitrogen	11.86	9.51	2.34	3.12	2.48	63.15–126.00	18
Water	44.96	28.82	4.14	19.88	20.75	322.04–644.22	18
Oxygen	7.61	8.88	3.20	1.28	1.35	90.21–149.82	12

Note : N = number of data points
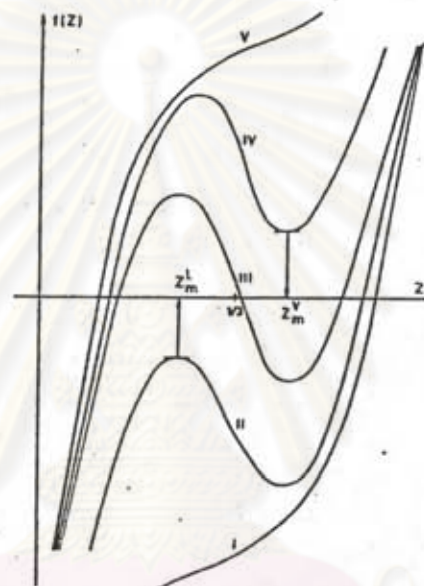
Figure 4.2   Possible form of f(Z)

Gundersen [26] proposed a method for avoiding trivial roots in VLE calculations with a cubic equation of state as show in Fig.4.3.
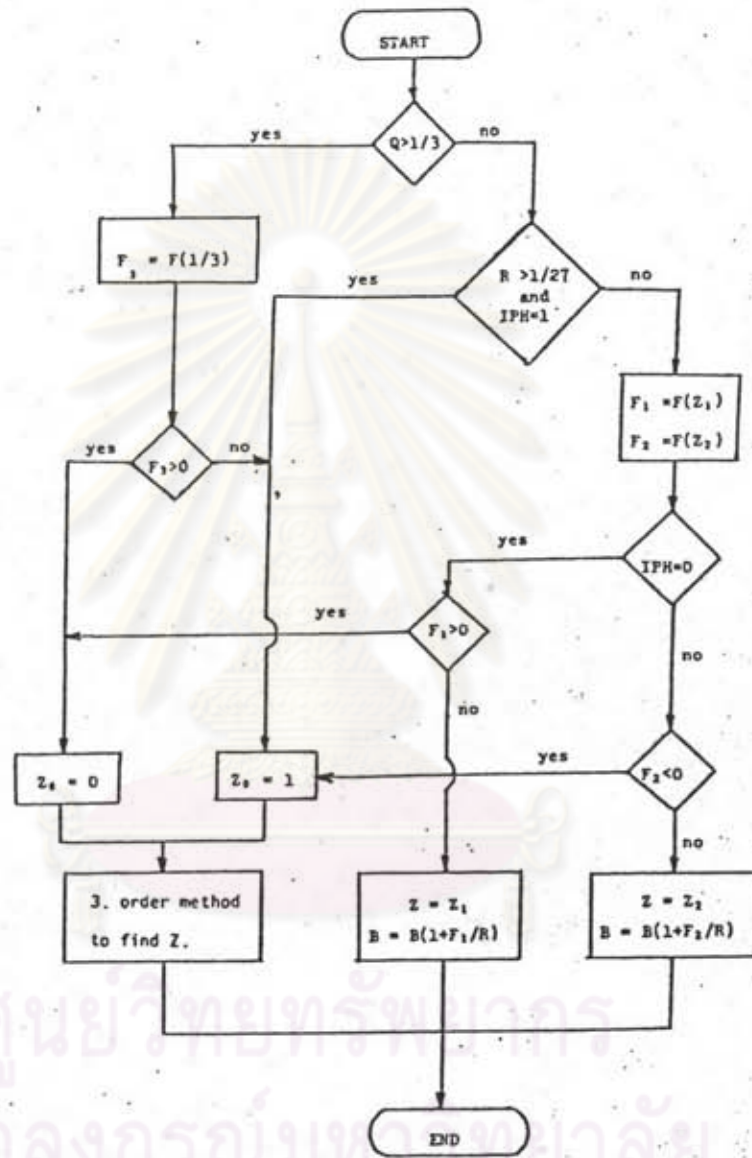

Fig. 4.3 Algorithm for the solution of the cubic SRK equation of state.

