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## APPLICATION OF GENERALIZED PRESSURE PERTURBATION PRINCIPLE TO CUBIC EQUATION OF STATE FORMULATION

Sunday O. Isehunwa, SPE; and Gabriel K. Falade, SPE, Department of Petroleum Engineering, U. of Ibadan

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### Abstract

Cubic equations of state are commonly used for predicting the properties of reservoir fluids. They are simple to use and require few parameters during computations. They have also been found to produce results that are comparable to the more rigorous multi-parameter equations. However, they are still regarded by many as mere comprehensive correlations of fluid properties because of a number of weaknesses and limitations. This work addresses two weaknesses of cubic equations of state commonly highlighted in literature, viz: that they do not seem to have deep theoretical foundations and are not as accurate as non-cubic equations. A pressure perturbation technique based on a simple adaptation of the Weirtheim's first order thermodynamic perturbation theory has been developed and used to formulate a cubic equation of state. The practical equation formulated was applied to pure fluids and samples of Niger Delta Petroleum fluids. The results show more accurate predictions than the commonly used SRK and PR equations. This work suggests that cubic equations could have deeper theoretical

roots than otherwise thought and provides a theoretical framework for improving the accuracy of cubic equations of state.

### Introduction

Equations of State probably originated in 1662 from Boyle who conducted experiments on air and deduced that at a given temperature, the volume of a fixed mass of gas is inversely proportional to its pressure<sup>(1)</sup>. However, the modern view of equations of state derives from the well-known van der Waals equation which describes the pressure of a system with contributions from the repulsive and attractive forces:<sup>(2)</sup>

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \dots(1)$$

There are several equations of state in use today<sup>(3-9)</sup> and majority of them are simple empirical modifications of the van der Waals expression which has three very important attributes as noted by Tsonopoulos and Heideman<sup>(10)</sup>: First, as  $P \rightarrow \infty$ ,  $V \rightarrow b$  unlike in most non-cubic equations. Second, the parameters **a** and **b** have physical meanings, and third, the equation of state is cubic in volume and easily solved analytically.

Although cubic equations have been found to yield good results for a number of systems, they are still regarded as comprehensive correlations of fluid properties because of the belief that they lack sound theoretical foundations and are not as accurate as non cubic equations such as those based on thermodynamic perturbation theory<sup>(11)</sup>. Many researchers have therefore directed efforts

in recent times, at developing equations of state that have sound theoretical foundations. These efforts have largely resulted in the development of accurate but complex non-cubic equations that cannot be readily deployed to routine engineering applications. One obvious way forward, which has been adopted in this study, is to develop a theoretically robust and accurate equation of state which can be simplified to a practical cubic equation without substantial loss of accuracy.

### THEORETICAL FRAMEWORK

In recent times, the use of Wertheim's first order perturbation theory<sup>(12-13)</sup>, has led to the development of highly accurate, Statistical Associating Fluid Theory (SAFT) equations of state for associating pure fluids and mixtures<sup>(14-17)</sup>. The success of the SAFT equations of state has been attributed to the sound theoretical foundation of describing fluid molecules as covalently bonded chain segments whose Helmholtz energy can be represented by expressions for repulsive, dispersion, association and/or solvation forces. Mathematically, the SAFT free energy can be expressed as:

$$\frac{A}{NkT} = \frac{A^{rep}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} \quad \dots(2)$$

Or,

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mono}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} \quad \dots(3)$$

Equations (2) and (3) lead to the general expression:

$$A = A^{ideal} + A^{mono} + A^{chain} + A^{assoc} \quad \dots(4)$$

But following Gibbs-Duhem principle, we define:

$$A = \sum n_i \mu_i - PV \quad \dots(5)$$

Thus,

$$\begin{aligned} (\sum n_i \mu_i - PV) &= (\sum n_i \mu_i - PV)^{ideal} + (\sum n_i \mu_i - PV)^{mono} + \\ &(\sum n_i \mu_i - PV)^{chain} + (\sum n_i \mu_i - PV)^{assoc} \end{aligned} \quad \dots(6)$$

By equating equivalent terms on both sides of Equation (6), we have:

$$\sum n_i \mu_i = (\sum n_i \mu_i)^{ideal} + (\sum n_i \mu_i)^{mono} + (\sum n_i \mu_i)^{chain} + (\sum n_i \mu_i)^{assoc} \quad \dots(7)$$

and,

$$PV = (PV)^{ideal} + (PV)^{mono} + (PV)^{chain} + (PV)^{assoc} \quad \dots(8)$$

For a closed thermodynamic system, equation (8) can be simplified to:

$$P = (P)^{ideal} + (P)^{mono} + (P)^{chain} + (P)^{assoc} \quad \dots(9)$$

Thus, it could be concluded that the thermodynamic perturbation principle may be extended, under some assumptions, to pressure perturbation.

In this study, unlike the classical thermodynamic perturbation approach in which each of the terms in equations (2) – (4) are derived using different rigorous statistical thermodynamic equations, we propose a simple pressure perturbation approach that ensures the same coherent theory for all the terms. This method is easy to apply to fluid mixtures using simple mixing rules.

