A New Cubic Equation of State for Improved Liquid Density Prediction

Christiana NP[1]*, Adewumi MA[2] and Ityokumbul MT[3]

[1]Department of Petroleum Engineering, University of Ibadan, Ibadan, Nigeria

[2]University Office of Global Programs, The Pennsylvania State University, University Park, US

[3]Department of Energy and Mineral Engineering, The Pennsylvania State University, University Park, USA

*Corresponding author: Nwankwo, Princess Christiana, Department of Petroleum Engineering, University of Ibadan, Ibadan. Nigeria, Tel: 2348025887320; Email: bigcycy@yahoo.co.uk

Abstract

Hydrocarbon fluid phase behaviours have numerous implications in natural gas and petroleum engineering and are often predictable from equations of state (EOSs). Equations of state methods are far less expensive (in terms of material cost and time) than laboratory or experimental forages and the results are interestingly within acceptable limits of accuracy. Several cubic EOSS have been presented in literature, most of Fluid PVT and phase behavior properties to good degrees of accuracy. However, most fail in predicting liquid phase densities accurately enough. A new three parameter cubic EOS was developed based on a modification of the van der Waals (vdW) attraction term contribution to pressure. The success of the new EOS was derived from recognizing that the attraction term of previous EOSs has been inadequate in capturing the dense fluid properties especially liquid densities and PVT properties at or near the critical region. The primary goal was to minimize the gap between experimentally derived-, and equation of state (EOS)- calculated PVT or fluid phase behavior data especially, liquid densities, for pure components and mixtures.

Volumetric and phase equilibria calculations were carried out with the new EOS for pure components, binary ternary and multicomponent mixtures and results compared to experimental data (available in literature) and results obtained from industry-popular cubic EOSs, in particular, the two parameter, Peng-Robinson's (PR) and the three parameter Patel-Teja's (PT) EOs. The results indicate that the new EOS predicts the liquid densities of pure hydrocarbon components and mixtures more accurately than the Peng Robinson's (PR) and Patel-Teja's (PT) EOS. The new EOS predicted liquid phase densities of pure components and mixtures with a grand average percent absolute deviation (AAPD) of 1.60% as opposed to 3.01% and 11.17% for PT and PR EOSs respectively.

Keywords: Equation of state; Liquid density; Mixture properties; phase behavior; Pure hydrocarbon systems; Gas condensate systems

Introduction

By way of definition, an equation of state (EOS) is a thermodynamic equation describing the state of matter under a given set of physical conditions. It is a constitutive equation which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or internal energy. Cubic equations of state are a class of equations of state that may be represented by a polynomial when referencing the volume or compressibility factor, in such a way that the highest power in the polynomial is to the third degree.

The states of matter of interest for which natural gas and gas condensates are handled in the industry involve only two (vapour and liquid) phases for which a cubic equation is suitable. Cubic equations of state (EOS) when solved for molar volumes (or compressibility factor) give three values; the highest value corresponds to the vapour phase property, the lowest value corresponds to the liquid phase property while the intermediate value has no known significance. The roots of cubic equations of state can be obtained analytically without the need for an iterative solution procedure, which simplifies the solution method. The popularity of cubic EOSs is further enhanced by their structural simplicity, requirement of only a few parameters for implementation and little computer resources, thus assuring low computational overhead, while providing good phase equilibrium correlations and saturated phase volumes and densities of acceptable accuracy.

Literature Review

The simplest known equation of state is the perfect gas law, which is used for thermodynamic calculations for ideal gases, also called perfect gases. The perfect or also called, ideal gas is the simplest kind of gas and is in fact, an idealization of real gases as no gas is truly ideal. Most of the early works with gases were carried out at conditions near standard conditions of temperature and pressure; that is $T = 60^o F = 520^o R = 288.72K$ and $P = 14.7\ psia = 101.325\ KPa$. At these conditions, gas behavior approaches the behavior of the hypothetical ideal gas. The analytical expression of the PVT behavior of the hypothetical perfect gas behavior is written as:

$$PV=RT \qquad (1.0)$$

Where, V is the molar volume of the container containing the fluid, P is the pressure of the fluid, T is the absolute temperature and R is the universal gas constant evaluated

from R= PV/nT. The value of R depends on the units in which the parameters P, V, and T are evaluated. For example, at standard conditions of 14.7psia and 60°F (i.e. 520 °R), $R = 10.73159 \frac{ft^3\ psi}{mol\ ^oR}$.

At low pressures ($\leq 400\ psia$) and moderately high temperatures (low densities), most real gases exhibit an almost ideal behavior, such that the volume varies directly with the absolute temperature and inversely with the pressure. Therefore, the ideal gas law would be able to approximately predict its PVT behavior. The closer, however, a gas is to a phase change, or when at high pressures (above about 400 psia) and at moderate temperatures; the more significant the deviation from ideal gas behavior. Also, the ideal gas law fails to predict condensation from a gas to a liquid.

