Predictions of fugacity coefficients of pure substances from equations of state

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Abstract. This aim of this paper is to predict fugacity coefficients from newly developed equations of state. The fugacity coefficients have been calculated for Methane and Carbon di-oxide from equations of state of Soave Redliche Kwong (SRK), Peng Robinson (PR) and Twu Sim Tassone (TST) taking reduced temperatures, $T_r$ of interest from each of the three ranges $0<T_r<1$, $1<T_r<3$ and $1<T_r<5.5$ together with the reduced pressures, $P_r$ in steps of 0.2 in the range $0<P_r<10$. The calculated results of fugacity coefficients were compared with the available fugacity coefficient data for Beattie-Bridgeman (BB) equation. The calculations suggest that the TST equation of state is most suitable in predicting the fugacity coefficient of pure substances.

Keywords: Cubic Equations of State, Compressibility Factor, Fugacity Coefficients, Beattie-Bridgeman (BB) equation

1. Introduction

In the petroleum engineering applications, the cubic equations of state are widely used because of its simplicity, solvability, accuracy and generalization [1-10]. Some cubic equations and their modifications have been proposed by many investigators. A simple equation of state such as van der Waals, cannot accurately model the dense or complex fluids mixtures. After formulation of vdw EOS (1973) numerous modifications have been made to improve its ability by modifying the repulsive and attractive terms. In all van der Waals type equation of state, we recognize a repulsion term that takes into account the volume of the molecules using parameter $b$, or covolumes, and secondly an attraction term, or internal pressure that is dependent on the parameter $a$. The unlikely hypothesis of van der Waals was that the repulsive term, expressed by a constant $b$ is more effective in predicting the fluid properties than the attractive term. But, modified attractive term $a$ for all the van der Waals type equation of state is found to be more promising in the theory of equations of state. The values for these parameters are determined by applying critical constraints. The equations of state is satisfied at the critical point as:

$$\left(\frac{\partial P}{\partial V}\right)_{T} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T} = 0, \text{ for } T = T_c \text{ and } P = P_c.$$  

1.1 Equations of state:

A unified form for most commonly used two parameter cubic equations of state with modified representation of attractive term is:

$$P = \frac{RT}{V - b} - \frac{a = a(T_c)}{V^2 + \Omega_2 b V + \Omega_3 b^2}$$

where $\Omega_1$ and $\Omega_2$ are two integer values specific for each cubic equation and are given in Table.1. The numerical values for the dimensional parameters $\Omega_1$ and $\Omega_2$, and the critical compressibility
The actual values of the critical compressibility factor are, however, between 0.26 and 0.28 for popular hydrocarbons. It is noted that the values of $z_c$ from the Soave-Redlich-Kwong [8, 9] and Peng-Robinson [10] models are both larger than 0.3 (0.333333 and 0.307401, respectively), but that for TST is slightly below 0.3 (0.297), which is closer to the typical value of critical compressibility factor for most compounds [1, 2]. The EOSs which are tabulated in Table 1 are more useful because they provide an analytical solution for the density.

### Table 1. Constants in equation (1) for cubic equations of state [6]:

|    | $\Omega_1$ | $\Omega_2$ | $a_c$ | $\alpha$ | $b$ | $z_c$ |
|----|-------------|-------------|-------|--------|-----|-------|
| VdW [7] | 0 | 0 | $\frac{27 R^2 T_c^2}{64 P_c}$ | 1 | $\frac{RT_c}{8P_c}$ | 0.375 |
| RK [8] | 1 | 0 | $\frac{0.42748 R^2 T_c^2}{P_c}$ | $T_r^{-1/2}$ | $0.08664 RT_c$ | 0.333 |
| SRK [9] | 1 | 0 | $\frac{0.42748 R^2 T_c^2}{P_c}$ | $f_w \left[1 - \frac{T_r^{1/2}}{1 - T_r^{1/2}}\right]^2$ | $0.08664 RT_c$ | 0.333 |
| PR [10] | 2 | -1 | $\frac{0.4572 R^2 T_c^2}{P_c}$ | $f_w \left[1 - \frac{T_r^{1/2}}{1 - T_r^{1/2}}\right]^2$ | $0.07780 RT_c$ | 0.307 |
| TST [1, 2] | 0.5 | 3 | $\frac{0.470507 R^2 T_c^2}{P_c}$ | $T_r^{N(M-1)} L \left[1 - T_r^{NM}\right]$ | $0.0740740 RT_c$ | 0.296 |
| LM [11] | 2 | : | $\frac{0.4572355 R^2 T_c^2}{P_c}$ | $T_r = \frac{T_c}{T_r - 1}$ | $0.077960 RT_c$ | 0.307 |