In this study, the pressure function P, is first expressed by a relation of the form:

$$P = P_R + P_A + P_{NP} \quad \dots(10)$$

Where,

$P_R$  = Pressure contribution by repulsive forces

$P_A$  = Pressure contribution by attractive forces and

$P_{NP}$  = Pressure contribution by other forces



Equation (10) can however, be replaced by a simple general form:

$$P = f(v, T, n) \quad \dots \quad (11)$$

In general, for a pure fluid where composition effect is neglected, Equation (11) can be expanded in a polynomial equation form to give:

$$P = \left(\frac{a_1}{V} + \frac{a_{11}}{V^2} + \frac{a_{111}}{V^3} + \dots\right) + \left(\frac{a_2 a_2 T}{V} + \frac{a_1 a_{22} T}{V^2} + \frac{a_1 a_{222} T}{V^3} + \dots\right) + \left(\frac{a_{11} a_2 T^2}{V} + \frac{a_{111} a_2 T^3}{V} + \dots\right) + (a_0 + a_a T + a_{22} T^2 + \dots) \quad \dots \quad (12)$$

Where,

$$\rho = \text{Molar density} = 1/V$$

Equation (12) can be expressed in general form as:

$$P = \sum_{i=1}^r \frac{a_i(T)}{V^i} + \sum_{i=1}^r \frac{a_{i2}(T, V)}{V^i} + \sum_{i=1}^r \frac{a_2(V)}{T^i} \quad \dots \quad (13)$$

Equation (13) is a generalized expression similar to the "generalized" cubic equation of state developed by Martin<sup>(18)</sup> for pure fluids:

$$P = \sum_{i=1}^r \frac{a_i(T)}{V^i} \quad \dots \quad (14)$$

Thus, using common parlance, equations (12) and (13) can be still simply be interpreted conceptually as:

$$P = P_R + P_A + P_{NP} \quad \dots \quad (10)$$

**SIMPLIFICATION AND APPLICATION**

In this work, the authors take a look at the procedure to use equations (12) and (13) to evaluate them using the van der Waals approach and using simple algebraic manipulation as shown in the appendix to obtain:

$$P_R = \frac{RT}{V(1-\eta)^r} \quad \dots \quad (15)$$

for the repulsive forces term,

$$P_A = \frac{-a_1 a_2(T)}{V^2(1-\zeta)^r} \quad \dots \quad (16)$$

for the attractive forces term, and

$$P_{NP} = \left(\frac{a_1 a_2}{V}\right)[e^{\beta T} - 1] \quad \dots \quad (17)$$

for the contribution from other forces. Equation (17) can further be simplified as:

$$P_{NP} = \frac{c(T)}{V} \quad \dots \quad (18)$$

Substituting equations (15) to (18) into equations (11) and (13) gives:

$$P = \frac{RT}{V(1-\eta)^r} - \frac{a(T)}{V^2(1-\zeta)^r} - \frac{c(T)}{V} \quad \dots \quad (19)$$

Where,

$$r = 4$$

Equation (19) is the final generalized van-der Waals type equation of state obtained. However, it is rather complex and strictly non-cubic in V. It can be further simplified to yield a simple, practical cubic equation.

To obtain an approximate cubic equation, we set  $r=1$ , and  $\eta = -\zeta = b/4V$  in Equation (19) to obtain:

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)} - \frac{c(T)}{V} \quad \dots \quad (20)$$

Where, following Soave and Peng-Robinson form as modified by Grasboski and Daubert<sup>(23)</sup>:

$$a(T) = a c \alpha(T) \quad \dots \quad (21)$$

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2 \quad \dots \quad (22)$$

$$m = 0.48508 + 1.55171\omega - 0.151613\omega^2 \quad \dots \quad (23)$$

Using a convention similar to the attractive term  $a(T)$ ,

$$c(T) = c^* \gamma(T) \quad \dots(24a)$$

$$\gamma(T) = \exp(-\beta (1-Tr)) \quad \dots(b)$$

and  $\beta$  is an empirical constant.

In this study, a simple optimization approach was used to establish  $\beta$  and to evaluate Equation (24b) as:

$$\gamma(T) = \exp(-40 (1-Tr)^{0.5})^2 \quad (c)$$

### Equation of State Parameters

Equation (20) gives a cubic equation in volume that can be expressed as:

$$V^3 - V^2 \left( \frac{RT}{P} - \frac{c}{P} \right) + V \left( \frac{a}{P} - b^2 - \frac{bRT}{P} \right) - \left( \frac{ab}{P} + \frac{b^2c}{P} \right) = 0 \quad \dots(25)$$

Solving, at near critical condition, we have:

$$c = RT_c - 3P_c V_c \quad (26)$$

$$a_c = 3P_c V_c^2 + b(bP_c + RT_c) \quad \dots(27)$$

and the parameter,  $b$ , is obtained using a well-known convention, from the smallest positive real root of the cubic equation:

$$b^3 - \left( 3V_c - \frac{2RT_c}{P} \right) b^2 + \left( 3V_c^2 b - V_c^3 \right) = 0 \quad \dots(28)$$

