

CHAPTER IV

SELECTED EQUATIONS OF STATE

4.1 Soave-Redlich-Kwong Equation Of State (SRK EOS).

4.1.1 Characteristics Of SRK.

SRK equation of state is two-parameter cubic equation of state. It can be expressed in the following general equation:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (4-1)$$

Rearranging Equation (4-1) into compressibility factor form then,

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

where

$$A = \frac{aP}{(RT)^2} \quad (4-3)$$

$$B = \frac{bP}{RT} \quad (4-4)$$

4.1.1.1 Mixing Rules.

The equations of state[11] are generally developed for pure fluids first, then extended to mixtures. The mixtures extension requires so-call mixing rules, which are simply means of calculating mixture parameters equivalent to those of pure substances. Except or those of virial coefficients, the mixing rules are more or less arbitrary rules that are to reflect the composition effect on system properties.

All the pure parameter symbols should have had subscript “i” which was omitted for simplicity. The subscript “i” will be retained to distinguish the pure fluid parameters from its mixture counterparts. Then, the mixing rule for b and a are

$$b = \sum_i^N x_i b_i \quad (4-5)$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \quad (4-6)$$

$$a = \sum_i^N \sum_j^N x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (4-7)$$

$$a_i = a_{ci} \alpha_i \quad (4-8)$$

$$a_{ci} = 0.42748 \frac{(RT_{ci})^2}{P_{ci}} \quad (4-9)$$

$$\alpha_i^{0.5} = 1 + m_i (1 - T_{ri}^{0.5}) \quad (4-10)$$

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \quad (4-11)$$

4.1.2 System Represented of SRK.

SRK equation of State is wide spread use of simple equations of state in hydrocarbon industries. It applies to all nonpolar compounds. And it can predict with a good degree of accuracy volumetric and thermal properties of pure compounds and of mixtures.

At reduced temperatures lower than 0.4, all the computed vapor pressure slightly deviated increasingly when dealing with mixtures containing very light components, particularly hydrogen. SRK equation fits the experimental curve well, particularly for the vapor phase. However, for the liquid phase also, the error in computed bubble-pressure is small.

It is noteworthy that the calculated vapor and liquid curves converge almost exactly at the experimental critical pressure and composition. This fact was verified in almost all cases examined, so it can be concluded that the SRK equation is able to predict the phase behavior of mixtures in the critical zone also. In all the tables, the OAD's are defined as

$\sum |(\text{calculated} - \text{experimental}) \text{ values}| / (\text{number of data points})$ and are given in J/g.

An overall comparison for pure, nonpolar fluids and their mixtures in the two-phase region for the SRK, and PR equations of state is presented in Table 4.1. In this state, the enthalpy departure is dependent on the temperature, pressure, vapor and liquid compositions, and also the phase distribution.

Table 4.1 Overall Comparison in the Two-Phase State[11].

system	OAD, J/g	
	SRK	PR
nonpolar: pure fluids	(47) 87.2	(47) 98.8
mixtures	(706) 29.0	(609) 29.9

The enthalpy departure for the two-phase system is then evaluated from the independently calculated vapor and liquid phase enthalpy departure and the estimated phase distribution. Thus, it is clear that the accuracy of the results in this case is dependent on the ability of the equation of state to establish the phase equilibria correctly. This result is extremely important, as it shows that the enthalpy calculations in the two-phase region are highly dependent on the equation of state's ability to predict the phase equilibria and can include considerable uncertainties. More and better equations of state developments and extensive and detailed evaluations of phase equilibrium predictions are therefore certainly required to improve the estimation of thermophysical properties that are required in process design and simulation.

4.2 Peng-Robinson Equation Of State (PR EOS).

4.2.1 Characteristics Of PR.

Soave has a common shortcoming, i.e. it predicts poor liquid densities and an unrealistic universal, Z_c of 1/3 for all substances. To alleviate this shortcoming, it is

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (4-12)$$

Rearranging Equation (4-12) to be compressibility factor form. Then it will give

$$Z^3 - (1-B)Z^2 + (A-2B-3B^3)Z - (AB-B^2-B^3) = 0 \quad (4-13)$$

where A, B are same as Equations (4-3) and (4-4) respectively.

