

Chapter VI

Discussions and Conclusion

In this work, we have studied the Liquid-Liquid-Vapor equilibrium of two ternary systems containing light gases, namely, methane, ethane, CO_2 , N_2 and heavy hydrocarbons namely, n-docosane, n-nonadecane. We have found that Liquid-Liquid-Vapor phases equilibria can be predicted with all cubic equations of state (SRK, H&K, P&R, G&D-EOS), especially the ability of the HK-EOS to predict molar volume very close to the experimental measures. It was found that all the cubic equations of state fail to predict equilibrium compositions of polar system ($\text{CO}_2 + \text{N}_2 + \text{n-Nonadecane}$). However, we have found that Harmens & Knapp equation of state could predict molar volume better than SRK-EOS in all phases.

Mole-Fraction of Methane+Ethane+n-Docosane system

The SRK, H&K, P&R and G&D equation of state generally overpredicts methane mole-fraction in L^I -phase and L^{II} -phase and increase as pressure increase. Absolute error which calculated by H&K equations is smaller than the other equations. All equations could predict methane mole fractions in L^I better than L^{II} . These results are shown in table 6.1. In the case of ethane mole fractions, absolute error of ethane mole

fractions in L^I, L^{II} phases smaller than absolute error of methane mole fraction in L^I, L^{II} phases. The results of absolute error are shown in table 6.2. Harmens & Knapp equation of state could predict ethane mole fraction very closed to measured values, absolute error deviation only 0.2284%. The results of prediction of all equation at $T=303.15$ K are similar to those at $T=298.15$ K as shown in table 6.4, 6.5 and 6.6.

$CO_2 + N_2 + n$ -Nonadecane system compositions

The system of polar-ternary which composed of $CO_2 + N_2 + n$ -Nonadecane, the results of absolute error deviation of CO_2, N_2 -mole fraction in L^I, L^{II}, V are shown in table 6.7, 6.8 ($T=294.15$ K), table 6.10, 6.11 ($T=297.15$ K) and table 6.13, 6.14 ($T=301.15$ K). We have found that all equation of state fail to predict CO_2, N_2 mole fraction in L^I, L^{II} phases, Especially N_2 mole fraction. However, in L^I, L^{II} phases H&K equation could predict best at all temperature. For vapor phase H&K equation could predict CO_2 mole fraction better than all equations at $T=294.15$ K absolute error of CO_2 mole fraction = 1.6099% and not more than 0.7786% for L^{II} phase.

Molar volume of Methane+Ethane+n-Docosane system

The ability of SRK, H&K, P&R, G&D equations of state to calculated molar volume of ternary Liquid-Liquid-Vapor system

for Methane+Ethane+n-Docosane mixture at $T=298.15$ K are shown in figure 5.6,5.7,5.8 for L^I, L^{II}, V respectively. H&K equation of state could predict liquid molar volume better than the other equations, especially in L^{II} -phase H&K equation could predict very close to the measured values(abs error=0.9804%). Except in vapor phase P&R equation could predict better than H&K equation(abs error, P&R=2.1490%, H&K=2.6586%). At $T=303.15$ K the result of calculation in molar volumes are shown in the same line as the result which calculate at $T=298.15$ K, P&R equation of state could predict very good in vapor phase, whereas H&K shown the best in liquid phases. Comparisons of experimental and predicted at this temperature are shown in figure 5.14,5.15,5.16. Behavior of molar volume which calculated by the model's predictions using the SRK, H&K, P&R, G&D equations of state increase with pressure in L^I, L^{II} phases whereas in vapor decrease.