Equation (25) can also be expressed in the form:

$$Z^3 - (1-C)Z^2 + (A-B^2-B)Z - (AB+B^2C) = 0 \quad \dots(29)$$

Where,

$$A = \frac{aP}{(RT)^2}$$

$$B = \frac{bP}{(RT)}$$

$$C = \frac{c}{(RT)}$$

### EXTENSION TO MIXTURES

Following the work of several earlier investigators, the simple van der Waals one fluid mixing rules were used for calculating mixture parameters so as to extend Equation (20) to mixtures. The mixture parameters are given as:

$$a = \sum \sum X_i X_j a_{ij} \quad \dots(30a)$$

$$b = \sum X_i b_i \quad (b)$$

$$c = \sum X_i c_i \quad (c)$$

$$a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij}) \quad (d)$$

Where  $X_i$  stands for mole fraction and  $k_{ij}$  is a binary interaction coefficient for interactions between components. In this work,  $k_{ij}$  were set at zero and there was no tuning.

### RESULTS AND DISCUSSION

From the foregoing, it is clear that the van der Waals equation of state and its several variants only incorporate the 'physical' repulsive and attractive forces. They do not incorporate possible contributions to pressure, of other forces such as quantum effects and the chemical forces. In other words, a truly generalized equation of state should account for all possible contributions to pressure beyond the commonly recognized repulsive and attractive forces.

Equation (19) is a generalized van der Waals-type equation of state from which most simple equations of state can be derived. Equation (20) on the other hand, can be considered as an approximate generalized model derived from equation (19). One major advantage of the generalized equation expressed in this form is the fact that it explains the physical significance of the EOS parameters in a three-parameter equation of state. Thus, while 'a' captures the attractive forces, 'b', the co-volume, 'c' in the form it appears in the equation represents a parameter that captures the contribution to pressure of other forces. This is different from the concept of 'c' in many equations of state where 'c' obviously represents an "after-the-fact" volume correction term.



Furthermore, unlike Bondi<sup>(19)</sup>, who suggested possible determination of non van der Waals forces from a different fluid theory, in this work, the non-physical effects represented by parameter 'c' has been derived using a theory that is consistent with the estimation of parameters 'a' and 'b'. It follows by extension that multi-parameter equations of state can be physically meaningful if the parameters are related to different forces in the system.

Equation (20) was first validated by applying it to pure hydrocarbons under various conditions of temperature and pressure. The results are as shown in the Figures 1 – 4. It was observed that for the very light compounds – methane, ethane, nitrogen, etc., the results from this model agree more with the SRK predictions which is known to be accurate for light compounds. However, for the heavier compounds such as Butane, the results are closer to the Peng-Robinson estimates.

### Binary Mixtures

Tables 1 and 2 as well as Figure 5 show the predicted Z-factors for K-Field-CO<sub>2</sub> mixtures. The results show that Equation (20) produced results that matched the experimental values more accurately than the SRK and PR equations.

### Application to Niger Delta Crude Oil Samples

The model developed in this study was used to simulate several fluid samples obtained from the Niger Delta. The results for three samples are presented in Figures 9–11. The three samples presented here have properties that vary over a wide range as shown in Table 3. The results as shown in Figures 9–11 compare very well with SRK and PR, even without any fine-tuning. One advantage of the model presented in this work is that it tends to combine the best properties of the SRK and PR equations.

### CONCLUSION

A Pressure perturbation principle has been used to develop a generalized van-der Waals-type equation of state. This equation demonstrates that van-der Waals type equations of state can be related to thermodynamic perturbation principles and could have sound theoretical foundations than previously thought. It was shown that a truly generalized and accurate model must include the effects of non-physical forces in addition to the van der Waals repulsive and attractive forces normally captured in most of the existing cubic equations of

state. However, such an equation will be rather complex and requires further simplification through some assumptions to generate simple, practical approximate solutions.

### NOMENCLATURE

|                  |  |
|------------------|--|
| a, b             | - constants in van der Waals equation  |
| $a_{ij}, b_{ij}$ | - equations of state coefficients      |
| A                | - Helmholtz energy                     |
| c                | - third constant in equation of state  |
| c                | - volume translation parameter         |
| k                | - Boltzmann constant                   |
| $k_{ij}$         | - binary interaction coefficients      |
| m                | - constant in EOS attractive term      |
| $n_i$            | - number of moles of component i       |
| N                | - total number of molecules            |
| P                | - Pressure, psia (MPa)                 |
| r                | - parameter of solid equation of state |
| R                | - universal gas constant, per mole     |
| T                | - temperature, °F (°R)                 |
| v                | - molar volume                         |
| $x_i$            | - mole fraction of component i         |
| Y                | - parameter defined as $b/4v$          |
| Z                | - compressibility factor               |

### Greek

|            |                                      |
|------------|--------------------------------------|
| $\alpha$   | - coefficient of attractive term     |
| $\beta$    | - empirical constant                 |
| $\zeta$    | - equation of state parameter        |
| $\gamma$   | - coefficient of EOS attractive term |
| $\gamma_o$ | - specific gravity                   |
| $\rho$     | - molar density                      |
| $\eta$     | - dimensional volume = $b/4v$        |
| $\omega$   | - Pitzer acentric factor             |