4.2.1.1 Mixing Rules.

Peng-Robinson equation of state has different values from Soave-Redlich-Kwong equation of state as the following:

$$b_i = 0.077796 \frac{RT_{ci}}{P_{ci}} \quad (4-14)$$

$$a_{ci} = 0.457235 \frac{(RT_{ci})^2}{P_{ci}} \quad (4-15)$$

$$m_i = 0.37646 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (4-16)$$

While b, a, a_i and m_i are same as Equations (4-5), (4-7), (4-8), and (4-10) respectively.

4.2.2 System Represented Of PR.

The development of a new-constant equation of state[8] in which the attractive pressure term of the semiempirical van der Waals equation has been modified is outlined. Examples of the use of the equation for predicting the vapor pressure and volumetric behavior of single-component systems, and the phase behavior and volumetric behavior of binary, ternary, and multicomponent systems are given. The proposed equation combines simplicity and accuracy. It performs as well as or better than the Soave-Redlich-Kwong equation in all cases tested and shows its greatest advantages in the prediction of liquid densities.

Although one can not expect a two-constant equation of state to give reliable predictions for all of the thermodynamic properties, the demand for more accurate predictions of the volumetric behavior of the coexisting phases in VLE calculations has prompted the present investigation into the possibility that a new simple equation might exist which would give better results than the SRK equation. An equation is presented which gives improved liquid density values as well as accurate vapor pressures and equilibrium ratios.

Both the SRK and PR equations are designed with a view to reproduce accurately the vapor pressures of pure nonpolar substances. Nevertheless PR equation gives better agreement between calculated vapor pressures and published experimental values.

Generally, saturated liquid density values calculated from the SRK equation are lower than literature values. This is true except for small molecules like nitrogen and methane at very low temperatures where the predicted values are slightly higher. PR equation predicts saturated liquid densities which are higher at low temperatures and

lower at high temperatures than the experimental values. The fact that PR equation gives a universal critical compressibility factor of 0.307 as compared with SRK's 0.333 has improved the predictions in the critical region.

Both equations yield acceptable values except that in the critical region better results have been obtained with PR equation. The improvement is more well for small molecules. Compare with the values calculated from the SRK and PR equation, the results are presented is fair to say that both equations generate enthalpy values of about the same reliability. Vapor-liquid equilibrium conditions for a number of paraffin-paraffin binaries were predicted using PR equation. It was found that the optimum binary interaction coefficients were negligibly small for components with moderate differences in molecule size. However, systems involving components having relatively large differences in molecular size required the use of a nontrivial interaction coefficient in order to get good agreement between predicted and experimental bubble point pressures. Although both the SRK and PR equations generate reliable equilibrium ratios, the PR equation predicts much more accurate volumetric behavior.

While the PR equation offers the same simplicity as the SRK equation and although both equations predict vapor densities and enthalpy values with reasonable accuracy, more accurate liquid density values can be obtained with the PR equation. In regions where engineering calculations are frequently required the PR equation gives better agreement between predictions and experimental PVT data.

Since two-constant equations have their inherent limitations, and the equation obtained is no exception, the justification for the PR equation is the compromise of its simplicity and accuracy.

Peng-Robinson equation of state can apply to all nonpolar compounds. The different values which were shown as above do affect the prediction of molar volumes in dense region, where PR, though not as accurate as desired, shows a marked improvement over the SRK equation.

It should be pointed out that, while there is a large improvement in liquid density predictions, the saturated vapor densities are slightly worse than with the usual Peng-Robinson parameters. This is a result of the fact that simple cubic equations of state, such as the Peng-Robinson one, are not of high accuracy; for example, $Z_c = 0.307$ for this equation. Therefore, by fitting the parameters as we have here, a compromise between the accuracy of the vapor and liquid predictions results. However, the increase in error in the vapor density is far smaller than the large decrease in error of the liquid density.

What is also impressive is that with the proposed fluid-specific parameters, the errors in volume predictions for water and methanol are reduced by almost an order of magnitude, so that the errors for these distinctly non-hydrocarbon fluids, using the Peng-Robinson equation of state, are of the same order as those for the hydrocarbons. Also, with the revised parameters, the errors in vapor pressure predictions for the polar fluids water and methanol are only slightly higher than for the hydrocarbons. Note that the overall improvement is so great with the parameters proposed here, that the errors

in the volume and vapor pressure predictions for water and methanol are significantly smaller than for the hydrocarbons with the original Peng-Robinson parameters.

The use of the Peng-Robinson equation with the proposed fluid-specific, temperature-dependent parameters results in a marked improvement in the prediction of volumes in the low-temperature, high-pressure, and saturated liquid regions. However, in the critical and saturated vapor regions, our proposed parameters result in almost the same deviations as the original Peng-Robinson parameters. The largest deviations with the proposed parameters are confined to the near proximity of the critical temperature, and are an inherent limitation of a cubic equation of state.