Gundersen [26] proposed a method for avoiding trivial roots in VLE calculations with a cubic equation of state as show in Fig.4.3.
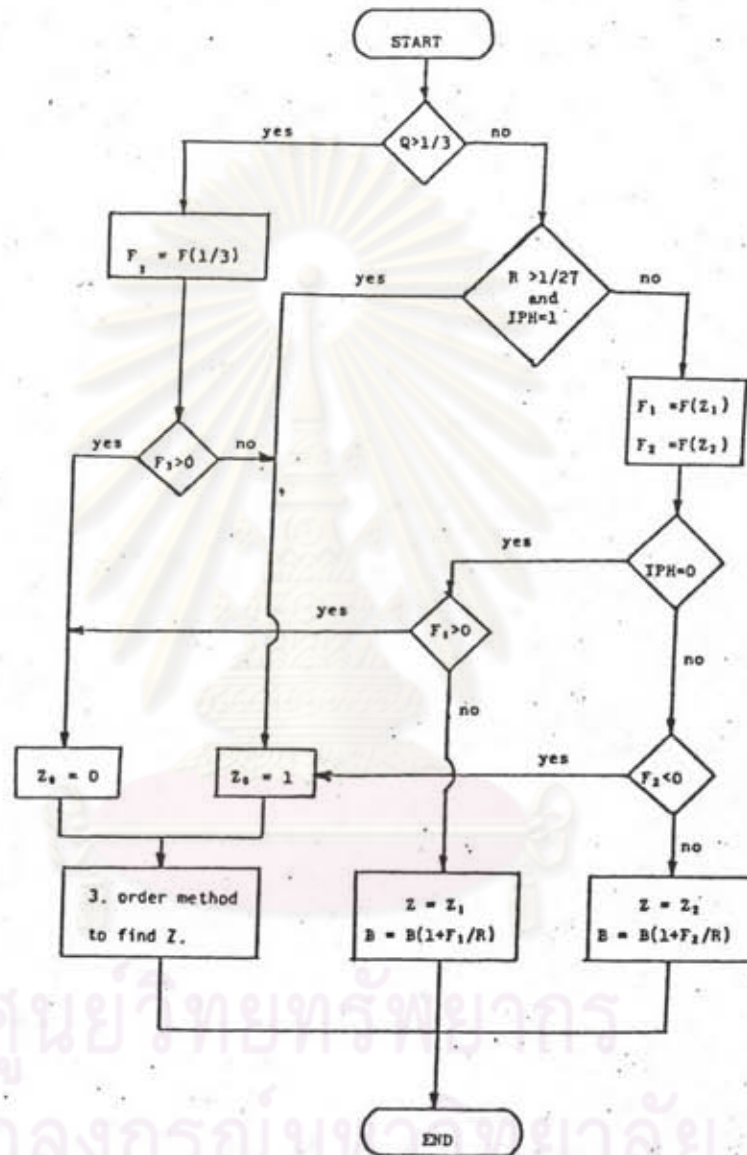

Fig. 4.3 Algorithm for the solution of the cubic SRK equation of state.

4.1.4 Consideration of Z-Chart Sum; Σ

Martin [15] defined Z-chart sum, Σ, as follow

$$\Sigma = \mathfrak{F} - \bar{B}c \qquad (4.18)$$

where $\mathfrak{F}$, the calculated critical compressbility factor,

$\bar{B}c$, the calculated reduced second virial coefficent at the critical isotherm

$$\bar{B}c = \frac{\bar{B}cPc}{RTc} = \Omega_{bc} - \Omega_{ac} \qquad (4.19)$$

Martin observed that the Z-chart sum is nearly the same for all substances, and of the order of 0.62. Table 4.6 are the Σ for a number of substances and Table 4.7 are the Σ from several cubic EOS. According to Martin [15], the lower the value of Σ, the better the equation of state.

