

A New Three Parameter Cubic Equation of State

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Abstract. A new three parameter Equation Of State (EOS) is developed based on well documented data, at three thermodynamic states of the critical point, the normal bubble point and standard condition. Besides these states, the EOS is designed to satisfy the condition of nearly zero Joule-Thomson (JT) coefficients at the normal boiling point. Critical properties and densities at the normal boiling point and a standard condition of more than 100 pure fluids were used. The new EOS is validated using experimental data and eight (8) of the popular EOSs, namely, SRK, PR, LLS, HK, MNM, SW, PT and ALS. The experimental data for pure fluids include 331 data points of vapor pressure covering 12 fluids and compressibility at the critical condition of 23 fluids. For mixtures, the data includes 129 PVT data points of 12 reservoir fluids [seven (7) of them are Sudanese crude oil considered for publication for the first time and five (5) from literature]. The new EOS is found to be superior to the existing EOSs in the prediction of PVT properties of mixtures with a grand average percent absolute deviation (AAPD) of 3.18%. It is also comparable to the existing EOSs in the prediction of vapor pressure despite the fact that existing EOSs are developed based on vapor pressure data; the grand average AAPD is 2.0. In terms of compressibility at the critical point with the exception of LLS, the new EOS yields better results than all other EOSs considered in this work.

Keywords: Equation of state; Joule-Thomson coefficient; PVT data; Sudanese reservoir fluids.

INTRODUCTION

Since the appearance of the Van Der Waals (VDW) Equation Of State (EOS) in 1873, numerous cubic (in volume or density) EOS have been developed. Most of these developments are based on the original VDW EOS [1]. These developments have the form of an extended VDW EOS as:

$$P = \frac{RT}{v-b} - \frac{a\alpha(T,\omega)}{v^2 + ubv + wb^2} \quad (1)$$

EOSs that assume this form include Peng Robison (PR) [2], Soave-Redlich-Kwong (SRK) [3], Schmidt-Wenzel (SW) [4], Patel-Teja (PT) [5], Harmens-Knapp (HK) [6], Adachi-Lu-Sugie (ALS) [7], Lawal - Lake - Silberberg (LLS) [8] and Modified-Nasrifar-Moshfeghian (MNM) [9] to mention a few. The first term in the

right hand side of Equation 1 represents the repulsive, and the second term represents the attraction term. Table 1 lists a number of cubic EOSs. The attraction term and the functional relationship of u and w are also given in Table 1; the repulsive term (not shown) is similar in all of these EOSs as defined in Equation 1. In most EOSs, the term a is constant. With the exception of VDW, the term $\alpha(T,\omega)$ is temperature (T) and acentric (ω) factor dependent. With few exceptions,

Table 1. Features of some cubic EOSs.

| EOS | Year | Attraction Term | u | w |
|-----|------|---|-------------|-------------|
| VDW | 1883 | $\frac{a}{v^2}$ | 0 | 0 |
| SRK | 1972 | $\frac{a(T)}{v(v+b)}$ | 1 | 0 |
| PR | 1976 | $\frac{a(T)}{v(v+b)+b(v-b)}$ | 2 | -1 |
| HK | 1980 | $\frac{a(T)}{v^2+c(\omega)bv-(c(\omega)-1)b^2}$ | $f(\omega)$ | $f(\omega)$ |
| SW | 1980 | $\frac{a(T)}{v^2+(1+3\omega)bv-3\omega b^2}$ | $1+3\omega$ | -3ω |
| PT | 1982 | $\frac{a(T)}{v(v+b)+c(v-b)}$ | $f(\omega)$ | $f(\omega)$ |
| ALS | 1983 | $\frac{a(T)}{(v-b_1(\omega))(v-b_2(\omega))}$ | $f(\omega)$ | $f(\omega)$ |
| MNM | 1988 | $\frac{a(T)}{v^2+2bv-2b^2}$ | 2 | -2 |
| LLS | 1990 | $\frac{a(T)}{v^2+\alpha bv-\beta(\omega)b^2}$ | $f(\omega)$ | $f(\omega)$ |

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the term $\alpha(T, \omega)$ has the following form:

$$\alpha(T, \omega) = \left[1 + m(\omega) \left(1 - \sqrt{Tr} \right) \right]^2. \quad (2)$$

At the critical point, $\alpha(T_c, \omega) = 1$. With the exception of LLS, the parameter b is acentric factor dependent only. Parameters u and w are constant in two parameter EOSs, such as VDW, PR, SRK, MNM. In three parameter EOSs, such as HK, SW and PT, u and w are dependent on each other. For the fourth parameters EOSs, such as LLS and ALS, the terms u and w are acentric factor dependent.