4.3 ALS EOS.

4.3.1 Characteristics Of ALS.

This is a new method[3] for the prediction of phase behavior in reservoir fluids using a four-parameter cubic equation of state. It seems natural to choose a cubic equation of state as thermodynamic basis for the model to be developed, since cubic equation of state 's are simple and fast models and easy to implement in any reservoir simulation program. Jensen (1987) found the ALS EOS (Adachi et al.,1983) to be the most accurate for prediction of the phase behavior of well-defined hydrocarbon mixtures with and without a considerable content of CO₂ or N₂. The ALS EOS seems to be well suited for calculation of the phase equilibria of reservoir fluids but often proves to give inaccurate predictions of the densities of hydrocarbon mixtures (Aasberg-Petersen, 1989). It was therefore decided to incorporate the volume

translation principle of Peneloux et al. (1982) into the ALS equation, resulting in the following new equation of state:

$$P = \frac{RT}{V - b_1} - \frac{a}{(V - b_2)(V + b_3)} \quad (4-17)$$

Rearranging Equation (4-17) into compressibility factor form then,

$$Z^3 - (1 + B_1 + B_2 - B_3)Z^2 + (A + B_2 - B_3 + B_1B_2 - B_2B_3 - B_1B_3)Z - (B_1 - B_2B_3 - B_1B_2B_3) = 0 \quad (4-18)$$

where

$$B_{k,i} = \frac{k_i}{RT} \quad k = 1, 2, 3 \quad (4-19)$$

The b parameters are calculated as follows:

$$b_1 = \beta_1 - C \quad (4-20)$$

$$b_2 = \beta_2 - C \quad (4-21)$$

$$b_3 = \beta_3 + C \quad (4-22)$$

For each component, the Peneloux-type parameter, C , is determined such that the equation of state gives the correct value of the liquid density at atmospheric pressure and at a temperature where the component is a liquid. The C parameters of

the C_{7+} fractions are determined by matching the equation of state to measure specific gravity data at 288.15 K and 1 atm.

4.3.1.1 Mixing Rules.

$$b_k = \sum_i^N x_i b_{k,i} \quad k = 1, 2, 3 \quad (4-23)$$

$$\alpha_i = \frac{\Omega_{ai} (RT)^2 \alpha_i}{P_{ci}} \quad (4-24)$$

$$\beta_{k,i} = \frac{\Omega_{bk,i} RT_{ci}}{P_{ci}} \quad k = 1, 2, 3. \quad (4-25)$$

The following expressions for calculation of Ω_a and Ω_{b_1} were obtained by Adachi et al. (1983) by fitting to pure component properties along the critical isotherm:

$$\Omega_a = 0.44869 + 0.04024\omega + 0.01111\omega^2 - 0.00576\omega^3 \quad (4-26)$$

$$\Omega_{b_1} = 0.08974 - 0.03452\omega + 0.0033\omega^2. \quad (4-27)$$

The value of m as function of ω was obtained by fitting to pure component vapor pressure:

$$m = 0.4070 + 1.3787\omega - 0.2933\omega^2. \quad (4-28)$$

Using the experimentally observed critical point criteria

$$\left(\frac{\delta P}{\delta V}\right)_c = \left(\frac{\delta^2 P}{\delta V^2}\right)_c = 0 \quad (4-29)$$

Jensen (1987) derived the following expressions for Ω_{b_2} and Ω_{b_3} :

$$\Omega_{b_2} = 0.5 \left[2(1 + \Omega_{b_1}) - 3\Omega_a^{1/3} + (4\Omega_a - 3\Omega_a^{2/3})^{1/2} \right] \quad (4-30)$$

$$\Omega_{b_3} = 0.5 \left[-2(1 + \Omega_{b_1}) + 3\Omega_a^{1/3} + (4\Omega_a - 3\Omega_a^{2/3})^{1/2} \right]. \quad (4-31)$$

T_c, P_c , and ρ_c , which are necessary input parameters for equation of state calculations, are not known for the C_{7+} fractions. These parameters are calculated by using the following functions:

$$T_c = d_1 SG + d_2 \ln MW + d_3 MW + d_4 / MW \quad (4-32)$$

$$\ln P_c = d_5 + d_6 SG + d_7 / MW + d_8 / MW^2 \quad (4-33)$$

$$\rho_c = d_9 + d_{10} MW + d_{11} SG + d_{12} MW^2. \quad (4-34)$$

The functional form of the equations for the calculation of T_c and P_c is the same as those used by Pedersen et al. (1988).