### Subscripts

|    |                       |
|----|-----------------------|
| A  | - attractive forces   |
| c  | - critical point      |
| k  | - convergence         |
| L  | - liquid              |
| m  | - mixture             |
| NP | - non-physical forces |
| r  | - reduced             |
| R  | - repulsive forces    |

### Superscripts

|       |                              |
|-------|------------------------------|
| Assoc | - associated chain           |
| a,b,c | - empirical constants        |
| ch    | - chemical                   |
| n     | - equation of state constant |
| L     | - liquid phase               |
| o     | - degree                     |
| seg   | - segment-segment chain      |



### Abbreviations

|                    |   |
|--------------------|---|
| EOS                | - equation of state                     |
| Exp                | - exponential                           |
| Expt               | - experimental value                    |
| $^{\circ}\text{F}$ | - degree Fahrenheit                     |
| $^{\circ}\text{R}$ | - degree Rankin                         |
| K                  | - Kelvin                                |
| ln                 | - natural logarithm                     |
| psia               | - pounds per square inch                |
| SAFT               | - Statistically Associated Fluid Theory |

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### APPENDIX DERIVATION OF APPROXIMATE CUBIC EQUATION OF STATE

The derivation of the equation of state for the cubic equation of state is given in the appendix. The equation of state is derived from the virial equation of state and the repulsive force is assumed to be of the form  $\frac{a}{r^6}$  and the attractive force is assumed to be of the form  $\frac{b}{r^3}$ .

$$P_R = \frac{RT}{V-b}$$

$$P_R = \frac{RT}{V(1-4y)}$$

$$y = \frac{b}{4V}$$

$$P_R = \frac{RT}{V} (1+4y+16y^2+64y^3+256y^4+\dots)$$

$$P_R = \frac{RT}{V} (1+4y+10y^2+18y^3+28y^4+40y^5+\dots)$$

$$P_R = \frac{RT(1+y+y^2-y^3)}{V(1-y)^3}$$

$$P_R = \frac{RT}{V(1-y)}$$

However, neither equation (A7) nor equation (A8) will yield a cubic equation. Therefore, we suggest a modification of equation (A7) to a cubic equation that can be easily adapted to a cubic equation in the form:

$$P_R = \frac{RT}{V(1-\eta)^r}$$

$$P_A = -\frac{a(T)}{V^2(1-\zeta)^r}$$

$$P_{NP} = \left(\frac{a_1 a_2}{V}\right) [e^{\beta T} - 1]$$

$$P_{NP} = \frac{c(T)}{V}$$

$$P = \frac{RT}{V(1-\eta)^r} - \frac{a(T)}{V^2(1-\zeta)^r} - \frac{c(T)}{V}$$

$$P_R = \frac{RT}{V} (1+4y+10y^2+20y^3+35y^4+\dots)$$

$$P = \frac{RT}{V(1-\eta)^r} - \frac{a(T)}{V^2(1-\zeta)^r} - \frac{c(T)}{V}$$

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)} - \frac{c(T)}{V}$$

where following Soave-Redlich-Kwong equation is modified by Gao and Wu (2002):

$$a(T) = a_0(T) \quad (16)$$

$$a_0(T) = (1 + \alpha) \left( \frac{RT}{T} \right)^2 \quad (17)$$

$$\alpha = 1 - \beta \left( \frac{RT}{T} \right)^2 \quad (18)$$

Using a convenient choice for the function  $\alpha(T)$ :

$$\alpha(T) = \frac{c}{RT} \quad (19)$$

$$\beta(T) = \frac{b^2}{RT} \quad (20)$$

and  $\beta$  is an arbitrary parameter.

In this study, a simple equation of state is used. The equation of state is established based on the following assumptions:

$$A = \frac{aP}{(RT)^2} \quad (21)$$

Equation of State Parameters:

Equation (15) gives a cubic equation in  $V$  that can be expressed as:

$$V^3 - V^2 \left( \frac{RT}{P} - \frac{c}{P} \right) + V \left( \frac{a}{P} - b^2 - \frac{bRT}{P} \right) - \left( \frac{ab}{P} + \frac{b^2c}{P} \right) = 0 \quad (22)$$

Using a convenient choice for the function  $\alpha(T)$ :

$$\alpha(T) = \frac{c}{RT} \quad (23)$$

$$b^3 - \left( 3V_c - \frac{2RT}{P} \right) b^2 + (3V_c^2 b - V_c^3) = 0$$

$$A = \frac{aP}{(RT)^2}$$

$$B = \frac{bP}{(RT)}$$

$$C = \frac{c}{(RT)}$$

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Z- Pressure Plot for Ethane at 60 oF