Molar volume of $CO_2 + N_2 + n$ -Nonadecane system

The molar volumes predicted by used of the SRK, H&K, P&R, G&D equations of state are compared to experimental results in figure 5.21,5.22,5.23 for L^I, L^{II}, V phases respectively. H&K could predict molar volumes better than the other equations, especially in vapor phase(abs error=1.2854% $T=294.15$ K). However, it should be noted that P&R equation could predict vapor molar volume very close to H&K result(abs

Table 6.1

Average absolute deviation of mole fraction of methane

T=298.15 K				
Phase	SRK	HK	PR	G&D
vapor*	-	-	-	-
Liquid I	22.6292	16.2042	28.3570	21.5706
Liquid II	9.4546	7.7067	13.5501	8.8347

Table 6.2

Average absolute deviation of mole fraction of ethane

T=298.15 K				
Phase	SRK	H&K	PR	G&D
vapor	0.6460	0.2284	1.0708	0.6720
Liquid I	1.8566	5.8052	1.3832	1.9179
Liquid II	0.8803	1.0212	1.2397	0.8259

Table 6.3

Average absolute deviation of molar volume [ml/g.mol]

T=298.15 K				
Phase	SRK	H&K	PR	G&D
vapor	4.1887	2.9781	2.1490	4.5656
Liquid I	25.0989	2.7576	12.0787	25.0875
Liquid II	16.3120	0.9804	5.8040	16.6847

Table 6.4

Average absolute deviation of mole fraction of methane

T=303.15 K				
Phase	SRK	HK	PR	G&D
vapor*	-	-	-	-
Liquid I	29.1261	28.4818	46.2888	28.4978
Liquid II	10.4463	23.5803	22.9075	9.8849

Table 6.5

Average absolute deviation of mole fraction of ethane

T=303.15 K				
Phase	SRK	H&K	PR	G&D
vapor	0.3428	0.5016	0.7141	0.3336
Liquid I	2.2188	4.5026	1.7497	2.2275
Liquid II	0.3924	0.9502	0.7416	0.3812

Table 6.6

Average absolute deviation of molar volume [ml/g.mol]

T=303.15 K				
Phase	SRK	H&K	PR	G&D
vapor	4.6352	2.2038	2.0142	4.7806
Liquid I	25.0590	3.1759	12.0145	25.0476
Liquid II	19.8505	2.4544	9.0305	19.8737

Table 6.7

Average absolute deviation of mole fraction of CO₂

T=294.15 K				
Phase	SRK	HK	PR	G&D
vapor	4.1804	1.6099	5.3889	4.1525
Liquid I	32.8675	37.8059	25.8304	32.8630
Liquid II	3.9600	0.7786	5.1608	3.8748

Table 6.8

Average absolute deviation of mole fraction of N₂

T=294.15 K				
Phase	SRK	H&K	PR	G&D
vapor*	-	-	-	-
Liquid I	151.4606	11.5077	185.2348	151.2185
Liquid II	44.2783	8.7680	62.1448	44.8058

Table 6.9

Average absolute deviation of molar volume [ml/g.mol]

T=294.15 K				
Phase	SRK	H&K	PR	G&D
vapor	8.0299	1.2854	1.6184	7.9858
Liquid I	45.8894	11.4822	30.4623	45.8692
Liquid II	17.6043	4.4258	6.0066	16.7777

Table 6.10

Average absolute deviation of mole fraction of CO₂

T=297.15 K				
Phase	SRK	HK	PR	G&D
vapor	2.5374	0.6060	3.9823	2.5194
Liquid I	34.4560	37.0476	27.0998	34.4972
Liquid II	2.7416	0.1286	4.2198	2.7140

Table 6.11

Average absolute deviation of mole fraction of N₂

T=297.15 K				
Phase	SRK	H&K	PR	G&D
vapor*	-	-	-	-
Liquid I	115.1702	14.9693	168.7608	113.2927
Liquid II	64.4732	11.2412	98.9349	63.8019

Table 6.12

Average absolute deviation of molar volume [ml/g.mol]

T=297.15 K				
Phase	SRK	H&K	PR	G&D
vapor	5.6325	3.5038	0.6817	5.7291
Liquid I	45.5794	11.1044	30.1977	45.5794
Liquid II	20.8554	2.1795	9.6836	20.9083

