

A SIMPLE GENERALIZED EQUATION OF STATE

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Abstract

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 generalized equation of state. The practical equation formulated was applied to pure fluids, binary systems and real samples of Niger Delta Petroleum fluids. Tuning of data is not required. The results show more accurate predictions than the commonly used SRK and PR equations. This work provides a theoretical framework for improving the accuracy of cubic equations of state. One major advantage of the generalized equation expressed in this work is the fact that it provides a theoretical framework for explaining the physical significance of the parameters in multi-parameter equations of state. Thus, in a three-parameter equation of state, while 'a' captures the attractive forces, 'b' is the co-volume, 'c' could represent non-physical forces. This is different from the concept of 'c' in such equations as Peng-Robinson EOS where 'c' obviously represents an "after-the-fact" volume correction term.

Introduction

Although cubic equations yield good results for a variety of systems, they are still regarded by many as mere correlations of fluid properties because of the belief that they lack sound theoretical foundations and are not as accurate as non cubic equations⁽¹⁾. Many researchers have therefore directed efforts in recent times, at developing equations of state that have sound theoretical foundations.

Wertheim's first order perturbation theory⁽²⁻³⁾, has been widely employed in recent times, to develop highly accurate, Statistical Associating Fluid Theory (SAFT) equations of state for associating pure fluids and mixtures⁽⁴⁻⁷⁾. The SAFT equations of state are believed to have sound theoretical foundation because they describe fluid molecules as covalently bonded chain segments whose Helmholtz energy can be represented by expressions for repulsive, dispersion, association and/or solvation forces. However, SAFT equations are still generally more complex than cubic equations when applied to fluid mixtures. Significant improvement in the accuracy of equations of state may be achieved by using pressure perturbation, while simplicity may be achieved by using reasonable approximation to obtain a practical, cubic equation.

THEORETICAL FRAMEWORK

A pressure function P, may be described by a relation of the form:

$$P = f(\rho, T, n) \quad (1)$$

Or, in general for a pure fluid where composition effect is neglected, by expanding in a general polynomial form, we have:

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

Where,

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

Equation (2) can be expressed as:

$$P = \sum_{i=1}^J \frac{a_i(T)}{V^i} + \sum_{i=1}^J \frac{a_{i2}(T,V)}{V^i} + \sum_{i=1}^J \frac{a_i(V)}{T^i} \quad \dots(3)$$

Equation (3) is a generalized expression similar to the "generalized" cubic equation of state (equation 4) developed by Martin⁽⁸⁾ for pure fluids:

$$P = \sum_{i=1}^J \frac{qi(T)}{V^i} \quad \dots (4)$$

Equations (2) and (3) can be simply interpreted conceptually in common parlance as:

$$P = P_R + P_A + P_{NP} \quad \dots(5)$$

Where,

$$P_R + P_A = P_{\text{physical forces}} \quad \dots(6)$$

SIMPLIFICATION AND APPLICATION

Each of the pressure terms in equations (2) and (3) can be evaluated using Taylors series expansion and simple algebraic manipulation to obtain:

$$P_R = \frac{RT}{V(1-\eta)^r} \quad \dots (7)$$

and,

$$P_A = \frac{-a_1 a_2(T)}{V^2(1-\zeta)^r} \quad \dots (8)$$

and similarly,

$$P_{NP} = \left(\frac{a_1 a_2}{V}\right) [e^{a_1/V} - 1] \quad \dots(9)$$

Where, r is a positive integer. Optimizing equations (7) and (8) and comparing with the Virial equation of state suggests r = 4, as first proposed by Guggenheim⁽¹⁾.

Equation (9) can further be simplified as:

$$P_{NP} = \frac{c(T)}{V} \quad \dots (10)$$

Where, using a familiar convention,

$$c(T) = c^* \gamma(T) \quad \dots(11a)$$

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

β is an empirical constant.

In this study, a simple optimization approach was used to establish β and to evaluate equation (11b) as:

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

Therefore, substituting equations (7) to (10) into equations (2) and (3) gives:

$$P = \frac{RT}{V(1-\eta)^r} - \frac{a(T)}{V^2(1-\zeta)^r} - \frac{c(T)}{V} \dots(12)$$

Equation (12) is a generalized van-der Waals type equation of state obtained. However, it is rather complex and strictly non-cubic in V . However, it can be further simplified to yield a simple, practical cubic equation. By setting $r=1$, and using appropriate values of η and ζ in equation (12), a number of common equations of state like the Peng-Robinson and Soave-Redlich-Kwong equations can be generated.