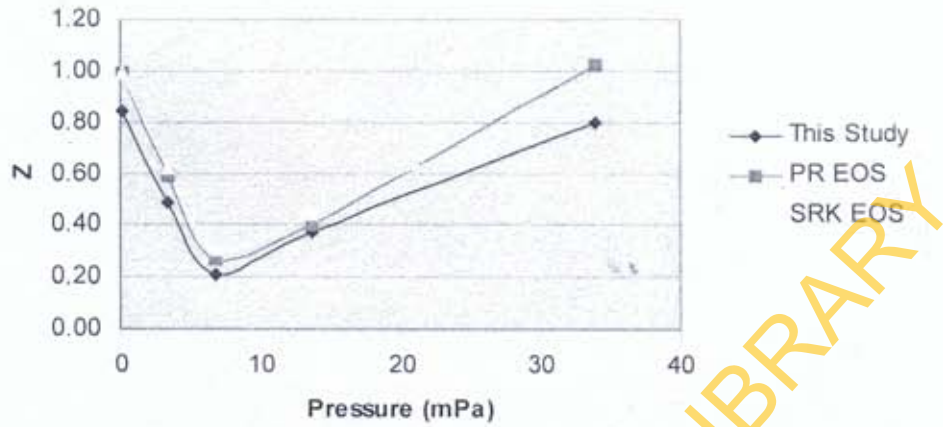


Figure 1: Pressure – Z Plot for Ethane at 60 oF

Z- Pressure Plot for Nitrogen at 60 oF

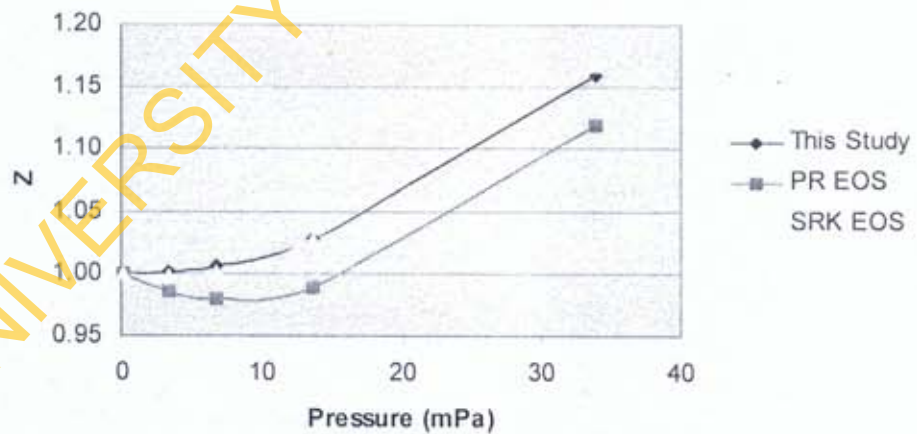


Figure 2: Pressure – Z Plot for Nitrogen at 60 oF

### Z- Pressure Plot for Methane at 200 °F

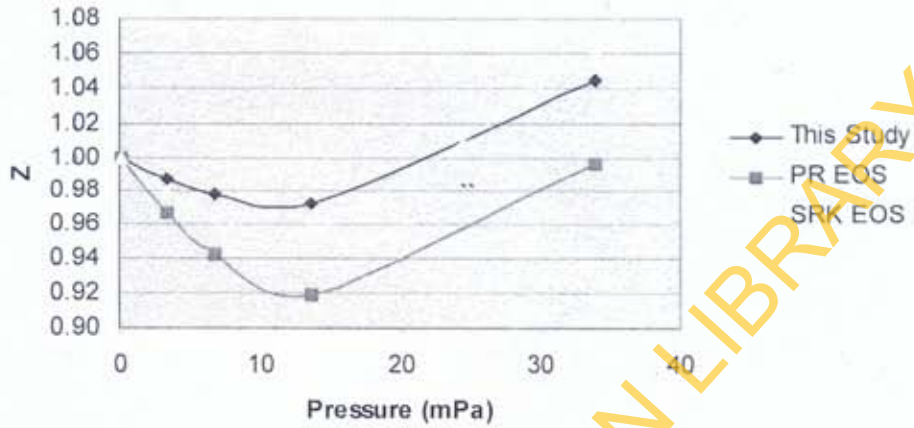


Figure 3: Z- Pressure Plot for Methane at 200 °F