Table 6.13

Average absolute deviation of mole fraction of CO₂

T=301.15 K				
Phase	SRK	HK	PR	G&D
vapor	2.0763	0.2064	3.3971	2.0555
Liquid I	32.7401	33.4378	25.8791	32.7685
Liquid II	2.0746	0.1948	3.4218	2.0473

Table 6.14

Average absolute deviation of mole fraction of N₂

T=301.15 K				
Phase	SRK	H&K	PR	G&D
vapor*	-	-	-	-
Liquid I	185.1709	5.7740	332.7663	182.5331
Liquid II	69.1459	4.8122	160.0232	67.4175

Table 6.15

Average absolute deviation of molar volume [ml/g.mol]

T=301.15 K				
Phase	SRK	H&K	PR	G&D
vapor	3.1689	6.7241	6.2169	3.3529
Liquid I	44.5060	10.1237	29.2363	44.1278
Liquid II	20.9783	2.8334	10.8649	19.8141

(-) Have no experimental data.

error=1.6184%) and better than SRK and G&D equations of state. At $T=297.15$ K and 301.15 K, it was found that H&K equation of state could predict molar volumes in L^I, L^{II} -phases better than the other equations of state, in L^{II} -phase absolute error not more than 3%. However, in vapor phase PR equation could predict better than H&K equation.

If we consider the following equation which generalized form of the van der Waals equation. Replacing the denominator V^2 in the attraction term of the original equation by an expression quadratic in volume, one obtains an equation of the following form:

$$P = RT/(V-b) - a/(V^2 + uV + wb^2) \quad (6.1)$$

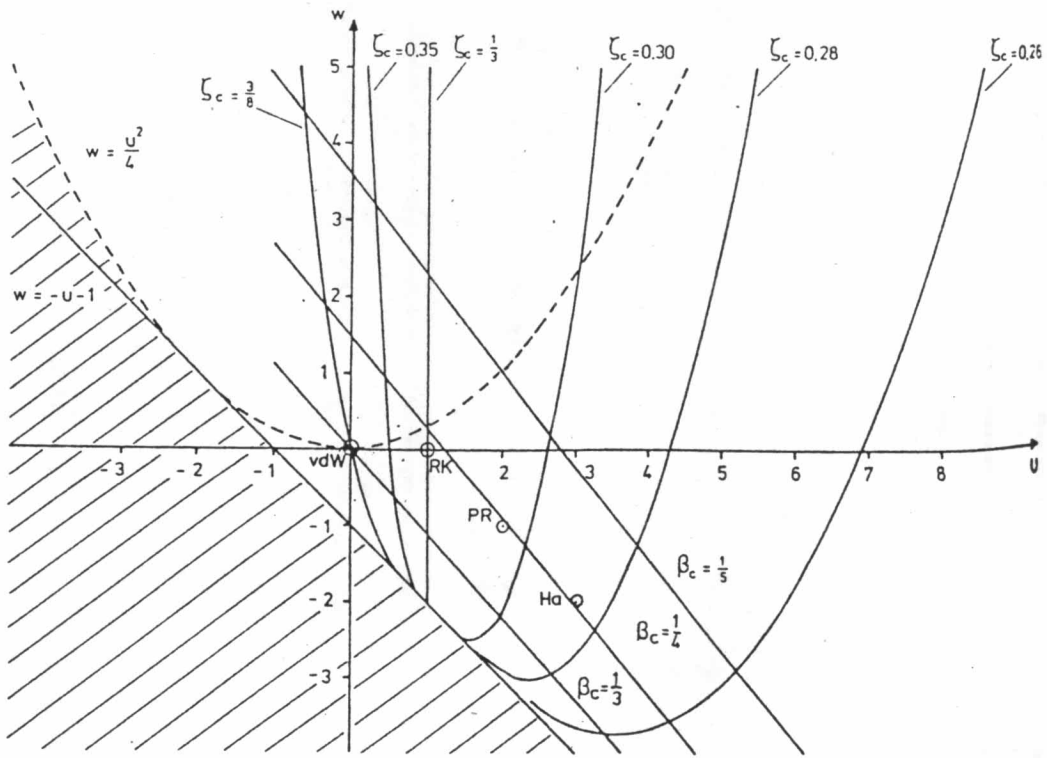
where $a=a(T)$ is a function of temperature and u, w and b are