RESULTS AND DISCUSSION

From the generalized expressions in equations (2), (3) and (12), it is clear that most van der Waals-type equations of state incorporate only the 'physical' repulsive and attractive forces. They do not incorporate the contributions to pressure, of other 'non-physical' effects such as quantum effects and chemical forces. In other words, using pressure perturbation principle, a truly generalized equation of state should account for all possible contributions to pressure beyond the commonly recognized repulsive and attractive forces.

One major advantage of the generalized equation of state derived from pressure perturbation principle 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' is the co-volume, 'c' in the form it appears in the equation represents a parameter that captures non-physical forces. This is different from the concept of 'c' in many three-parameter equations of state where 'c' represents an "after-the-fact" volume correction term.

Furthermore, comparing equations (12) and (13) suggests that van der Waals-type equations of state could possibly be related to equations of state derived from statistical thermodynamics such the SAFT equations of state expressed as:

$$\frac{A}{NkT} = \frac{A^{scc}}{NkT} + \frac{A^{chem}}{NkT} + \frac{A^{assoc}}{NkT} \dots(13)$$

Or,

$$\frac{A}{NkT} = \frac{A^{ideal}}{NkT} + \frac{A^{mix}}{NkT} + \frac{A^{chem}}{NkT} + \frac{A^{assoc}}{NkT} \quad (14)$$

However, unlike thermodynamic perturbation, pressure perturbation is easy to apply to fluid mixtures since there is no need to employ different mixing rules for each of the terms

Equation (12) was first validated by applying it to pure hydrocarbons under various conditions of temperature and pressure. Two of the results are as shown in Figures 1 and 2. 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 and Pentane, the results are closer to the Peng-Robinson estimates. Figures 3 and 4 show the predicted Z-factors for n-Butane–CO₂ system. The generated results 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 3 samples are presented in Figures 5 -10. The three samples presented here have properties that vary from volatile to heavy as shown in Table 1. The results as shown in Figures 5-10 indicate that this model performs very well when compared with SRK and PR equations, 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. Obviously, better match could be achieved by making the value of β in equation (11) substance dependent.

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 could have sound theoretical foundations than previously thought. A truly theoretically sound, generalized and accurate equation must include the effects of several other forces in addition to the conventional van der Waals repulsive and attractive forces. However, such equations could become rather complex and would require further simplification through some assumptions to generate simple, practical approximate equations of state.

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

α	- coefficient of attractive term
β	- empirical constant
ζ	- equation of state parameter
γ	- coefficient of EOS attractive term
γ_0	- specific gravity
ρ	- molar density
η	- dimensional volume = $b/4v$
ω	- Pitzer acentric factor

Subscripts

A	- attractive forces
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φ	- 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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Table 1: Composition and PVT Data for Three Niger Delta Case Studies

PARAMETER	CASE 1	CASE 2	CASE 3
C1	53.51	55.38	39.20
C2	4.66	9.95	2.27
C3	1.95	7.12	0.07
IC4	1.89	1.71	0.31
NC4	2.61	2.52	0.02
IC5	1.09	1.13	0.10
NC5	1.13	1.01	0.05
C6	1.61	1.34	0.29
C7+	31.34	19.31	55.80
CO2	0.21	0.29	1.75
N2	0.00	0.24	0.14
FLUID MW	95.68	55.18	175.68
GOR (scf/stb)	232	2242.5	288
Oil Visc (cp)	3.73	0.94	9.58
Pb (psia)	1460	4229	996
Res Press(psia)	3317	2497	2635
Res. Temp (R)	616	600	605
Crude Type	Medium	Volatile	Heavy