For two parameter EOSs, such as VDW and RK, parameters a and b are determined using VDW critical point conditions. This criterion is expressed mathematically by the following three equations [1]:

$$\left. \frac{\partial P}{\partial v} \right|_{T_c} = 0, \quad (3a)$$

$$\left. \frac{\partial^2 P}{\partial v^2} \right|_{T_c} = 0, \quad (3b)$$

$$f(T_c, P_c, V_c) = 0. \quad (3c)$$

For three and four parameter EOSs, where additional boundary conditions are needed, the parameters are determined by fitting the EOS to experimental data. Vapor pressure data is common to all EOSs. Other fitted properties include liquid and vapor density and compressibility factor [5-7].

Experimental data and prediction methods for the thermodynamic states at critical point, normal boiling point and standard condition ($T = 15^\circ\text{C}$ [60°F] and $P = 1$ atm [14.67 psia]) for a wide range of fluids are well documented. The objective of this work is to use the thermodynamic properties at those three points, coupled with the inflection point criteria of temperature, isotherm and isenthalpic (Joule Thomson inversion curve) to develop a three parameter equation of state similar to Equation 1.

MODEL DEVELOPMENT

Equation 1 can be written in a reduced form as:

$$P_r = \frac{T_r}{v_r - \beta} - \frac{a_c \alpha(T, \omega)}{v_r^2 + u\beta v_r + w\beta^2}, \quad (4)$$

where:

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}, \quad \beta = \frac{bP_c}{RT_c},$$

$$a_c = \frac{aP_c}{(RT_c)^2}, \quad Z_c = \frac{P_c v_c}{RT_c},$$

$$v_r = \frac{vP_c}{RT_c} = \frac{v}{v_c} Z_c.$$

With $\alpha(T, \omega)$ defined by Equation 2, Equation 4 contains six parameters (a_c, β, u, w, Z_c and m) and hence six boundary conditions are needed. The boundary conditions chosen to evaluate the parameters are (1) critical point, (2) normal boiling point and (3) standard condition. These points are selected, because over years, the thermodynamic states at these points are well documented for pure fluids. The boundary conditions at these three points are characterized as:

1. **Critical Point:** At this point, three constraints are written by VDW as given by Equations 3a to 3c. In fact, VDW critical point conditions are common to all cubic EOSs.
2. **Normal Boiling Point:** The EOS is assumed to give the correct volume at the normal boiling point, hence:

$$f(T_b, P_b, v_b) = 0. \quad (5)$$

Equation 5 represents the fourth boundary condition. It should be emphasized that the calculation methods of T_b and v_b are well established. It is also assumed that the JT coefficient vanishes or becomes nearly zero at the normal boiling point:

$$\underbrace{\mu \equiv \left. \frac{\partial T}{\partial P} \right|_h}_{\text{normal boiling point}} = 0. \quad (6)$$

The point at which JT vanishes is called the inversion point and the locus of these points is called a JT inversion curve. Experimental data of the JT inversion curve is very limited in the literature; it does not cover a wide spectrum of fluids. This is attributed to the fact that direct measurement of an inversion curve is difficult and unreliable [10]. Nevertheless, close scrutiny of the isenthalpic line (cf. Figure 1) reveals an interesting fact. It is noticeable that at low pressure ($P \rightarrow 1$ atm), the turning point of isenthalpic lines (i.e. $\mu = 0$) lies exactly at or close to the bubble point curve. The question is, how close is it to the boiling curve? Under all circumstances, the deviation is in the order of magnitude of experimental error. For example, for water at the normal boiling point $\mu = -0.18$ K/MPa. Hence, it is safe to consider that the JT coefficient is approximately zero at the normal boiling point.