For $T_r < 1.0$;  

$T^* = \frac{T_c/T_b - 1}{T_c/T_b - 1}$

For $T_r > 1.0$;  

$T^* = \frac{T/T_c - 1}{T_c/T_b - 1}$

$p, q, L, M$ and $N$ are substance dependent constants [1, 6].

The parameter $a$ is a function of temperature. The value of $a$ at any temperature $\alpha(T_r)$ can be calculated from $a(T) = \alpha(T_r) a_c$, where the alpha, $\alpha(T_r)$, is a function only of reduced temperature, $T_r = T / T_c$. We use the Twu alpha function [1, 2] which is given in Table 1 has three parameters, $L, M$ and $N$. These parameters are unique to each component and can be determined from the regression of pure component vapor pressure data. Table 2 lists the $L, M$ and $N$ parameters for
CH₄, CO₂, N₂, H₂S and H₂O. In this work we have only interest on the pure substance CH₄ and CO₂.

1.2 The Beattie-Bridgeman (BB) equation:

The graphical and the analytical methods are the main tools for the calculation of fugacities. In both the methods the knowledge of P-V-T data is necessary. The condition of employing analytical method is that the P-V-T data must be fitted to an analytical expression for the equation of state so that it can be integrated. It is found that the Beattie-Bridgeman equation [3, 4, 5] is of such a form and with the proper constants closely represents the P-V-T data for many gases over a wide range of temperatures and pressures.

It is written as:

\[ PV^2 = RT \left( 1 - \frac{c}{VT^5} \right) \left( V + B_0 \frac{bB_0}{V} \right) - A_0 \left( 1 - \frac{a}{V} \right) \]  

(2)

where \( A_0, B_0, a, b, \) and \( c \) are empirical constants to be determined experimentally for a particular gas and \( P, V, R, \) and \( T \) have their usual meanings. Values of the constants of the Beattie-Bridgeman equation of state for CH₄: \( A_0 = 2.2769 \), \( a = 0.01885 \), \( b = -0.01587 \), \( c = 12.83 \times 10^4 \) and for CO₂: \( A_0 = 5.0065 \), \( a = 0.07132 \), \( b = 0.07235 \), \( c = 66 \times 10^4 \), respectively [3, 4, 5]. Equation (1) can be rearranged in a quadratic form in \( V \) which can be further solved for one real positive root must found close to the experimental value. In this EOS, the fugacity, \( f \), can be determined by the expression:

\[ \ln \left( \frac{f}{P} \right) = -\frac{1}{RT} \int_0^P \alpha dP, \]

where, \( \alpha = \frac{RT}{P} - V \). The equations used for calculating the fugacity coefficients, \( \phi = f / P \) are given in Table 2. The paper is organized in such a way that the second section represents the theory for calculating the fugacity coefficients for pure substances and the third section explains the results and discussion and finally the conclusions.

2. Theory

In statistical mechanical theory, the fugacity defines the grand canonical ensemble (a system that may exchange particles with the environment). G.N. Lewis (1923), the American chemist, introduced Gibbs energy using an auxiliary property fugacity. Its logarithm, multiplied by \( k_B \), is the chemical potential, \( \mu = k_B T \log f \) where, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. In other words, fugacity, \( f = \exp \left( \frac{\mu}{k_B T} \right) \). Actually, fugacity coefficient is relatively abstract value and is used in place of fugacity for pure substance. For Gibbs energy, fugacity plays the same role for a real fluid as pressure plays for ideal gas. This means that when a system approaches the ideal gaseous state

\[ \frac{f}{P} \rightarrow 1 \quad \text{if} \quad P \rightarrow 0 \]  

(3)
Thus fugacity is equal to effective pressure which is useful in order to preserve the expressions for ideal gas when it is substituted for pressure.