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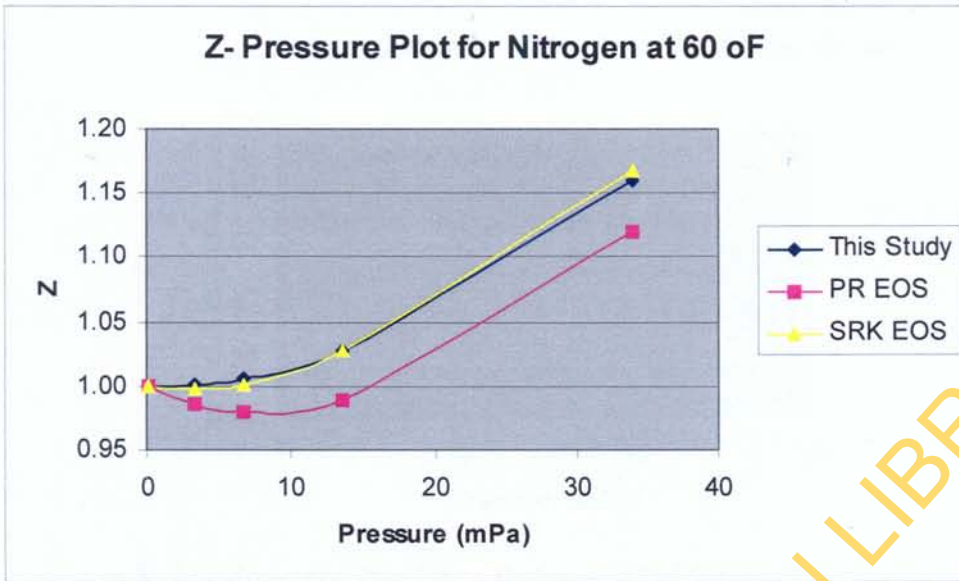


Figure 1: Pressure - Z Plot for Nitrogen at 60 oF

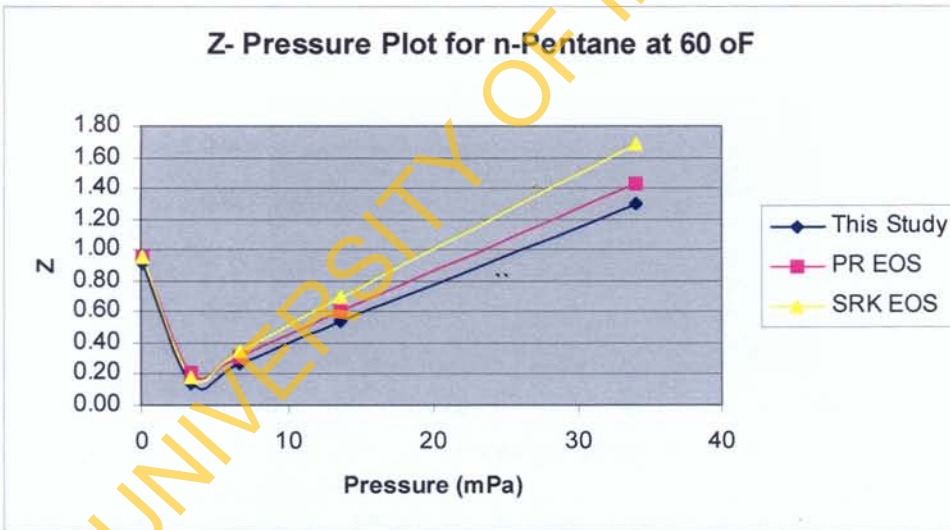


Figure 2: Z- Pressure Plot for n-Pentane at 60 oF

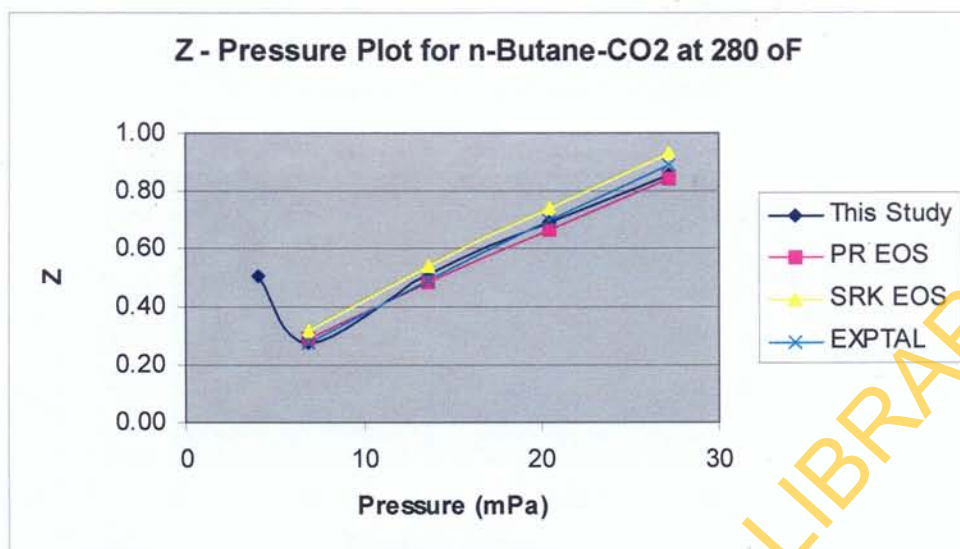


Figure 3: Z - Pressure Plot for n-Butane-CO2 System (% mole of CO2 = 10%)