Using the definition of enthalpy:

$$dh = Cp dT - \left[T \left(\frac{\partial V}{\partial T} \right)_p - v \right] dp. \quad (7)$$

The JT coefficient is:

$$\mu = \left. \frac{\partial T}{\partial P} \right|_h = \frac{1}{Cp} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right]. \quad (8)$$

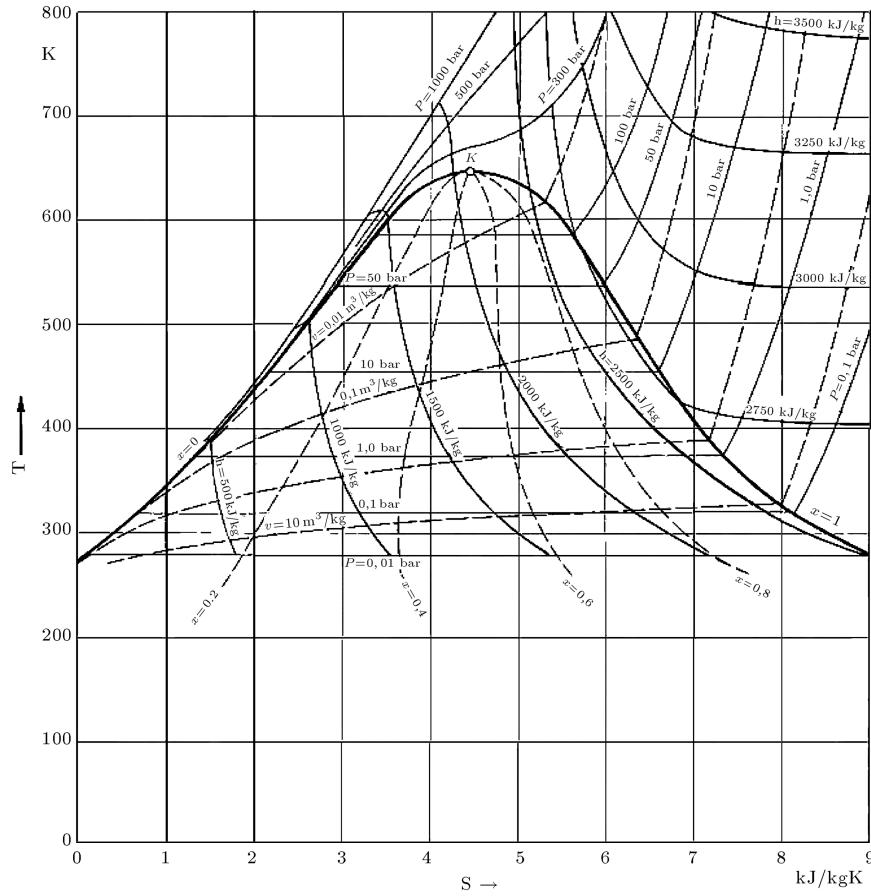


Figure 1. Temperature-entropy (T-s) diagram (source: [11]).

At the normal boiling point, Equation 7 becomes:

$$\left[T_b \left(\frac{\partial v}{\partial T} \right)_{p_b} - v_b \right] \rightarrow 0, \quad (9)$$

where the subscript b stands for normal boiling point. Equation 9 represents the fifth boundary condition.

3. **Standard Condition Point:** To close the system of equations, Equation 4 is considered to give the correct value of the liquid density under standard conditions:

$$f(T_{sc}, P_{sc}, v_{sc}) = 0, \quad (10)$$

where the subscript sc stands for standard condition.

With these six boundary conditions (three at critical point, two at normal boiling point and one at standard condition) the six parameters (a_c, β, u, w, Z_c and m) can now be evaluated.

Evaluation of Parameters

Applying the critical point conditions given by Equations 3a to 3c to Equation 4, and solving a_c, β and Z_c , in terms of u and w , results in:

$$Z_c = \frac{p_c v_c}{RT_c} = \frac{1}{3} [1 + (1 - u) \beta], \quad (11)$$

$$a_c = 3Z_c^2 + (u - w) \beta^2 + u\beta, \quad (12)$$

$$(u + 2)^3 \beta^3 + 3(9w - u + 5u + 5) \beta^2 + 3(u + 2) \beta - 1 = 0. \quad (13)$$

The value of β is the smallest root of Equation 13. Details of the derivation of Equations 11 to 13 are available in [11].