2.1 Fugacity coefficients using available experimental data:

When sufficient data on the compressibility factor, $Z$, and pressure, $P$, are available, the fugacity coefficient can be obtained from the numerical integration:

$$\ln \phi = \int_0^{\frac{P}{Z}} \frac{Z-1}{P} dP$$

(4)

| Table 2. Physical property of the component and parameters of Twu alpha function [6]: |
|-----------------------------------|
| Component | $T_c$ (K) | $P_c$ (atm) | $T_b$ (K) | $L$ | $M$ | $N$ | $\omega$ |
|----------|----------|-------------|----------|-----|-----|-----|-----|
| CO$_2$   | 304.21   | 72.80       | 194.70   | 0.945951 | 0.88652 | 0.65000 | 0.225 |
| CH$_4$   | 190.564  | 45.99       | 111.70   | 0.081382 | 0.905296 | 2.13000 | 0.008 |
| N$_2$    | 126.20   | 34.00       | 77.40    | 0.064994 | 0.892385 | 2.34000 | 0.040 |
| H$_2$S   | 373.53   | 89.62       | 212.875  | 0.231877 | 0.784346 | 0.65000 | 0.225 |
| H$_2$O   | 647.13   | 22.05       | 373.15   | 0.430058 | 0.870932 | 1.67211 | 0.344 |

| Table 3. Expression of fugacity coefficients for different EoS: |
|-----------------------------------|
| EOS | log $\phi$ |
|---|---|
| VW[7] | $Z - 1 - \ln \left( \frac{Z - 1}{V} \right) - \frac{a}{RTV}$ |
| RK[8] | $Z - 1 - \ln \left( \frac{Z - 1}{V} \right) - \frac{a}{aRT} \ln \left( 1 + \frac{b}{V} \right)$ |
| SRK[9] | $Z - 1 - \log(Z - B) + \frac{a}{bRT} \ln \left( \frac{Z}{Z + B} \right)$ |
| PR[10] | $Z - 1 - \log(Z - B) + \frac{A}{2\sqrt{2B}} \ln \left( \frac{Z - 0.414B}{Z + 2.414B} \right)$ |
| ML[11] | $Z - 1 - \log(Z - B) + \frac{A}{2\sqrt{2B}} \ln \left( \frac{Z - 0.414B}{Z + 2.414B} \right)$ |
| TST[1,2] | $Z - 1 - \log(Z - B) + \frac{A}{3.5B} \ln \left( \frac{Z - 0.5B}{Z + 3B} \right)$ |
| BB[4] | $\ln \left( \frac{RT}{V} \right) + \left( B_0 - \frac{c}{T^3} - \frac{A_0}{RT} \right) \frac{2}{V} + \left( bB_0 - \frac{cB_0}{T^3} - \frac{aA_0}{RT} \right) \frac{3}{2V^2} + \frac{cbB_0}{T^3} \frac{4}{3V^3}$ |
1.5 \text{ cm} \times 1.5 \text{ cm} \text{.}

Here, \( A = \frac{aP}{RT^2} \) and \( B = \frac{bP}{RT} \) can be determined from the three parameters of the gas: critical pressure, \( P_c \); critical temperature, \( T_c \) and the eccentric factor \( \omega \).

Table 4. Represents the coefficients of the equation, \( Z^3 + a_2Z^2 + a_1Z + a_0 = 0 \), used for the calculation of largest root of compressibility factor \( Z \) for different EOS:

| EOS     | \( a_2 = B - 1 \) | \( a_1 = -A \) | \( a_0 = -AB \) |
|---------|-------------------|----------------|-----------------|
| VW[7]   | \( a_2 = -1 \)    | \( a_1 = A - B - B^2 \) | \( a_0 = -1 \)  |
| SRK[9]  | \( a_2 = B - 1 \) | \( a_1 = A - 2B - 3B^2 \) | \( a_0 = B^3 + B^2 - AB \) |
| PR[10]  | \( a_2 = B - 1 \) | \( a_1 = A - 2B - 3B^2 \) | \( a_0 = B^3 + B^2 - AB \) |
| ML[11]  | \( a_2 = B - 1 \) | \( a_1 = A - 2.5B - 4B^2 \) | \( a_0 = 1.5B^3 + 1.5B^2 - AB \) |
| TST[1,2] | \( a_2 = 1.5B - 1 \) | \( a_1 = A - 2.5B - 4B^2 \) | \( a_0 = 1.5B^3 + 1.5B^2 - AB \) |