4.3.2 System Represented of ALS.

The ALS equation is shown that P-V-T properties and phase equilibria can be accurately predicted even in the near-critical region and can predict liquid volumes of mixtures including those with a considerable content of N_2 . This model preserves the good qualities of the model of Pedersen et al. with respect to phase equilibrium predictions and at the same time improves liquid dropout and liquid density

calculations. The model should also be able to accurately predict the phase behavior of fluids with a considerable content of CO₂ or N₂. This is of special importance in the simulation of miscible or immiscible gas injection processes. The model can calculate the phase behavior of oil and gas condensate mixtures.

The thermodynamic framework is a four parameter cubic equation of state. The necessary parameters in the employed C₇₊ -characterization procedure are calculated with only measured molecular weights and specific gravities. The model has been used for prediction of a number of different P-V-T properties for a wide variety of reservoir fluids ranging from light gas condensates and near critical mixtures to heavy oils. The model is able to predict simultaneously phase compositions and phase densities. This results in very accurate liquid dropout predictions even in the near critical region.

The new model has also been applied for the prediction of phase behavior for a number of mixtures with a significant content of CO₂ or N₂. Predicted saturation points agree well with experimental data, and the new model is able to accurately predict liquid volumes of mixtures with a considerable content of N₂.

The results that have been described up to now are all for mixtures which were used in estimating the parameters in Equation (4-32) to (4-34). In order to test the predictive capabilities of the model, various properties were calculated for fluids not included in the parameter estimation.

Accurate predictions of phase equilibria and related properties for oil and gas condensate mixtures have been the main objective for developing the new model. No attempt has been made to calculate physical properties of the individual C₇₊

components. The functions for the calculation of T_c, P_c , and ρ_c (Equations (4-32) to (4-34)) should therefore not be used for quantitative conclusions regarding the phase behavior of oil fractions.

Table 4.2 Measured and Predicted Liquid- and Vapor-Phase Compositions of Mixture 7 at $T=394$ K and $P=12.4$ MPa^a[3].

component	liquid phase			vapor phase		
	Expt	SRK	ALS	Expt	SRK	ALS
C ₁	0.2885	0.3138	0.3001	0.7771	0.7812	0.7688
C ₂	0.0570	0.0598	0.0581	0.0737	0.0753	0.0769
C ₃	0.0532	0.0529	0.0523	0.0446	0.0413	0.0433
n-C ₄	0.0833	0.0803	0.0804	0.0385	0.0390	0.0419
n-C ₅	0.0919	0.0900	0.0912	0.0283	0.0281	0.0308
C ₆	0.1087	0.1045	0.1068	0.0211	0.0214	0.0238
C ₇₊	0.3174	0.2987	0.3111	0.0167	0.0138	0.0145

^aTotal vapor mole fraction: experimental 0.38, SRK 0.344, ALS 0.373.

In Table 4.2, The liquid-phase composition is predicted with greater accuracy by using the new model, while the gas-phase composition is predicted slightly better by using the SRK EOS. Aasberg-Petersen (1989) has made a more thorough comparison between the two models with experimental data for a number of fluids. It concluded that the two models are of comparable quality regarding the prediction of phase compositions.

4.4 TCC Equation Of State.

4.4.1 Characteristics of TCC EOS.

In summary, the optimum three-parameter cubic equation of state[15] based on the assumption discussed is proposed as the following:

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+4b)+c(V+b)}. \quad (4-35)$$

Equation (4-35) can be expressed in terms of compressibility factor,

$$Z^3 + (3B+C-1)Z^2 + (A-4B-C-4B^2)Z - (A+BC+C)B = 0 \quad (4-36)$$

where

$$A = Pa/R^2T^2 \quad (4-37)$$

$$B = Pb/RT \quad (4-38)$$

$$C = Pc/RT. \quad (4-39)$$

Expression of the critical conditions results in:

$$C_c = 1 - 3(Z_c + B_c) \quad (4-40)$$

$$A_c = 3Z_c^2 + B_c + (1 - 3Z_c) + 4B_c^2 \quad (4-41)$$

where B_c is the smallest positive real root of the cubic equation:

$$B_c^3 - (3Z_c + 1)B_c^2 + (3Z_c^2 - 6Z_c + 2)B_c - Z_c^3 = 0. \quad (4-42)$$

The parameters A_c , B_c and C_c are all functions of Z_c .