Table 4.6   Z-Chart Sum, from several cubic EOS

EOS	$\mathfrak{F}$	Ω_{bc}	Ω_{ac}	Σ
Redlich-Kwong	1/3	0.08664	0.42746	0.6742
Peng-Robinson	0.30741	0.07780	0.45724	0.6868
Harmens	0.28619	0.07072	0.48487	0.6900
Ishikawa-Chung-Lu	0.3152	0.10876	0.4671	0.6736

Table 4.7   Z-Chart Sum, for a number of substances [13]

Substance	Z_c	B_c	Σ
Ne	0.309	0.325	0.634
H2	0.305	0.325	0.630
CO	0.295	0.330	0.625
O2	0.294	0.324	0.618
CH4	0.291	0.330	0.621
N2	0.288	0.339	0.621
i-C4H10	0.283	0.341	0.624
C2H4	0.281	0.337	0.618
CO2	0.274	0.345	0.619
C6H6	0.271	0.345	0.616
i-C5H12	0.270	0.352	0.622
n-C6H14	0.264	0.368	0.624
n-C7H16	0.260	0.360	0.620
n-C8H18	0.259	0.366	0.614
Average			0.62

4.2 SELECTED EOS

Referring to Section 4.1, there are not much difference in numerical values of various properties produced from the mentioned cubic EOS. For instance, one EOS may give a better value of saturated liquid volume than others while it may give the same value of calculated vapor pressure.

From the computation solution point of view, the SRK EOS is certainly the best choice since it contains only two parameters. Unfortunately, saturated liquid volumes calculated from the SRK EOS are greater than values in the literature, it gives a prediction result twice as greater as others equations such as Peng Robinson [18] and Fuller [19] as indicalted in Table 4.6.

The Leiva EOS [17] is very attractive from the viewpoint that it contains only two parameters and remains in the same form of equation as that of SRK and thus its solution is equally simple. According to Table 4.5 the Leiva equation gives better results for saturated liquid volume than those given by the SRK.

Accuracy in predicting saturated liquid volume is important for high pressure VLE calculations, since the partial molar volume determines the effect of pressure on the partial fugicity as shown in Equation 4.21

$$\left(\frac{\partial \ln f_i}{\partial P} \right)_T = \frac{\overline{V}_i}{RT} \qquad (4.21)$$

Equation 4.21 may be integrated to give f_i, at the system pressure.

Consequently, Leiva EOS was selected for further study in this work.

Leiva EOS has the following form :

$$P = \frac{RT}{(v - b)} - \frac{a}{v(v + b)} \qquad (4.22)$$

The quantities a and b are related to the critical properties, as :

$$a = \Omega_a R^2 Tc^2 /Pc \qquad (4.23)$$

$$b = \Omega_b RTc/Pc \qquad (4.24)$$

The pure - component parameters Ω_a and Ω_b were considered as temperature - dependent as well as substance - dependent. The generalized correlations developed by Leiva et.al [17] are

$$\Omega_a = \Omega_{ac} \exp(a_1 + a_2 Tr) \qquad (4.25)$$

$$\Omega_b = \Omega_{bc} \exp(b_1 + b_2 Tr) \qquad (4.26)$$

where a_1, a_2 and b_1, b_2 are characteristic constants of each substance.

$$a_1(\omega) = 0.60424 + 0.95362\omega - 0.33760\omega^2$$
$$a_2(\omega) = -0.65870 - 1.09907\omega + 0.46498\omega^2$$
$$b_1(\omega) = 0.15389 - 0.73725\omega + 0.15117\omega^2$$
$$b_2(\omega) = -0.23715 + 0.56228\omega - 0.10689\omega^2$$