There are, in total, six equations (Equations 5 and 9 to 13), with six unknown parameters (a_c, β, u, w, Z_c and m). Using an algebraic method, parameters a_c and Z_c are eliminated and the number of equations is reduced to four non-linear equations with four unknown parameters (β, u, w and m).

The non-linear equations are solved numerically using the Jacobian method and the values of the four parameters are calculated for 102 fluids. For all these fluids, the critical properties (T_c, P_c), acentric factor (ω), molar volume at the standard condition (v_{sc}) and the normal boiling point temperature (T_b) are obtained from a standard table presented in Danesh [12]. The

molar volume at the normal boiling point (v_b) is evaluated using the modified Rackett equation [13].

It is convenient and common practice (cf. Table 1) to write u and m as a function of the acentric factor and w as a function of u . This exercise results in:

$$u = 1.7574 + 4.0951\omega + 1.7176\omega^2, \quad (14)$$

$$m = 0.0967 - 0.4442\omega + 0.8267\omega^2 - 0.6621\omega^3 + 0.1903\omega^4, \quad (15)$$

$$w = 0.01871u^2 - 1.42111u + 1.6165. \quad (16)$$

Since u and w are related by an exact mathematic relationship, similar to HK, SW and PT EOSs, the new model is a three parameter EOS.

Application to Mixtures

Equation 4 with the parameters defined by Equations 11 to 16 may be used for mixture with the conventional VDW mixing rules as:

$$X = \sum_i y_i X_i, \quad (17)$$

$$a = \sum_i y_i y_j \sqrt{a_i a_j} (1 - k_{ij}), \quad (18)$$

where X can be β , u or w and y is the liquid or vapor mole fraction, and k_{ij} is the binary interaction parameter.

RESULTS AND DISCUSSION

To compare the new EOS to experimental data and the available EOSs, numerous quality measurements based on statistical error analysis are computed. These include the Percent Deviation (PD), the Average Absolute Percent Deviation (AAPD), the minimum Absolute Percent Deviation (APD_{\min}), the maximum Absolute Percent Deviation (APD_{\max}) and the grand average AAPD. The percent deviation is defined as:

$$PD_i = \frac{X_{\text{exp},i} - X_{\text{EOS},i}}{X_{\text{exp},i}} \times 100\%, \quad (19)$$

and the average absolute percent deviation (AAPD) is defined as:

$$\text{AAPD} = \frac{1}{N} \sum \left| PD_i \right|, \quad (20)$$

where X_{exp} is the experimental value, X_{EOS} is the calculated value using EOS, N is the number of the data points and i is a dummy index. Besides these statistical parameters, a Consistency Parameter (CP) is introduced in this work. The CP is defined as the

difference between the maximum and the minimum APD.

The new EOS is compared with experimental data and eight (8) of the most popular EOSs, namely, SRK, PR, LLS, HK, MNM, SW, PT and ALS EOSs. The data include published and unpublished experimental works of pure components and mixtures. For pure components, these data include the compressibility at the critical point and vapor pressure. For mixtures, PVT data of the reservoir fluids under undersaturated conditions are used.

Compressibility

Table 2 shows the critical at the critical point (Z_c) of some components common to reservoir fluids predicted by the EOSs including the new one. The statistical parameters of AAPD, APD_{\min} and APD_{\max} are also shown. The new EOS predicts critical compressibility with an AAPD of about 4.0% while the AAPD of the existing EOSs with the exception of LLS exceeds 20. LLS has an AAPD of 1.37. The higher error associated with EOSs, such as SRK, PR and MNM, is not surprising, since Z_c is constant, i.e. independent of the fluid. For ALS, SW, PT and HK, no justification could be given to the inaccuracy in the prediction of Z_c . The superiority of LLS by the prediction of Z_c could be attributed to the fact that parameter b is a function of temperature, contrary to the rest of the EOSs including the new model.