3. Results and discussion

We know that the curves are the guides for the eye. Plotting has been performed for every inspection for the nature of the drawn curve. For plot of these curves, the fugacity coefficients have been calculated for Methane and Caron di-oxide from equations of state of Soave Redlich Kwong (SRK), Peng Robinson (PR) and Twu Sim Tassone (TST) taking reduced temperatures, \( T_r \) of interest from each of the three ranges \( 0 < T_r < 1 \), \( 1 < T_r < 3 \) and \( 3 < T_r < 5.5 \) together with the reduced pressures, \( P_r \) in steps of 0.2 in the range \( 0 < P_r < 10 \). Let us first consider the plot of calculated fugacity coefficients of methane from considered EOSs for \( T_r = 3.149 \) and \( T_r = 5.248 \), belonging to the range \( 1 < T_r < 5.5 \), and varying \( P_r \) from 0 to 8. By a close look into the Fig. 1 we find that the continuous curve represents the TST data, which agrees to some extent to the data what BW EOS. The SRK EOS is predicting well for \( T_r = 5.248 \) but for \( T_r = 3.149 \) it completely fails to predict the data of BW. The reverse result is obtained in case of the PR EOS, which is predicting to some extent for \( T_r = 3.149 \) while for \( T_r = 5.248 \) it fails completely to predict the data of BB EOS. In Fig. 2 the plot has been performed for \( T_r = 1.574 \) and \( T_r = 2.099 \) which belonging to \( 1 < T_r < 3 \). For both of these \( T_r \) values the TST EOS predicting well with the BB data. The dashed curve of SRK EOS gives the coefficient values more than the BB data for each \( T_r \). The curve PR has exact coincidence with BB data these reduced temperature and for \( 0 < P_r < 1 \). In Fig. 3, for \( T_r = 0.84 \) and \( T_r = 0.945 \), the SRK EOS again reproducing the fugacity coefficients value more than the BB data for the considered pressure range i.e., \( 0 < P_r < 0.6 \). But both the TST EOS and SRK EOS have an exact match with the BB data for the considered pressures range.

Similarly, for plot of \( CO_2 \) fugacity coefficient curves, we find in Fig. 4 that the continuous curve represents the TST data, which agrees to some extent to the data of BW for \( T_r = 2.17 \) and

\[\text{Table 4.}\]
$T_r = 3.287$ both and the range of $P_r$. For the same $T_r$ values, the dashed curve of SRK and the dotted curve of PR EOS show a complete disagreement behavior with BB data. The SRK EOS is predicting well for $T_r = 2.17$, but for $T_r = 3.287$ it completely fails to predict the data of BW. The reverse result is obtained in case of the PR EOS, which is predicting to some extent for $T_r = 2.17$ while for $T_r = 3.287$ it fails completely to predict the data of BB. In Fig. 5 the plot has been performed for $T_r = 1.315$ and $T_r = 2.972$ which belonging to $1 < T_r < 3$. For both of these $T_r$ value the TST EOS predicting well with the BB data. The dashed curve of SRK EOS gives the fugacity coefficient values more than the BB data for each $T_r$. The curve PR has exact coincidence with BB data these $T_r$ values and for $0 < P_r < 1$. In Fig. 6, for $T_r = 0.986$ and $T_r = 0.945$, the SRK EOS again reproducing the fugacity coefficients value more than the BB data for the considered pressure range i.e., $0 < T_r < 0.6$. But both the TST EOS and SRK EOS have an exact match with the BB data for the considered range of $P_r$. In Fig. 7, for $T_r = 3.149$ and $T_r = 5.248$, the comparative plots has been performed for methane from each equation of state to observe it as a eye wink.

Figure 1. Plot for the pure substance methane: for $T_r = 3.149$ curve [5], its plots against $P_r$ represent the TST EOS (first continuous curve), the SRK EOS (first dashed curve), and the PR EOS (first dotted curve), respectively and for $T_r = 5.248$ curve [5], its plots against $P_r$ represent the TST EOS (second continuous curve), the SRK EOS (second dashed curve), and the PR EOS (second dotted curve), respectively. For higher values of $T_r$ ($3 < T_r < 5.5$) the values of fugacity coefficient increase with $P_r$.  