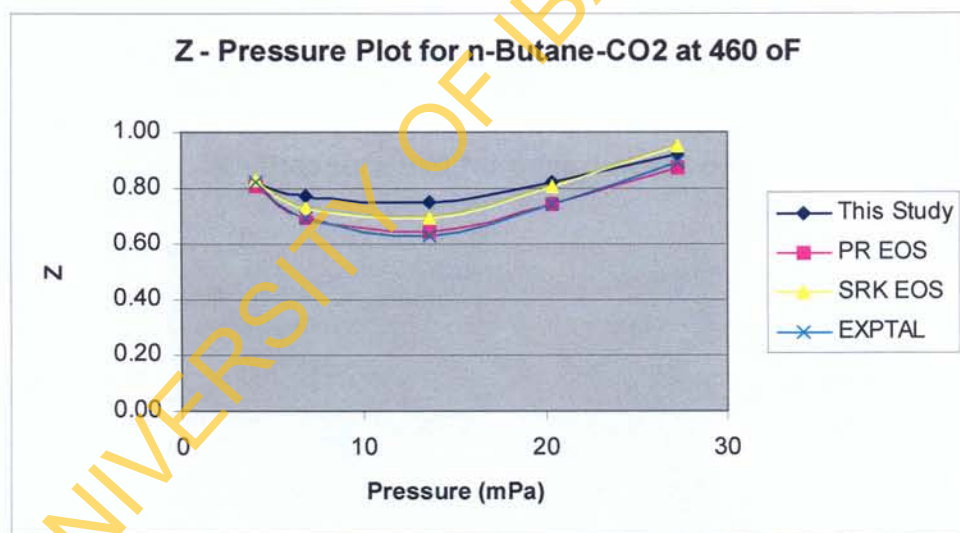


Figure 4: Z - Pressure Plot for n-Butane-CO2 System (% mole of CO2 = 90%)