VAPOR PRESSURE

The vapor pressure is calculated using Maxwell criteria:

$$P^s = \frac{1}{v_v - v_l} \int_{v_l}^{v_v} P(T, v) dv, \quad (21)$$

where P^s , v_v and v_l are the vapor pressure, vapor molar volume and liquid molar volume, respectively. Table 3 shows a summary of AAPD for some 13 fluids, comprising about 331 vapor pressure data points from the literature. The reported values may be slightly different from similar calculations available in the literature [14]. This difference is due to the covered ranges and, hence, the number of data points involved in the comparison. The covered range is limited to $Tr \leq 0.9$. This range is selected to maintain comparison consistency, because some EOSs, such as SW, are valid for a vapor pressure within this range only. All EOSs, including the new EOS, produced comparable results with a consistent grand average AAPD of about 2.0. The APD_{\max} for all EOSs is more than 3.0. However, this is obtained for few fluids; namely, H_2S and $i\text{C}_4$. This could not be explained but, in part,

Table 2. Accuracy of EOSs in the prediction of Z_c (data source: [12]).

| Name | Exp. | This Work | SRK | PR | LLS | MNM | HK | SW | ALS | PT |
|--------------------------|-------|-----------|-------|-------|-------|-------|-------|-------|-------|-------|
| N ₂ | 0.292 | 0.309 | 0.333 | 0.307 | 0.291 | 0.295 | 0.318 | 0.330 | 0.319 | 0.326 |
| CO ₂ | 0.274 | 0.288 | 0.333 | 0.307 | 0.273 | 0.295 | 0.305 | 0.315 | 0.314 | 0.313 |
| H ₂ S | 0.284 | 0.304 | 0.333 | 0.307 | 0.286 | 0.295 | 0.315 | 0.326 | 0.321 | 0.323 |
| C ₁ | 0.286 | 0.312 | 0.333 | 0.307 | 0.288 | 0.295 | 0.320 | 0.332 | 0.325 | 0.328 |
| C ₂ | 0.279 | 0.302 | 0.333 | 0.307 | 0.288 | 0.295 | 0.314 | 0.325 | 0.320 | 0.322 |
| C ₃ | 0.276 | 0.296 | 0.333 | 0.307 | 0.288 | 0.295 | 0.310 | 0.321 | 0.312 | 0.318 |
| <i>i</i> C ₄ | 0.282 | 0.294 | 0.333 | 0.307 | 0.288 | 0.295 | 0.308 | 0.319 | 0.316 | 0.316 |
| <i>n</i> C ₄ | 0.274 | 0.291 | 0.333 | 0.307 | 0.288 | 0.295 | 0.307 | 0.317 | 0.315 | 0.315 |
| <i>i</i> C ₅ | 0.270 | 0.288 | 0.333 | 0.307 | 0.288 | 0.295 | 0.305 | 0.315 | 0.313 | 0.313 |
| <i>n</i> C ₁₀ | 0.247 | 0.256 | 0.333 | 0.307 | 0.245 | 0.295 | 0.291 | 0.297 | 0.297 | 0.296 |
| <i>n</i> C ₁₃ | 0.232 | 0.241 | 0.333 | 0.307 | 0.231 | 0.295 | 0.286 | 0.289 | 0.291 | 0.290 |
| <i>n</i> C ₁₄ | 0.226 | 0.238 | 0.333 | 0.307 | 0.225 | 0.295 | 0.286 | 0.288 | 0.290 | 0.288 |
| <i>n</i> C ₁₅ | 0.224 | 0.232 | 0.333 | 0.307 | 0.224 | 0.295 | 0.284 | 0.285 | 0.287 | 0.286 |
| <i>n</i> C ₁₇ | 0.219 | 0.221 | 0.333 | 0.307 | 0.220 | 0.295 | 0.282 | 0.280 | 0.279 | 0.282 |
| C ₁₇ | 0.233 | 0.238 | 0.333 | 0.307 | 0.235 | 0.295 | 0.286 | 0.288 | 0.290 | 0.288 |
| C ₁₈ | 0.231 | 0.234 | 0.333 | 0.307 | 0.229 | 0.295 | 0.285 | 0.286 | 0.288 | 0.287 |
| C ₂₀ | 0.226 | 0.226 | 0.333 | 0.307 | 0.225 | 0.295 | 0.283 | 0.282 | 0.280 | 0.284 |
| C ₂₁ | 0.224 | 0.223 | 0.333 | 0.307 | 0.223 | 0.295 | 0.283 | 0.281 | 0.278 | 0.283 |
| C ₂₂ | 0.221 | 0.219 | 0.333 | 0.307 | 0.219 | 0.295 | 0.282 | 0.279 | 0.280 | 0.282 |
| C ₂₃ | 0.220 | 0.216 | 0.333 | 0.307 | 0.222 | 0.295 | 0.281 | 0.278 | 0.274 | 0.281 |
| C ₂₄ | 0.217 | 0.212 | 0.333 | 0.307 | 0.218 | 0.295 | 0.281 | 0.277 | 0.273 | 0.279 |
| C ₂₅ | 0.215 | 0.208 | 0.333 | 0.307 | 0.217 | 0.295 | 0.281 | 0.275 | 0.276 | 0.278 |
| C ₂₆ | 0.213 | 0.205 | 0.333 | 0.307 | 0.214 | 0.295 | 0.280 | 0.274 | 0.270 | 0.277 |
| AAPD | | 4.03 | 36.88 | 26.19 | 1.37 | 21.26 | 20.42 | 21.68 | 20.86 | 21.71 |
| APD _{min} | | 0.00 | 14.16 | 5.25 | 0.22 | 1.13 | 9.02 | 12.96 | 9.36 | 11.76 |
| APD _{max} | | 9.01 | 56.34 | 44.13 | 6.63 | 38.50 | 31.46 | 28.64 | 28.41 | 30.05 |
| CP | | 9.01 | 42.18 | 38.88 | 6.41 | 37.37 | 22.44 | 15.68 | 19.05 | 18.29 |