### Z- Pressure Plot for Propane at 200 °F

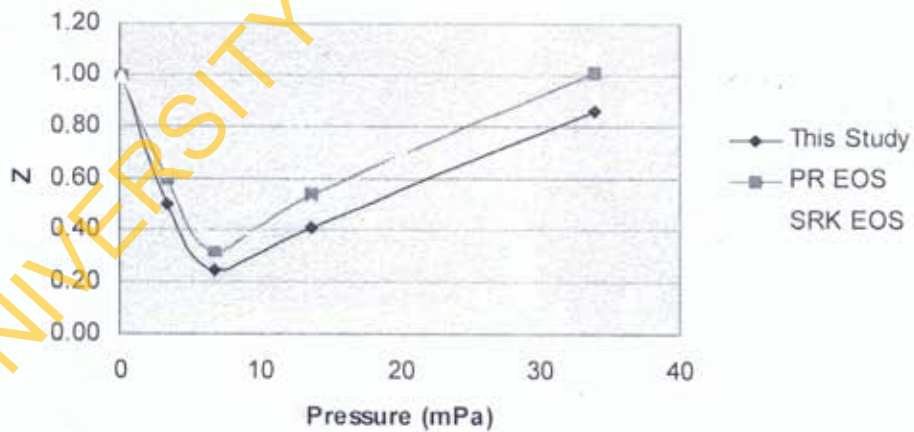


Figure 4: Z- Pressure Plot for Propane at 200 °F



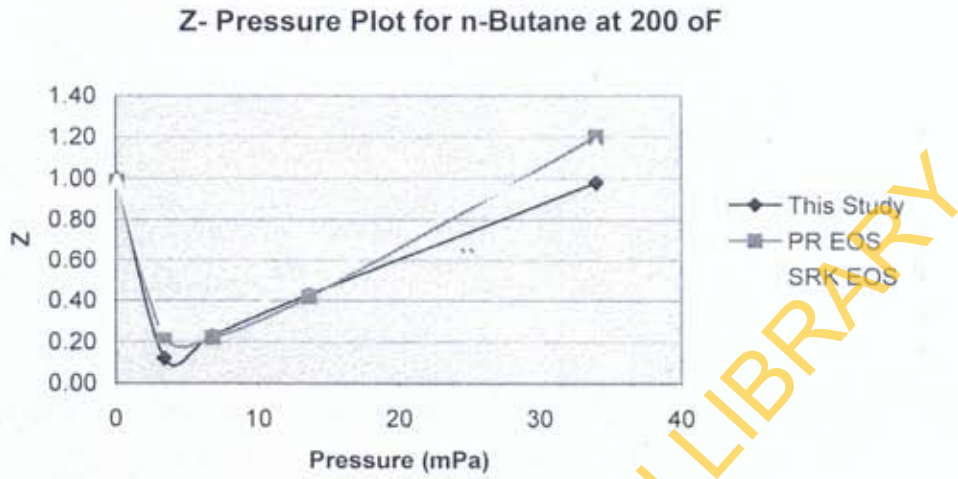


Figure 5: Z- Pressure Plot for n-Butane at 200 °F

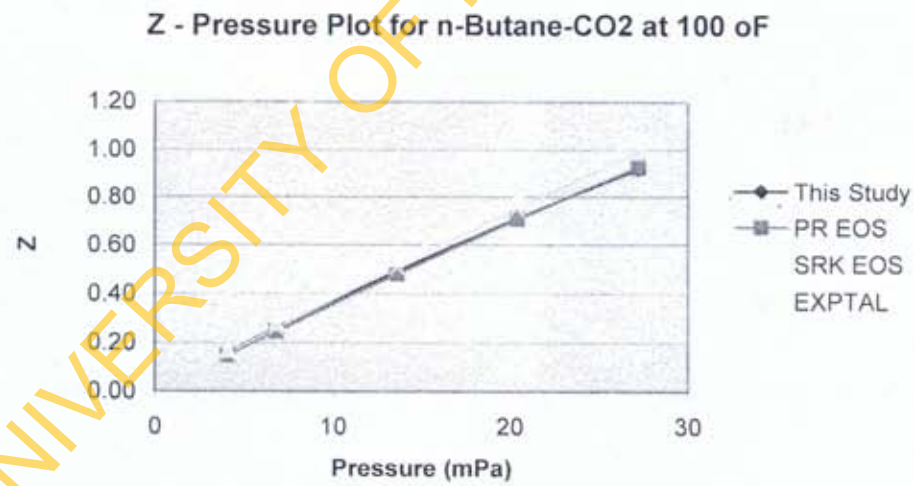


Figure 6: Z – Pressure Plot for n-Butane-CO2 System (% mole of CO2 = 10%)