Table 6.16 Values of u and w from eqn (6.1) and corresponding equations of state

u	w	Equation of state
0	0	van der waals
1	0	Soave-Redlich-Kwong
2	-1	Peng-Robinson
3	-2	Harmens
u	$u^2/4$	Clausius

independent of temperature. Equation (6.1) is cubic in volume and such is still relatively easy to handle mathematically. For particular values of u and w equation (6.1) reduces to some known equation of state as shown in table 6.16. The properties of equation (6.1) as a function of u and w are conveniently represented in diagram of u vs. w as shown in figure 6.1. To avoid that $V^2 + ubV + wb^2 = 0$ for $V \geq b$ it can be shown that u and w must satisfy the following constraints.

$$\begin{aligned}
 w &> -u-1 && \text{for } u \geq -2 \\
 w &> u^2/4 && \text{for } u \leq -2
 \end{aligned}
 \tag{6.2}$$



u - w -Diagram, with u and w defined in eqn (1), ζ_c calculated value of the critical compressibility factor, $\beta_c = b/V_c$ with b volume parameter in eqn (1) and V_c calculated critical volume.

Figure 6.1

The shaded area in fig 6.1 is that excluded by equation(6.2) and the points representing the equation of state of table 6.1 are circled, Once the parameters u and w are assigned particular values, the critical compressibility factor Z_c and the critical volume V_c are determine by equation (6.1) the parameters a and b being fitted to the critical temperature T_c and the critical pressure P_c , using the critical condition.

$$(dP/dV)_T = (d^2P/dV^2)_T = 0$$

Example for Peng-Robinson at critical point

$$a(T_c) = 0.45724R^2T_c/P_c$$

$$b(T_c) = 0.07780RT_c/P_c$$

$$P_c V_c = Z_c RT_c$$

$$Z_c = 0.307$$

Fig 6.1 shown that in principle u and w can be selected so as to match any experimental value of Z_c and this leaves Z_c to be defined. For an equation with only two adjustable parameters. The simultaneous solution of system referred to above yields a fixed value of Z_c which is characteristic for the equation. So we have SRK($Z_c=0.3333$), P&R($Z_c=0.3074$) and G&D($Z_c=0.3333$). In the case of Harmens & Knapp equation of state which defined Z_c by studied the critical isotherm

of seven substances from Argon to n-Decane, going from atmospheric pressure up to about $P_r = 5$. For each substance a value of Z_c was derived which made the average relative error in predicted volume along the critical isotherm zero. So for each substance the Z_c was chosen so as to give on average the best calculated critical isotherm. This led to relation

$$Z_c = 0.3211 - 0.080w + 0.0384w^2$$

$$\beta = b/V_c$$

$$a = \Omega_a R^2 T_c^2 / P_c$$

$$b = \Omega_b R T_c / P_c$$

$$c = 1 + (1 - 3Z_c) / \beta Z_c$$

in which

$$\Omega_a = 1 - 3Z_c + 3Z_c^2 + \beta Z_c (3 - 6Z_c + \beta Z_c)$$

$$\Omega_b = \beta Z_c$$

The parameters a , b and c are all functions of β and Z_c . The temperatures other than the critical, the parameter a will now be modified by a coefficient α which depends on T_r , so that

$$a = \alpha(T_r) R^2 T_c^2 / P_c$$

The parameters b and c retain their critical point value throughout. The Harmens & Knapp equation of state presented critical compressibility factor in term of substance dependent this is reason why Harmens & Knapp equation is able

to predict vapor, liquid-molar volume more accurately than does the SRK, P&R, G&D.