*Note:* This document is a excerpt from a scientific paper discussing the behavior of EOS (EoS) models in predicting fugacity coefficients for methane at different temperatures and pressures. The SRK EOS is shown to predict well for $T_r = 2.17$, while the PR EOS fails completely at $T_r = 3.287$. The TST EOS shows a reasonable agreement with BB data across different ranges of $T_r$. The plots illustrate the comparison between measured (BB) data and predicted values for each EOS at various pressure values. The fugacity coefficients increase with pressure for higher temperatures.
Figure 2. Plot for the pure substance methane: for $T_r = 1.574$ curve [5], its plots against $P_r$ represent the TST EOS (first continuous curve), the SRK EOS (first dashed curve), and the PR EOS (first dotted curve), respectively and for $T_r = 2.099$ curve [5], its plots against $P_r$ represent the TST EOS (second continuous curve), the SRK EOS (second dotted curve), and the PR EOS (second dashed curve), respectively. For middle values of $T_r$ ($1 < T_r < 3$) the values of fugacity coefficient decrease in small steps with $P_r$.

Figure 3. Plot for the pure substance methane: for $T_r = 0.84$ curve [5], its plots against $P_r$ represent the TST EOS (first continuous curve), the SRK EOS (first dashed curve), and the PR EOS (first dotted curve, respectively and for $T_r = 0.945$ curve [5], its plots against $P_r$ represent the TST EOS (second continuous curve), the SRK EOS (second dotted curve), and the PR EOS (second dashed curve), respectively. For lower values of $T_r$ ($0 < T_r < 1$) the values of fugacity coefficient decrease in big steps with $P_r$. 
Figure 4. Plot for the pure substance CO₂: for $T_r = 2.17$ curve [5], its plots against $P_r$ represent the TST EOS (first continuous curve), the SRK EOS (first dotted curve), and the PR EOS (first dashed curve), respectively and for $T_r = 3.287$ curve [5], its plots against $P_r$ represent the TST EOS (second continuous curve), the SRK EOS (second dotted curve), and the PR EOS (second dashed curve), respectively. For higher values of $T_r$ ($2 < T_r < 5.5$) the values of fugacity coefficient increase with $P_r$.

Figure 5. Plot for the pure substance CO₂: for $T_r = 1.315$ curve [5], its plots against $P_r$ represent the TST EOS (first continuous curve), the SRK EOS (first dotted curve), and the PR EOS (first dashed curve), respectively and for $T_r = 1.972$ curve [5], its plots against $P_r$ represent the TST EOS (second continuous curve), the SRK EOS (second dotted curve), and the PR EOS (second dashed curve), respectively. For middle values of $T_r$ ($1 < T_r < 3$) the values of fugacity coefficient decrease in small steps with $P_r$ and for $T_r = 1.972$ curve [5] ($1 < T_r < 3$) the values of fugacity coefficient decrease in somewhat larger steps with $P_r$. 
Figure 6. Plot for the pure substance $CO_2$: for $T_r = 0.986$, its plots against $P_r$ represent the TST EOS (continuous curve), the SRK EOS (dashed curve), and the PR EOS (dotted curve), respectively. For lower values of $T_r$ ($0 < T_r < 1$) the values of fugacity coefficient decrease in big steps with $P_r$.

Figure 7. Plot for the pure substance methane: for $T_r = 3.149$ curve [5], its plots against $P_r$ represent the LM EOS (first dotted curve), the PR EOS (first dashed curve), the TST EOS (first continuous curve), the VW EOS(first dashed dotted curve), and for SRK EOS (first bigger dashed curve), respectively. For $T_r = 5.248$ curve [5] its plots against $P_r$ represent the LM EOS (first dotted curve), the PR EOS (first dashed curve), the TST EOS (second continuous curve), the VW EOS(second dashed dotted curve), and for SRK EOS (second bigger dashed curve), respectively. For higher values of $T_r$ ($3 < T_r < 5.5$) the values of fugacity coefficient increase with $P_r$. 

4. Conclusions

The fugacity coefficients from different equations of state and with different $T_r$ values have been compared with the calculated values of BB [3, 4, 5]. The outcome of this study is that the calculated fugacity coefficients for selected different $T_r$ values in the region of interest were found either of increasing or decreasing nature with $P_r$. It is interesting to note that the TST EOS among all others shows its ability to reproduce the data as predicted by BB. Finally, the comparison of the fugacity coefficient values obtained for $CH_4$ and $CO_2$, it can be concluded that among all the equations of state the newly developed EOS of Twu Sim Tassone the is most authentic.

5. References

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