The deviation of real gases from ideal behaviour is captured by introducing a factor called the gas deviation factor, or gas compressibility factor or z factor since it is denoted by the letter, z. The resulting real gas equation is:

$$PV=zRT \qquad (1.1)$$

By definition, z-factor is the ratio of the actual volume occupied by a mass of gas at some pressure and temperature to the volume the gas would occupy if it behaved ideally. The compressibility factor of an ideal gas is 1.0, i. e. for an ideal gas, z=1.0. In real applications, deviations from ideal behavior can be as large as 30% and such deviations must be corrected to improve accuracy. The value of the correction factor Z generally increases with pressure and decreases with temperature. At high pressures molecules are colliding more often. This allows repulsive forces between molecules to have a noticeable effect, making the molar volume of the real gas $(V_m)_{real\ gas}$ greater than the molar volume of the corresponding ideal gas $(V_m)_{ideal\ gas}$, which causes Z to exceed one.[56] When pressures are lower, the molecules are free to move. In this case attractive forces dominate, making Z<1.0. The closer the gas is to its critical or boiling points, the more Z deviates from the ideal case. If the gas deviation factor is accurately determined, the actual gas law can give tolerable estimates of gas thermodynamic behavior, but like the perfect gas law, it too, fails to predict the condensation of liquid from gas. This was one of the motivating factors in early equations of state research.
The earliest attempt to correct for the departure of real gases from ideal gas behavior and extend the use of the ideal gas equation of state (EOS) to account for vapor-liquid co-existence was made by Johannes Diderick van der Waals in 1873, with his work on "the equation of state

for gases and liquids" which won a Nobel prize in 1910. Van der Waal's (vdW) EOS is written as

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \qquad (1.2)$$

Where, the parameters, a is the "specific attraction" and b is the "hard sphere volume" or co-volume, so that molar volume cannot be smaller than b.Equation (1.2) is based on the fact that the pressure on the walls of a container on which gas molecules collide is decreased because of attraction by the molecules in the bulk gas and the volume in which the molecules move is less than the total volume by the excluded volume, b, due to the size of the molecules themselves. Therefore, the constants a and b have positive values and are characteristic of the individual gas. The vdW's EOS expressed in pressure-explicit form, as in Eq. (1.2), has the repulsive term as $\frac{RT}{(V-b)}$ and the attractive term as $\frac{a}{V^2}$ thus indicating that pressure can be regarded as the sum of two terms: a hard sphere term and an attraction term that is [1]

$$P = P^{repulsion} + P^{attraction} \qquad (1.3)$$

Which by implication, implies that compressibility factor can be expressed as?

$$Z = Z^{repulsion} + Z^{attraction} \qquad (1.4)$$

The phase diagrams using the vdW EOS to model hydrocarbon fluid behavior reveals that, at temperatures equal to or greater than the critical temperature (T_c), only single roots exist. However, at temperatures below T_c, three roots exist. The smallest root represents liquid-like volume, the intermediate root has no known significance and the largest root represents the vapour-like volume.

The vdW EOS has limitations which include the facts that it provides inaccurate vapour pressure predictions because the attraction term parameter, a, is not optimized to fit vapour pressure. Also, it provides inaccurate critical point predictions. The critical compressibility factor, z_c from the vdW EOS has a fixed value of $z_c = \frac{P_c V_c}{RT_c} = 0.375$.

This value is quite greater than that obtained for real hydrocarbon fluids (0.24 to 0.29). The vdW's EOS however, has significant historical relevance since it provides the basic foundation over which most other researchers have built their framework by either modifying the attractive term or repulsive term of the original van der Waals Equation or both.

Redlich and Kwong's (RK) EOS made the first significant improvement on the vdW's EOS [2]. By modifying the volume dependence on the attraction parameter, a slightly improved critical compressibility factor value of z_c=0.3333 was obtained. However, the predictions on vapour pressure and liquid density values were still inaccurate. The RK EOS has the form

$$P = \frac{RT}{(V-b)} - \frac{a}{T^{1/2}V(V+b)}$$

To further improve prediction performance of EOSs, Wilson in 1964 introduced temperature dependency of the a parameter. Wilson's EOS has the form: $P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)}$

Where, $a(T) = a_c \alpha(T)$, $\alpha = T_r \left[1 + (1.57 + 1.62\omega)\left(\frac{1}{T_r} - 1\right)\right]$ and ω is the acentric factor, introduced by Pfizer and defined as
$\omega = -1.0 - log\left(P_r^{sat}\right)(at\ T_r = 0.7)$.