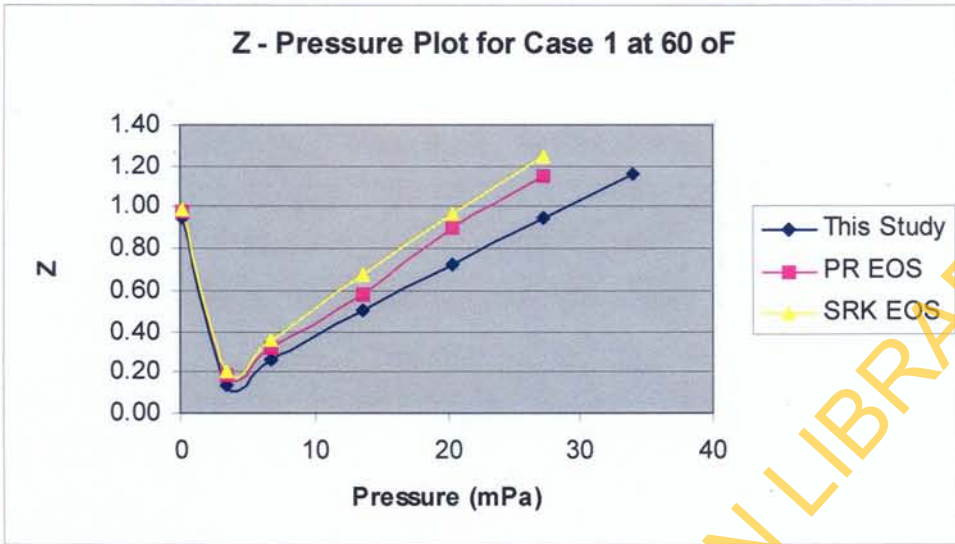


Figure 5: Z – Pressure Plot for Case 1 at Surface Conditions

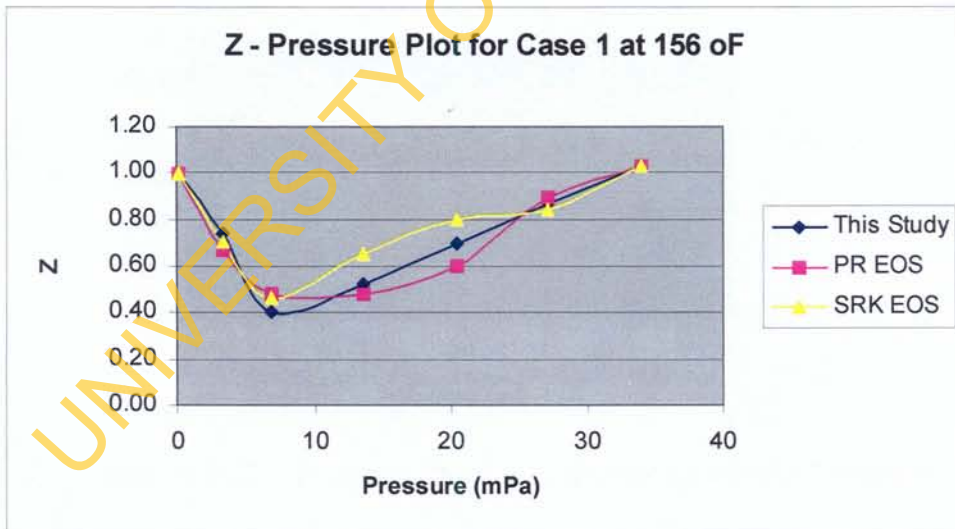


Figure 6: Z – Pressure Plot for Case 1 at Reservoir Temperature

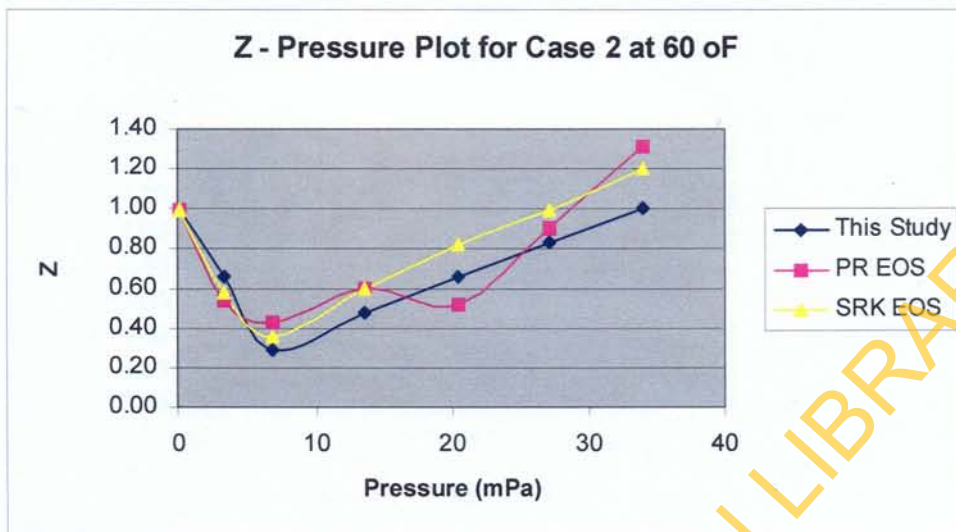


Figure 7: Z – Pressure Plot for Case 2 at Ambient Temperature