If we consider accuracy of calculation in molar volume of P&R equation which could predict better than SRK and G&D equation, The critical compressibility factor is the main reason which used for explanation. The Peng & Robinson equation the critical compressibility is $Z_c = 0.307$ this value is nearer the values of many substances, particularly nonpolar ones, than are the Z_c s of some other two-parameter equation of state this is a partial explanation of the fact that more accurately that does the SRK or G&D equations and improved prediction of liquid densities. The SRK equation yields a critical compressibility factor $Z_c = 0.3333$ whereas experimental critical compressibility factor Z_c range between 0.24-0.30. As a result, both the predicted densities of the saturated liquid and the critical volumes deviate noticeably from experimental values. Soave (1972) original proposed a modification of the Redlich-Kwong equation of state which introduced the temperature dependent term a/\sqrt{T} of the Redlich-Kwong equation was replaced by a function $a(T, w)$ involving the temperature and the acentric factor by Soave. The equation fit the vapor pressure data of hydrocarbons, with the result

$$a(T, w) = \alpha a = 0.42748 R^2 T_c^2 / P_c \alpha$$

where $\alpha^{0.5} = 1 + (1 - T_r^{0.5}) (0.480 + 1.574w - 0.176w^2)$

By accurately correlating vapor pressure, the equation of state is capable of accurately predicting the fugacity of fluids and therefore the phase equilibrium behavior. Specifically, Soave used the critical point and the vapor pressure at a reduced temperature of 0.7 for a number of compounds to determine the function required to correlate vapor pressures. A limited set of critical pressures, critical temperatures and acentric factors which are not totally consistent with the recommended American Petroleum Institute Data Book parameters were used in the original development. Thus Graboski and Gaubert proposed equation was refit with the expanded property set. Instead of anchoring the equation at $T_r = 0.7$. Then, the coefficients of this term were modified by Graboski and Daubert (1978) to

$$\alpha^{0.5} = 1 + (1 - T_r^{0.5}) (0.48508 + 1.55171w - 0.15613w^2)$$

The " α " function was determined as a function of reduced temperature and acentric factor for the API vapor pressure data set.

Conclusion

Every equation of state that has been proposed has more or less severe limitations with regard to the kind of substances that it could represent, or the range of operating conditions or the phases. Some equations are better for PVT,

others for phase equilibria. There is little hope that a universal equation of state of moderate complexity ever will be discovered.

Increasing the number of constants in the equation has often, but not always, served to improve coverage. There are instances where a two-parameter equation is superior to some with eight or more parameters; this can not be depended on in general, however, so the multiparameter equations are used extensively, particularly since computers have made them tractable.

The Harmens and Knapp equation of state was a great improvement over Soave-Redlich-Kwong, Peng and Robinson, modified SRK (Graboski and Daubert) equations in the prediction of liquid volumes. The following are the main conclusions of this work.

1. For Methane+ethane+n-Docosane system, H&K equation could predict liquid molar volume better than the other equations of state (SRK, P&R, G&D) not more than 4% for this system at both fixed temperature ($T=298.15, 303.15$ K). For vapor phase P&R equation shows the best results. In the same time P&R equation could predict molar volumes in all phases better than SRK equation, these results corresponding with above discussions.

2. For polar mixture $\text{CO}_2 + \text{N}_2 + \text{n-Nonadecane}$. The H&K equation could predict liquid molar volume at $T=294.15, 297.15, 301.15$ K better than the other equations of

state, not more than 5% in L^I phase and not more than 5% in L^{II} phase. However in vapor phase P&R equation could predict better than H&K equation, P&R equation shows very good results, especially at $T=297.15$ K (abs error=0.6817%). For SRK and G&D equation both gave nearly identical results in calculated molar volumes. we have found that all cubic equations of state fail to predict phases equilibrium compositions of N_2 , CO_2 mole fraction in polar ternary mixtures at every temperature. However, Harmens & Knapp equation show ability better than the other equations of state. For hydrocarbon mixture all equations of state show satisfied results.