4.6.1.1 Mixing Rules.

Equation (4-35) can be extended to the calculation of mixture properties if the constants a , b , and c are replaced by any usual set of mixing rules, such as the classical quadratic one:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (4-43)$$

$$b = \sum_i x_i b_i \quad (4-44)$$

$$c = \sum_i x_i c_i \quad (4-45)$$

where x_i is the mole fraction of component i and a_{ij} is not equal to a_{ji} . For a binary system, the following mixing rule is used for a_{12}

$$a_{12} = (a_1 a_2)^{0.5} \left[\left(1 - \frac{k_{12}}{T} \right) + \left(\frac{H_{12} G_{12} x_2^2}{x_1 + G_{12} x_2} \right) \right] \quad (4-46)$$

where

$$H_{12} = \frac{k_{21} - k_{12}}{T} \quad (4-47)$$

$$G_{12} = \exp(-\beta_{12}H_{12}). \quad (4-48)$$

The expression for γ_{12} , which is similar to Equation (4-46), can be obtained by interchanging subscript 1 and 2. Equation (4-46) has four adjustable parameters, and β_{12} . These four parameters all have meanings (Twu et al., 1992)[15] or nonpolar/nonpolar systems, where deviations from ideality are not large or only weakly asymmetric, two parameters, and β_{12} are sufficient to fit binary data. For other polar/polar or polar/nonpolar systems, where the nonideality is large or strongly asymmetric, it may be necessary to include the additional parameters, β_{11} and β_{22} in Equation (4-46). However, for polar/polar systems, β_{12} generally can be set equal to β_{11} , or polar/nonpolar systems, which have the greatest deviation from an ideal solution, β_{12} is usually not equal to β_{11} . Equation (4-46) can be simplified, if β_{12} is zero, to the following,

$$a_{12} = (a_1 a_2)^{0.5} \left[\left(1 - \frac{k_{12}}{T} \right) + \frac{(k_{21} - k_{12})}{T} x_2^2 \right]. \quad (4-49)$$

Equation (4-49) is not quite the same as that proposed by Panagiotopoulos and Reid (1986), whose mixing rule is given below,

$$a_{12} = (a_1 a_2)^{0.5} \left[(1 - k_{12}) + (k_{12} - k_{21}) x_1 \right]. \quad (4-50)$$

Although Equation (4-49) does not appear to be the same as Equation (4-50), the properties calculated from either equation, using Equation (4-43), are identical for a binary isotherm. However, the Panagiotopoulos-Reid mixing rule is not readily generalized to multicomponent solutions.

Unlike the conventional mixing rule which can be obtained at a temperature by setting the asymmetric definition of in the new mixing rule[14] provides a powerful way to fit binary data. It should be noted that a temperature-dependent function is built into Equation (4-46). As a result, Equation (4-46) gives not only an expression for the mixing rule as a function of composition but also an estimation of the variation of the mixing rule with temperature. This is an important practical advantage in isobaric calculations where the temperature varies as the composition changes.

For a multicomponent system, Equation (4-46) is generalized as:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} \left(1 - \frac{k_{ij}}{T}\right) + \sum_i x_i \frac{\left[\sum_j H_{ij}^{1/3} G_{ij}^{1/3} (a_i a_j)^{1/6} x_j \right]^3}{\sum_j G_{ij} x_j} \quad (4-51)$$

where

$$H_{ij} = \frac{k_{ji} - k_{ij}}{T} \quad (4-52)$$

$$G_{ij} = \exp(-\beta_{ij} H_{ij}). \quad (4-53)$$

4.4.2 System Represented of TCC.

TCC equation of state can be modified to allow a simultaneous calculation of all thermodynamic properties for polar and nonpolar systems. To significantly improve the accuracy of liquid density calculations, adjusting the volume function of a EOS by the addition of a third parameter. The volume function chosen gives the best fit for

liquid hydrocarbon densities and also improves the predicted liquid densities for polar components. The range of application for the TCC EOS is extended to polar/nonpolar systems by combining an appropriate function and advanced mixing rule.