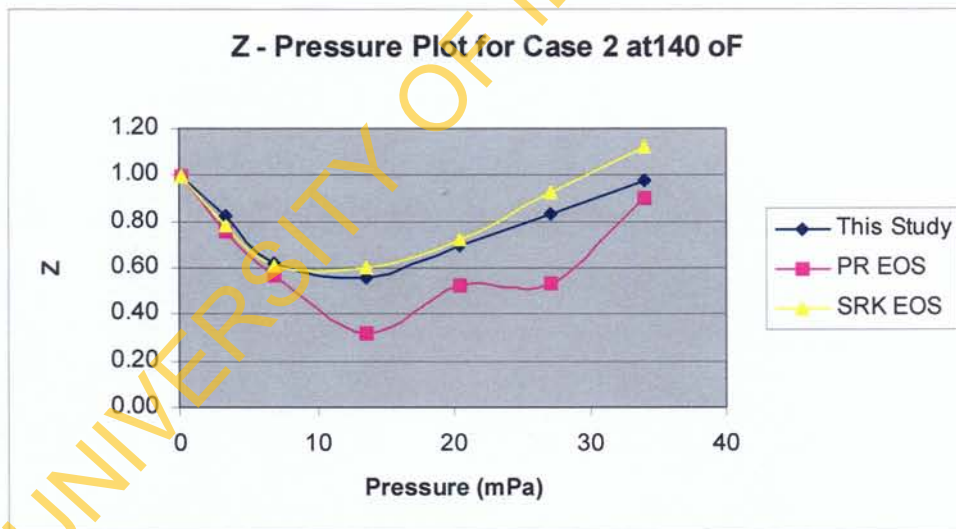


Figure 8: Z – Pressure Plot for Case 2 at Reservoir Temperature

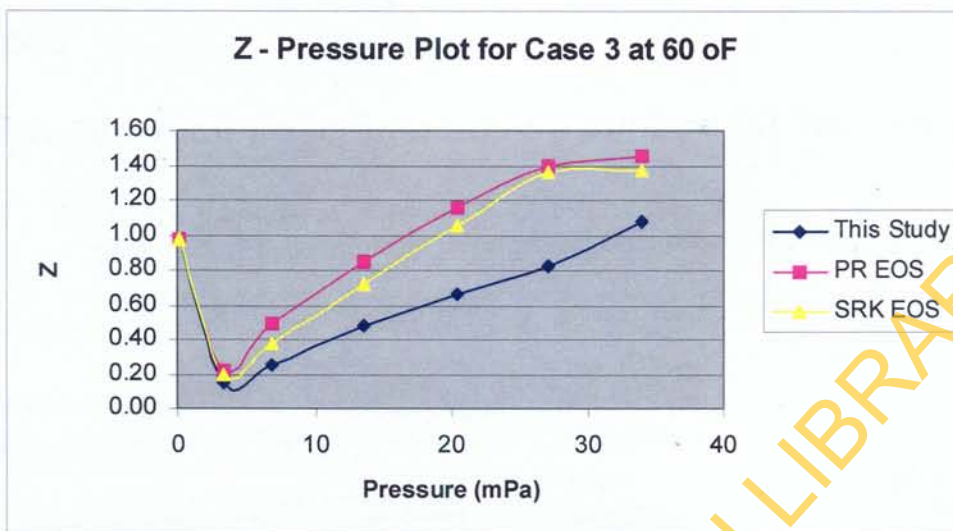


Figure 9: Z - Pressure Plot for Case 3 at Surface Temperature

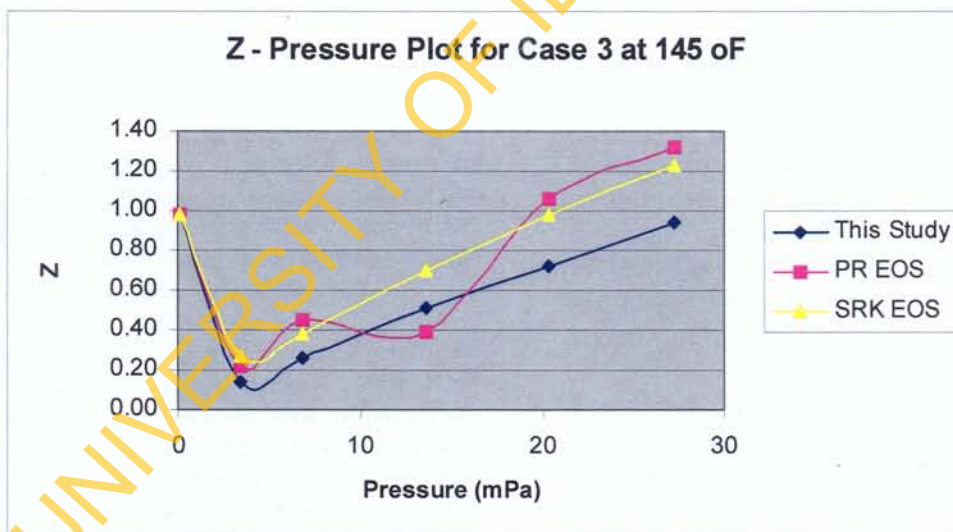


Figure 10: Z - Pressure Plot for Case 3 at Reservoir Temperature