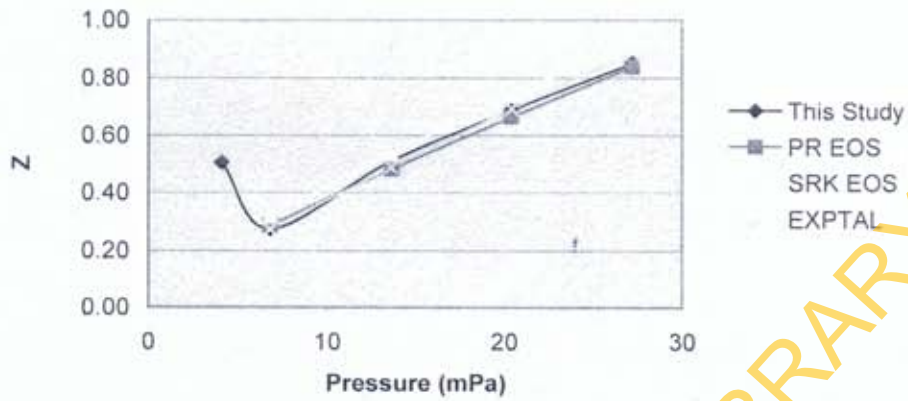
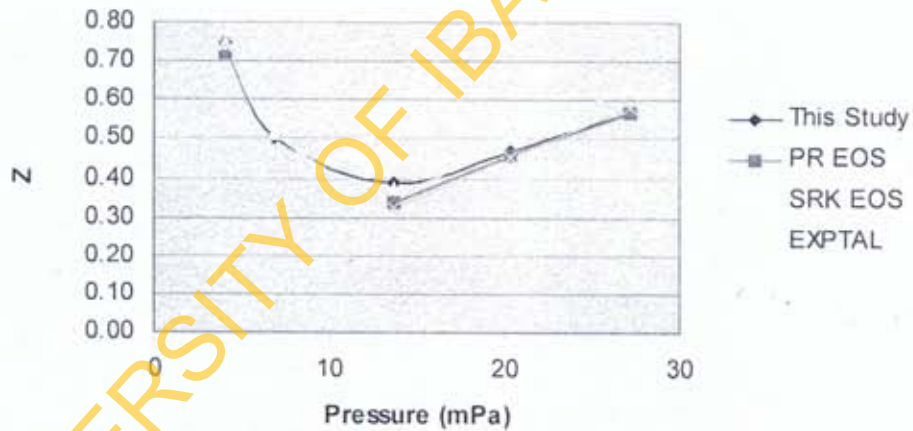
Z - Pressure Plot for n-Butane-CO<sub>2</sub> at 280 oFFigure 7: Z - Pressure Plot for n-Butane-CO<sub>2</sub> System (% mole of CO<sub>2</sub> = 10%)Z - Pressure Plot for n-Butane-CO<sub>2</sub> at 100 oFFigure 8: Z - Pressure Plot for n-Butane-CO<sub>2</sub> System (% mole of CO<sub>2</sub> = 90%)



TABLE 1: Z Factor vs Pressure for n-Butane (0.90)

| Pressure<br>Psia | Z Factor         |       |              |               |
|------------------|------------------|-------|--------------|---------------|
|                  | SRK <sup>2</sup> | PR    | Experimental | This<br>Study |
| 500              | 0.720            | 0.720 | 0.658        | 0.658         |
| 1000             | 0.720            | 0.720 | 0.658        | 0.658         |
| 2000             | 0.710            | 0.707 | 0.648        | 0.648         |
| 3000             | 0.704            | 0.701 | 0.637        | 0.637         |
| 4000             | 0.697            | 0.694 | 0.629        | 0.629         |

(Mole fraction n-Butane = 0.90)

TABLE 2: Z Factor vs Pressure for n-Butane (0.10)

| Pressure<br>Psia | Z Factor         |       |              |               |
|------------------|------------------|-------|--------------|---------------|
|                  | SRK <sup>2</sup> | PR    | Experimental | This<br>Study |
| 500              | 0.720            | 0.720 | 0.658        | 0.658         |
| 1000             | 0.721            | 0.719 | 0.627        | 0.627         |
| 2000             | 0.702            | 0.705 | 0.634        | 0.634         |
| 3000             | 0.671            | 0.668 | 0.630        | 0.630         |

(Mole fraction n-Butane = 0.10)

Table 3: Composition and PVT Data for Three Case Studies

| PARAMETER                    | CASE 1 | CASE 3 | CASE 6 |
|------------------------------|--------|--------|--------|
| C1                           | 41.83  | 47.47  | 7.81   |
| C2                           | 3.51   | 6.51   | 1.75   |
| C3                           | 5.4    | 4.93   | 0.71   |
| IC4                          | 1.84   | 1.03   | 0.25   |
| NC4                          | 3.36   | 2.11   | 0.22   |
| IC5                          | 1.69   | 0.92   | 0.16   |
| NC5                          | 1.65   | 1.06   | 0.13   |
| C6                           | 2.24   | 1.7    | 0.27   |
| C7+                          | 38.25  | 31.6   | 88.46  |
| CO2                          | 0.2    | 2.54   | 0.11   |
| N2                           | 0.03   | 0.13   | 0.13   |
| Fluid Mol Wt.                | 83.98  | 79.48  | 234.9  |
| GOR, scf/stb                 | 806    | 1197   | 42.9   |
| Oil Viscosity, cp            | 0.86   | 0.82   | 5.79   |
| Saturation<br>pressure, Psia | 2747   | 3652   | 415    |
| Reservoir<br>Pressure, psia  | 3960   | 3663   | 4218   |
| Reservoir<br>Temperature °R  | 648.1  | 720    | 631    |