Soave provided a more refined temperature dependency of the parameter of the original RK EOS [3]. The resulting effort, called, Soave-Redlich-Kwong (SRK) EOS improved results of vapour-pressure calculations. The SRK EOS has the same structural form as the RK EOS, however, the a parameter is defined as;

$a(T) = a_c \alpha(T)$, $\alpha(T) = \left[1 + m\left(1 - \sqrt{T/T_c}\right)\right]^2$ and $m = 0.48509 + 1.55171\omega - 0.15613\omega^2$.

Peng and Robinson proposed additional modifications to more accurately predict the vapor pressure, liquid density, and equilibria ratios [4]. Peng and Robinson's (PR) EOS has the form: $P = \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b)+b(V-b)}$.

Patel and Teja presented a three parameter EOS called Patel-Teja (PT) EOS in 1982, which further improved prediction of phase equilibria and volumetric properties [5]. The EOS has the form:

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

Equations of state based on modifications of the attraction term of the original vdW's EOS, such as those described above and several others in literature are called van der Waal's family of EOSs and usually can be shown to be cubic polynomials when expressed in terms of molar

volume or compressibility factors. They are therefore categorized as cubic EOSs.

Cubic EOSs have been known to predict fluid phase equilibria data with appreciable accuracy though their ability to predict volumetric data, especially liquid densities has remained poor. To assure high accuracy, researchers sometimes have to use two or more equations to calculate densities and phase equillibria separately. Thieryet used the Soave-Redlich-kwong cubic equation (SRK) (1972) to model phase equilibria and a virial type equation to calculate equilibrium volumes [6-8]. This approach has the obvious disadvantage of inconsistency of various fluid parameters as first pointed out by Bakker and Diamond [9].

Some authors (Carnahan and Starling, Guggenheim, and Boublik) have also modified the repulsion term of vdW's EOS to obtain more accurate expressions for hard body repulsion [10-12]. Other researchers like Chen and Kreglewski, Christoforakos and Franck, Heilig and Franck modified both the attractive and repulsive terms of the van der Waals Equation of state to obtain improved thermodynamic property estimations for hard convex geometries [13-14].

Summaries of some popular equations of state based on repulsion term modifications are shown in Tables 1 below:

Repulsive Term	Reference
$(1 + \eta + \eta^2)/(1 - \eta)^3$	Reiss [15]
$1/(1 - \eta)^4$	Guggenheim [11]
$(1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3$	Carnahan-Starling [10]
$(RT(V + b))/V(V - b)$	Scott [16]
$[1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha^2\eta^3]/(1 - \eta)^3$	Boublik, 1981 [12]

Table 1: Modifications of vdW Repulsive Term.

Where $\eta = \frac{b}{4V} = packing\ fraction$; $b = covolume\ of\ vdW$.

Other forms of equations of state exist besides those based on modifications of vdW's EOS and based on formulation and functionality can be categorized as virial or complex. A tree of EOS relationships based on intermolecular interactions is shown in Figure 1 below:
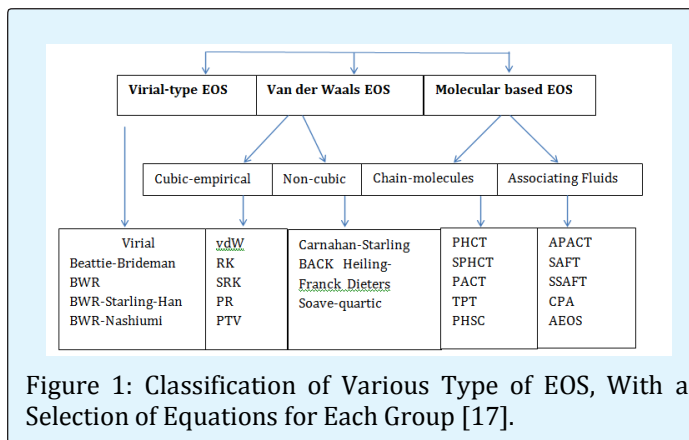

Figure 1: Classification of Various Type of EOS, With a Selection of Equations for Each Group [17].

Methodology

Development and Formulation Considerations for New EOS

Formulation considerations were based mainly on the fact that two parameter EOSs cannot be considered since they give a fixed value for the calculated critical compressibility factor, ζ_c, which hardly agrees with the experimental compressibility factor values, Z_c [18]. For example, whereas actual experimental values for pure hydrocarbon compounds vary from 0.23 to 0.29, $\zeta_c=1/3$, for Redlich-Kwong EOS and ζ_c =0.307401 for Peng-Robinson's EOS. Three parameter equations of state however, exhibit variable values of ζ_c over a temperature range, so they are more flexible in force fitting operation on experimental volumetric data.