Two-parameter cubic equation of state are analyzed and a new three-parameter cubic equation of state is proposed with the critical compressibility factor taken as substance dependent. An apparent critical compressibility factor is determined by optimizing the calculation of saturated liquid densities while the equality of fugacities along the saturation curve is imposed. TCC equation of state, combined with a previously proposed function and mixing rule, proves to be a powerful equation for predicting properties of pure components and mixtures. The new equation not only improves volumetric property calculations relative to either efforts, but also achieves high degree of accuracy in the calculation of vapor-liquid equilibria for highly nonideal systems such as polar/nonpolar mixtures. Alcohol/hydrocarbon mixtures are used as an extreme test of the new equation of state.

The results of predicting vapor pressures and saturated liquid densities from the new cubic EOS are shown in Table 4.3. The accuracy for the majority of components is generally within 0.5% for vapor pressure and 1.5% for liquid density for reduced temperature less than 0.7. Also listed in Table 4.3 are the calculated saturated liquid densities calculated with RK and PR.

Table 4.3 Average absolute deviation percents(AAD%) when predicting saturated vapor pressures (VP) and saturated liquid densities (DENS) from the triple point to critical temperature using the TCC[15].

Component	TCC		DENS (up to T_c)		
	VP	DENS ($T_c \leq 0.7$)	TCC	RK	PR
Argon	0.23	0.83	1.83	4.39	10.06
Methane	0.08	0.70	2.04	5.64	8.94
Ethane	0.20	1.73	2.29	6.53	7.00
Propane	0.69	2.02	2.45	8.00	5.18
n-Butane	0.18	1.67	2.46	9.52	4.49
n-Pentane	0.32	1.61	2.36	11.21	2.91
n-Hexane	0.15	1.38	2.25	12.66	2.30
n-Heptane	0.14	1.43	2.36	14.34	3.41
n-Octane	0.13	1.23	2.54	15.99	5.25
n-Nonane	0.83	1.51	2.80	16.54	5.86
n-Decane	0.16	1.38	2.62	17.22	6.64
n-Undecane	0.09	1.46	2.79	18.33	7.92
n-Dodecane	0.24	1.40	2.80	19.50	9.22
n-Tridecane	0.10	1.86	3.04	19.08	8.76
n-Tetradecane	0.17	1.28	3.33	21.37	11.37
n-Pentadecane	0.18	1.69	3.03	20.63	10.52
n-Hexadecane	0.08	1.72	4.08	22.30	12.42
n-Heptadecane	0.48	1.36	3.27	24.89	15.33
n-Octadecane	1.22	1.34	2.59	28.57	19.41
n-Nonadecane	0.19	1.65	4.18	30.78	21.97
Eicosane	1.20	1.91	4.50	32.87	24.28
Cyclohexane	0.08	0.77	2.33	10.22	5.00
Benzene	0.18	0.80	2.42	11.73	3.95
Acetone	0.15	1.44	3.33	23.72	13.96
Methanol	0.30	2.21	5.04	26.92	17.63
Ethanol	0.72	2.07	4.55	20.08	9.79
Water	0.13	3.63	6.80	28.65	19.50
EG	1.59	1.30	4.47	17.77	7.19
DEG	0.99	1.98	5.43	25.27	15.77
TEG	1.54	1.36	3.46	24.69	15.12

Table 4.4 The binary interaction parameters for binaries[15].

System*	case	k_{12} (K)	k_{21} (K)	β_{12}	β_{21}	AAD%		
						P	K_1	K_2
BZ(1)/ CH(2)	1	6.964	7.393	0.0	0.0	0.26	0.58	0.48
DMK(1)/ H2O(2)	1 2	-91.72 -92.83	-33.83 -39.67	0.0 5.793	0.0 5.793	2.75 1.56	2.42 1.12	3.70 1.64
ETOH(1)/ NC7(2)	1 2	36.86 57.00	-1.455 -0.9193	0.0 -8.154	0.0 -82.74	4.41 1.19	5.46 1.38	7.14 2.15
ETOH(1)/ BZ(2)	1 2	41.10 46.40	14.69 17.66	0.0 -11.84	0.0 -38.75	1.46 0.65	3.96 1.71	2.62 0.92
MEOH(1)/ NC7(2)	1 2	66.12 101.7	-11.95 -7.030	0.0 -4.977	0.0 -28.66	4.43 0.59	3.03 0.26	8.22 0.66

* BZ is benzene, CH is cyclohexane, DMK is acetone, ETOH is ethanol, NC7 is n-heptane, and MEOH is methanol

The effect of the interaction parameter can be visualized in Table 4.4, where the results of the prediction from the equation of state are shown in two cases for polar/polar and polar/nonpolar systems: case 1: for nonpolar/nonpolar, and case 2: for polar/polar or for polar/nonpolar

The accuracy for case 2 is improved significantly over case 1. The results clearly indicate that the use of additional parameters, for a nonideal system is justified.