may be attributed to the literature data. The good accuracy of existing EOSs on the prediction of vapor pressure is not surprising, since vapor pressure values have been used to determine the values of parameter “ a ”. On the contrary, vapor pressure data are not involved in the development of the new EOS. Despite this fact, the new EOS is comparable to existing EOSs in terms of vapor pressure. This is indicative in the consistency of the new EOS.

Molar Volume of Reservoir Fluids

Table 4 gives the composition and code names for 12 reservoir fluids. Reservoir temperature, bubble point, and plus heptanes (C₇₊) molecular weight and specific gravity are also given in Table 4. Data of mixtures coded A to F are supplied by the Ministry of Energy and Mining, Sudan. These data have been considered for publication for the first time. For these data, the

experimental error of pressure is ± 5 psi, temperature is $\pm 0.5^\circ\text{F}$ and cell volume is ± 0.3 cc as reported in PVT studies. Reservoir fluids, G to M , are obtained from the literature; their sources are indicated in the footnote of Table 4.

For C₇₊, the critical properties and acentric factor are estimated for a given molecular weight and specific gravity from Lawal-Tododo-Heinze [15] correlations. Binary Interaction Parameters (BIPs) are taken as $k_{ij} = 0$.

Table 5 gives a summary of the statistical parameters of comparison of new EOS with experimental data and other EOSs in term of the molar volume of reservoir fluid. Table 5 reveals some interesting findings:

1. Although HK, ALS and PR do yield good results, the new EOS is superior to all EOSs under consideration, in terms of the grand average AAPD.

Table 3. AAPD of the new EOS in the prediction of vapor pressures.