Z - Pressure Plot for CASE 1 at 60 oF

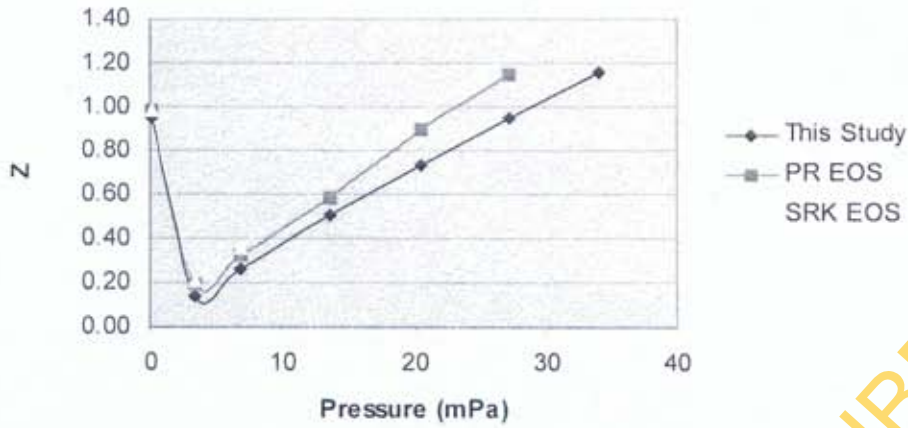


Figure 9: Z – Pressure Plot for Case 1 at Surface Conditions

Z - Pressure Plot for CASE 1 at 188 oF

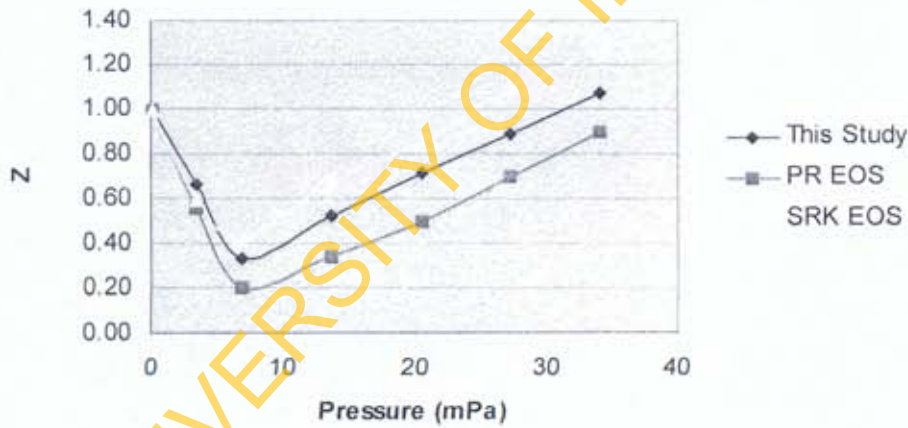


Figure 10: Z – Pressure Plot for Case 1 at Reservoir Temperature

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Z - Pressure Plot for CASE 3 at 260 oF

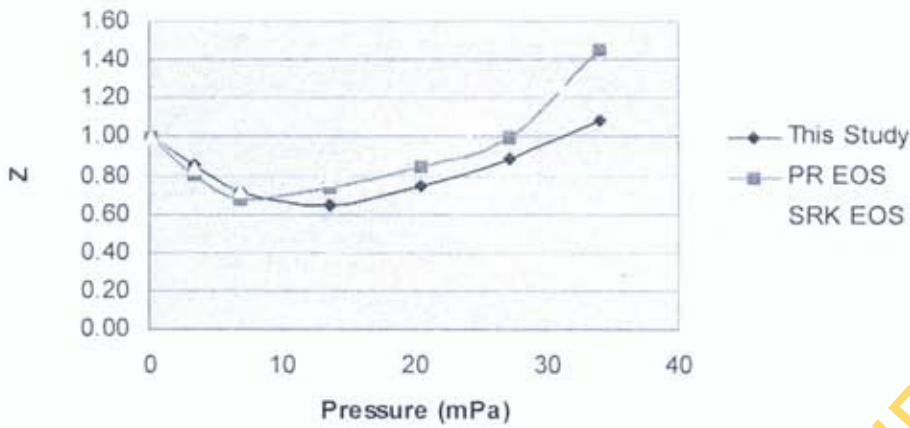


Figure 13: Z - Pressure Plot for Case 3 at Reservoir Temperature

Z - Pressure Plot for CASE 6 at 171 oF

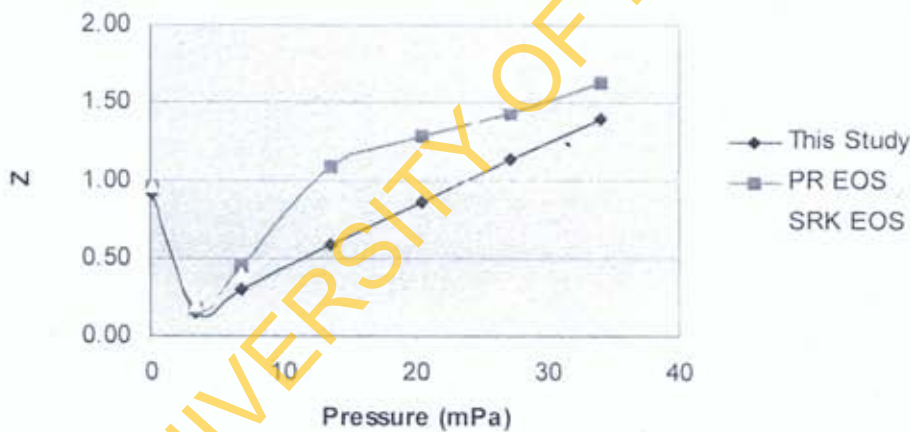


Figure 11: Z - Pressure Plot for Case 6 at Reservoir Temperature

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