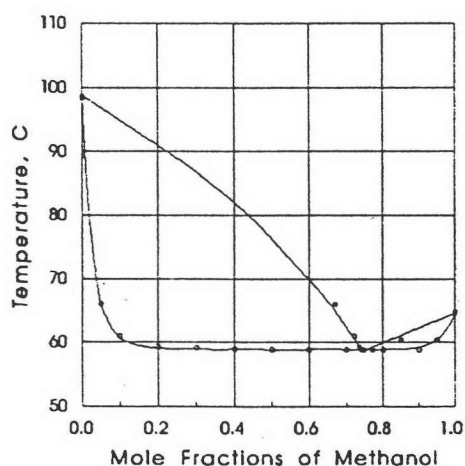


Figure 4.1. Methanol/n-heptane system; comparison of predicted T-x and T-y curves (lines) with experimental data (symbols) at 760 mmHg from Budantseva, I.S., Lesteva, T.M., and Nemstov, M.S., *Zh. Fiz. Khim.*, 49, 1844 (1975)[15]

The result for these binaries are plotted in Figure 4.1. The system, methanol/n-heptane, which has the strongest deviations from Raoult's law, is shown in Figure 4.1 to demonstrate the temperature-dependence of the interaction parameters given in the mixing rule. The system is at atmospheric pressure. The usual treatment of the system at isobaric conditions is to set the interaction parameters to be functions of temperature, Since a temperature-dependent function is automatically built into

Equation (4-66), no modification of to include additional parameters is needed in the mixing rule. The result for this strongly asymmetric system is in excellent agreement with data. The reason for choosing the methanol/n-heptane system for demonstration is that alcohol/hydrocarbon mixtures are highly non-ideal and can be used as an extreme test of an equation of state.

4.5 SBC Equation of State.

4.5.1 Characteristics of SBC EOS.

SBC equation of state is a noncubic equation[10] that contains four parameters which depend on three properties of the fluid-critical temperature, critical volume, and acentric factor. The equation of state can be written as:

$$P = \frac{RT}{(V - k_0\beta)} + \frac{\beta k_1 RT}{(V - k_0\beta)^2} - \frac{aV + k_0\beta c}{V(V + e)(V - k_0\beta)}. \quad (4-50)$$

The equation of state can be rewritten as a quartic:

$$V^4 + q_3V^3 + q_2V^2 + q_1V + q_0 = 0 \quad (4-51)$$

where

$$q_3 = \left(-2k_0\beta + e - \frac{RT}{P} \right) \quad (4-52)$$

$$q_2 = \left[\frac{RT}{P} (\beta(k_0 - k_1) - e) + k_0\beta(k_0\beta - 2e) \right] + \frac{a}{P} \quad (4-53)$$

$$q_1 = e \left[k_0^2 \beta^2 + \frac{RT}{P} \beta (k_0 - k_1) \right] + \left[\frac{k_0 \beta (c - a)}{P} \right] \quad (4-54)$$

$$q_0 = -\frac{ck_0^2 \beta^2}{P} \quad (4-55)$$

A temperature dependence was incorporated into β according to Nezbeda and Aim (1984):

$$\beta = \beta_c \left\{ \exp \left[-0.03125 \ln(T_r) - 0.0054 [\ln(T_r)]^2 \right] \right\}^3 \quad (4-56)$$

where $\beta_c = 0.165V_c$ (4-57)

and e is a constant, and a and c are temperature-dependent. A temperature dependence was incorporated into a and c in the following manner:

$$a = a_c \alpha(T_r) \quad (4-58)$$

where for $T_r \leq 1$

$$(T_r) = \left[1 + X_2(1 - \sqrt{T_r}) + X_3(1 - \sqrt{T_r})^2 + X_4(1 - \sqrt{T_r})^3 \right]^2 \quad (4-59)$$

and for $T_r > 1$

$$(T_r) = \left[1 + X_2(1 - \sqrt{T_r}) + X_5(1 - \sqrt{T_r})^2 + X_6(1 - \sqrt{T_r})^3 \right]^2 \quad (4-60)$$