| Component | Data Source | AR | SRK | PR | LLS | HK | ALS | SW | PT | MNM | No of Data Points |
|--------------------------|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------------------|
| H ₂ S | [16] | 3.786 | 3.978 | 3.771 | 3.892 | 3.765 | 3.797 | 3.941 | 4.095 | 3.765 | 19 |
| N ₂ | [17] | 1.287 | 1.262 | 1.252 | 1.406 | 1.309 | 1.283 | 1.839 | 1.280 | 1.421 | 10 |
| CO ₂ | [17,18] | 0.734 | 0.732 | 0.733 | 0.741 | 0.732 | 0.733 | 7.227 | 0.733 | 0.732 | 9 |
| C ₁ | [19] | 1.303 | 1.288 | 1.314 | 1.305 | 1.303 | 1.317 | 1.305 | 1.303 | 1.579 | 39 |
| C ₂ | [17] | 1.677 | 1.519 | 1.675 | 2.340 | 1.545 | 1.720 | 2.591 | 1.461 | 3.425 | 28 |
| C ₃ | [17] | 1.462 | 1.403 | 1.462 | 1.462 | 1.463 | 1.462 | 1.586 | 1.546 | 1.472 | 20 |
| <i>i</i> C ₄ | [16] | 3.051 | 3.103 | 3.042 | 3.537 | 3.085 | 3.145 | 3.350 | 3.114 | 3.579 | 24 |
| <i>n</i> C ₄ | [17,18] | 1.871 | 1.876 | 1.872 | 1.859 | 1.876 | 1.873 | 1.726 | 1.998 | 1.836 | 33 |
| <i>i</i> C ₅ | [16] | 0.977 | 0.965 | 0.977 | 0.938 | 0.954 | 0.962 | 0.935 | 0.882 | 1.147 | 23 |
| <i>n</i> C ₆ | [16,17] | 1.579 | 1.918 | 1.488 | 1.863 | 1.514 | 1.683 | 1.644 | 1.565 | 2.160 | 54 |
| <i>n</i> C ₇ | [16] | 1.561 | 1.351 | 1.184 | 1.742 | 1.320 | 1.688 | 1.435 | 1.375 | 1.604 | 22 |
| <i>n</i> C ₈ | [16] | 1.848 | 2.287 | 1.520 | 2.403 | 1.700 | 1.445 | 1.932 | 2.074 | 2.246 | 26 |
| <i>n</i> C ₁₀ | [19] | 1.466 | 1.591 | 1.651 | 1.695 | 1.696 | 1.630 | 1.842 | 1.766 | 2.158 | 18 |
| Grand average AAPD | | 1.694 | 1.735 | 1.648 | 1.930 | 1.671 | 1.697 | 2.317 | 1.734 | 2.011 | 331 |
| AAPD _{min} | | 0.734 | 0.732 | 0.733 | 0.741 | 0.732 | 0.733 | 0.935 | 0.733 | 0.732 | |
| AAPD _{max} | | 3.786 | 3.978 | 3.771 | 3.892 | 3.765 | 3.797 | 7.227 | 4.095 | 3.765 | |
| <i>C_P</i> | | 3.052 | 3.246 | 3.038 | 3.151 | 3.033 | 3.064 | 6.292 | 3.362 | 3.033 | |

Table 4. Mixture compositions and reservoir conditions.

| Components | A | B | C | D | E | F | G | H | K | L | M |
|-------------------------|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| H ₂ S | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| N ₂ | 0.35 | 0.08 | 0.07 | 0.18 | 0.20 | 8.70 | 6.94 | 4.52 | 0.91 | 0.49 | 0.16 |
| CO ₂ | 0.94 | 0.68 | 26.99 | 1.26 | 2.00 | 0.25 | 0.23 | 0.21 | 0.16 | 0.53 | 1.94 |
| C ₁ | 21.05 | 29.04 | 0.29 | 1.44 | 1.69 | 1.75 | 1.45 | 1.31 | 36.47 | 38.83 | 25.50 |
| C ₂ | 4.44 | 10.00 | 0.31 | 0.27 | 0.27 | 0.16 | 0.39 | 0.06 | 9.67 | 9.86 | 7.37 |
| C ₃ | 4.53 | 7.75 | 0.37 | 0.31 | 0.25 | 0.11 | 0.66 | 0.05 | 6.95 | 9.53 | 11.21 |
| <i>i</i> C ₄ | 3.17 | 1.23 | 0.50 | 0.13 | 0.12 | 0.02 | 0.25 | 0.02 | 1.44 | 1.23 | 3.49 |
| <i>n</i> C ₄ | 3.29 | 4.10 | 1.08 | 0.33 | 0.27 | 0.04 | 0.39 | 0.03 | 3.93 | 4.31 | 4.17 |
| Neopentane | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| <i>i</i> C ₅ | 2.70 | 1.15 | 1.53 | 0.23 | 0.22 | 0.01 | 0.31 | 0.01 | 1.44 | 1.20 | 2.18 |
| <i>n</i> C ₅ | 2.23 | 2.25 | 1.74 | 0.41 | 0.37 | 0.02 | 0.38 | 0.02 | 1.41 | 1.87 | 2.76 |
| C ₆ | 3.57 | 2.74 | 2.95 | 1.08 | 1.04 | 0.02 | 0.97 | 0.03 | 4.33 | 2.82 | 3.67 |
| C ₇₊ | 53.73 | 40.97 | 64.16 | 94.36 | 93.57 | 88.92 | 88.03 | 93.74 | 33.29 | 29.33 | 37.55 |
| | | | | | | | | | | | |
| T (°F) | 249 | 224 | 172 | 242 | 243 | 234 | 236 | 231 | 220 | 162 | 138 |
| Pb (psia) | 1818.7 | 1999.7 | 809.7 | 129.7 | 150.7 | 309.7 | 359.7 | 186.7 | 2634.7 | 2677.7 | 1689.7 |
| S.G. C ₇₊ | 0.816 | 0.855 | 0.909 | 0.887 | 0.886 | 0.8952 | 0.845 | 0.896 | 0.8515 | 0.8413 | 0.8467 |
| MW C ₇₊ | 180.596 | 321.9 | 389.49 | 373.00 | 363.00 | 336.50 | 220.59 | 320.93 | 218.00 | 252.0 | 209.00 |