Other formulation considerations were based on the findings of Aadachi and Zhi suggest improvements in the attractive term are influenced by the number of terms present when the EOS is expressed in terms of a ?(V) function and the relationship between the numerators of the various terms [19].

The $\pi(V)$ function is derived by first noting that all vdW type EOSs can be represented in the form:

$$P = \frac{RT}{V-b} - \frac{a_w}{\pi(V)} \qquad (1.4)$$

Where b and a, are constants with their usual meanings and subscript w means 'associated with the vdW EOS.' This was derived by noting that the van der Waals EOS can be written in the form:

$$P = \frac{RT}{V-b} - \frac{a_w}{V^2} \qquad (1.5)$$

The first improvement over the vdW's EOS to be reckoned with was by Redlich and kwong which though written as:

$$P = \frac{RT}{V-b} - \frac{a(\sqrt{T})^{-1}}{V(V+b)} \qquad (1.6)$$

can be expressed in $\pi(V)$ function as:

$$P = \frac{RT}{V-b} - \frac{a_{RKS}}{V(V+b)} \qquad (1.7)$$

Where a_{RKS} is dependent on temperature.

Assuming that a_w is not a constant, and making Equation (1.7) equal to Equation (1.5), i.e.

$$\frac{a_w}{V^2} = \frac{a_{RKS}}{V(V+b)} \qquad (1.8)$$

Then, after rearranging, the a_w can be calculated as

$$a_w = \frac{a_{RKS}}{1+b/V} = \frac{a_{RKS}}{\pi_{RKS}(V)} \qquad (1.9)$$

Where $\pi(V)$ is a new function which expresses the influence of volume on the attractive parameter, a_w. The $\pi(V)$ function which in general, has the form:

$$\pi(V) = 1 + \frac{k}{V} + \frac{l}{V^2} + \cdots \qquad (1.10)$$

is a major determinant of EOS accuracy. The more the numbers of terms present in the $\pi(V)$ function, the better the accuracy of the corresponding EOS. For the PR and PT EOSs,

Peng Robinson's EOS is: $\quad P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$
$$(1.11)$$

Patel-Teja EOS is : $\quad P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+c(V-b)}$
$$(1.12)$$

The $\pi(V)$ functions are respectively:

$$\pi_{PR}(V) = 1 + \frac{2b}{V} - \frac{b^2}{V^2} \qquad (1.13)$$

$$\pi_{PT}(V) = 1 + \frac{(b+c)}{V} - \frac{cb}{V^2} \qquad (1.14)$$

When compared to the $\pi(V)$ form of the PR EOS, the $\pi(V)$ form of the PT EOS is more elastic, powerful and so more competent for the regression of data. By this hypothesis, the PT EOS should give better accuracy when compared to the accuracies of the PR EOS. Also, the relations between the parameter k, l,... in Eq.(1.10) also influence the capability of an EOS in predicting vapor-liquid thermodynamic properties. The stronger the

relation between k and l, the poorer the predictive ability of the EOS and vice versa. For example, the relation between the parameters k and l in $\pi_{PR}(V)$ is very strong which therefore, limits the capabilities of PR EOS, while the parameters k and l in $\pi_{PT}(V)$ is relatively weak, guaranteeing better performance in the calculation of various properties of fluids.

The new equation that guarantees better performance based on above theory is of the form:

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T)}{V(V+b)+c(V-b)+c(c-b)} \qquad (1.15)$$

or also expressed as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2+(b+c)V-(2bc-c^2)} \qquad (1.16)$$

The proposed EOS was extended to VLE calculations of binary and multi-component mixtures by using the well-known conventional mixing rules with the binary interaction parameter K_{ij}, as an adjustable parameter [20].

$$a = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j a_{ij}, \qquad (1.17)$$

$$b = \sum_{i=1}^{n_c} x_i b_i, \qquad (1.18)$$

$$c = \sum_{i=1}^{n_c} x_i c_i, \qquad (1.19)$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}}(1 - K_{ij}). \qquad (1.20)$$

The $\pi(V)$ function is: $\pi_{NEW}(V) = 1 + \frac{(b+c)}{V} - \frac{(2bc-c^2)}{V^2}$
$$(1.21)$$

The NEW EOS expressed in terms of compressibility factor is:

$Z^3 + (C-1)Z^2 + (A - B - C - 3BC - B^2 + C^2)Z + (2BC + 2B^2C - BC^2 - C^2 - AB) = 0$ Where, $A = \frac{aP}{(RT)^2}$, $B = \frac{bP}{RT}$ and $C = \frac{cP}{RT}$.
$$(1.22)$$

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