Finally,

$$c = c_c \xi(T_r) \quad (4-61)$$

and

$$\xi(T_r) = [1 + X_7(1 - \sqrt{T_r})]^2 \quad (4-62)$$

where X_2, X_3, X_4, X_5, X_6 and X_7 are constants. The equation of state was extended to nonspherical fluids with the introduction of the acentric factor, ω , as the third property to characterize the fluid. The parameters a, c and e , and the constants X_1 through X_7 were made functions of the acentric factor. The parameters a_c, c_c and e were defined and related to the acentric factor as shown in Equations (4-63) to (4-68).

$$a_c = \frac{a_r RT_c}{\rho_c} \quad (4-63)$$

$$c_c = \frac{c_r RT_c}{\rho_c} \quad (4-64)$$

$$e = \frac{e_r}{\rho_c} \quad (4-65)$$

$$a_r = a_{r0}(1 + a_{r1}\omega + a_{r2}\omega^2) \quad (4-66)$$

$$a_c = \frac{a_r RT_c}{\rho_c} \quad (4-67)$$

$$c_c = \frac{c_r RT_c}{\rho_c} \quad (4-68)$$

$$e = \frac{e_r}{\rho_c} \quad (4-69)$$

$$a_r = a_{r0}(1 + a_{r1}\omega + a_{r2}\omega^2) \quad (4-70)$$

$$e_r = e_{r0}(1 + e_{r1}\omega + e_{r2}\omega^2) \quad (4-71)$$

$$c_r = c_{r0}(1 + c_{r1}\omega + c_{r2}\omega^2) \quad (4-72)$$

where a_c and c_c are the values of a and c at the critical temperature. Equations (4-67) to (4-68) were required to keep the critical compressibility, calculated by the equation of state, dependent on the nature of the fluid. The constants X_2 to X_7 were made functions of ω as:

$$X_i = X_{i1} + X_{i2}\omega \quad \text{for } i = 2,3,4,5,6,7. \quad (4-73)$$

4.5.2 System Represented of SBC EOS.

SBC equation of state models the forces between molecules correctly, unlike the cubic equations of state. The equation of state has been generalized for simple and nonpolar fluids. Only three properties of a fluid need to be specified to reproduce P-V-T and thermodynamic properties accurately. The identification of the roots obtained on solving the equation of state is very easy as one of them is always negative. Hence, the rules used to identify the roots of a cubic equation of state can be used with the SBC EOS.

A multiproperty nonlinear regression analysis was employed using data from 16 nonpolar fluids to determine all of the constants necessary to specify the equation of state. Second virial coefficient data, high-temperature residual enthalpy data, and density data were used for parameter evaluation.

The performance of SBC EOS is substantially superior to those of the Peng-Robinson (PR) equation. PR EOS overpredict densities at high pressures and supercritical temperatures. At subcritical temperatures the SBC EOS performs better, particularly for liquid density calculations. For argon the PR equation gives too high a liquid density at lower reduced temperatures. For nonpolar hydrocarbons, as the chain length of molecule increases from methane to n-octane, the performance of the PR EOS becomes comparable to that of the SBC EOS for orthobaric liquid densities and saturated vapor pressures.

The SBC EOS is more accurate in predicting derived thermodynamic properties such as specific heat, the Joule-Thomson coefficient and the adiabatic coefficient of bulk compressibility. In general, the SBC EOS is better and more accurate than or comparable to the Peng-Robinson EOS in estimating derived thermodynamic properties.

Table 4.5 presents the absolute average deviation (AAD) for various physical properties calculated from the SBC EOS, the PR EOS. The AAD summary was generated using data from all 16 fluids used in the regressions. Table 4.5 shows that the SBC EOS is remarkably superior to the other two equations. The PR EOS is slightly better than the SBC EOS with regard to saturated vapor pressure representation. The SBC EOS, however, gives a much better overall representation of fluid behavior than either the PR equation.

Table 4.5 Comparison of Physical and Thermodynamic Properties: AAD Summary

[10].

Property*	SBC	PR	Data Points
P_{sat}	1.52	1.31	409
ρ_{sv}	2.00	2.20	409
ρ_l	3.46	6.31	581
ρ_g	0.60	1.67	2,763
B_{vir}	6.09	46.46	537
H_r	4.03	22.27	1,204

* P_{sat} = saturated vapor pressure; ρ_{sv} = saturated vapor density; ρ_l = liquid density; ρ_g = single-phase gas density; B_{vir} = second virial coefficient; H_r = residual enthalpy, J/mol.