Data sources:

1. Mixtures A to F: Ministry of Energy and Mining, Sudan.
2. Mixtures G and H: [20]
3. Mixture L: [21]
4. Mixtures K and M: [22]

Table 5. Summary of AAPD in the prediction of the molar volume of the reservoir fluids.

| Mixture | No. of Data Points | This Work | PR | SRK | LLS | ALS | SW | PT | MNM | HK |
|--------------------|--------------------|-----------|-------|-------|-------|------|-------|-------|-------|------|
| A | 13 | 1.19 | 4.06 | 16.53 | 14.42 | 0.77 | 16.94 | 15.65 | 2.34 | 2.48 |
| B | 9 | 3.17 | 5.96 | 18.21 | 31.29 | 7.21 | 18.51 | 16.58 | 2.98 | 4.51 |
| C | 7 | 0.84 | 10.32 | 23.38 | 18.15 | 2.76 | 11.93 | 10.20 | 7.13 | 0.40 |
| D | 16 | 4.00 | 16.11 | 29.60 | 3.36 | 9.14 | 7.47 | 5.11 | 14.87 | 1.80 |
| E | 16 | 2.66 | 16.99 | 30.61 | 3.88 | 7.53 | 6.48 | 4.22 | 14.90 | 2.67 |
| F | 18 | 5.54 | 10.83 | 23.78 | 4.63 | 9.59 | 10.48 | 8.66 | 6.15 | 2.33 |
| G | 10 | 5.14 | 3.32 | 15.76 | 4.92 | 5.80 | 14.26 | 13.27 | 2.04 | 6.07 |
| H | 13 | 5.51 | 10.13 | 23.07 | 0.73 | 8.82 | 10.27 | 8.63 | 4.47 | 2.70 |
| K | 9 | 3.15 | 0.41 | 11.28 | 28.23 | 4.19 | 23.08 | 21.63 | 4.06 | 7.01 |
| L | 9 | 0.67 | 3.57 | 15.68 | 28.44 | 3.14 | 18.82 | 17.32 | 1.78 | 4.47 |
| M | 9 | 3.15 | 0.41 | 11.28 | 28.23 | 4.19 | 23.08 | 21.63 | 4.06 | 7.01 |
| AAPD | | 3.18 | 7.46 | 19.93 | 15.12 | 5.74 | 14.67 | 12.99 | 5.89 | 3.77 |
| APD _{min} | | 0.67 | 0.41 | 11.28 | 0.73 | 0.77 | 6.48 | 4.22 | 1.78 | 0.40 |
| APD _{max} | | 5.54 | 16.99 | 30.61 | 31.29 | 9.59 | 23.08 | 21.63 | 14.90 | 7.01 |
| CP | | 4.87 | 16.58 | 19.33 | 30.56 | 8.82 | 16.60 | 17.41 | 13.12 | 6.61 |

2. Despite the fact that the mixtures under consideration vary in composition (mixtures A, B, K, L and M are characterized with high content of C₁ and low content of C₇₊), the new EOS is consistent in the prediction of the molar volume of reservoir mixtures. It has a CP of 4.87, while CP is 6.61 for HK, CP is 8.82 for ALS and CP > 13 for the rest of the EOSs.

CONCLUSION

The work produced a new EOS based on well documented data at three thermodynamic states of critical point, normal boiling point and standard condition. The new EOS is also made to satisfy JT inversion criteria. The new EOS is superior to the existing EOSs and consistent in the prediction of the thermodynamic properties of mixtures and pure fluids. The derivation of the EOS is straightforward and educational.

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