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# Comparative Study of Equations of State

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**Abstract**: The objective of this work is to predict thermodynamic properties of pure component using equation of state (EOS). Six EOSs used in this study, namely Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Schmidt-Wenzel (SW), Patel-Teja (PT), Lawal-Lake-Silberberg (LLS), and Adachi-Lu-Sugie (ALS). The pure component used include eleven hydrocarbon compounds from methane to normal decane and four non-hydrocarbon compounds namely water, hydrogen sulphide, nitrogen, and carbon dioxide. The predicted properties include vapor pressure, saturated vapor and liquid volumes, in temperature range from triple to critical point. A computer code using Matalab software is written to facilitate the calculation. The predicted resulted is compared with experimental data. The results reveled with exception SW EOSs all EOSs are inconsistent in the prediction of thermodynamics properties of the fluids under consideration. SW predicted all properties with absolute average percent deviation (AAPD) of less that 3**.**

**Keywords:** *Equation of state; saturated properties.*

## 1. INTRODUCTION

Numerous cubic equations of state have been developed since the appearance of Van der Waals (VDW) equation in 1873. A number of modifications of the VDW equation were made through the developments of its attractive term, $\frac{a}{V^2}$ .The general form of this type of modifications is

$$p = \frac{RT}{(V-b)} - \frac{a\alpha(T)}{(V^2 + ubV + wb^2)} \quad (1)$$

**Table (1 )**. modifications of attractive term of VDW EOS

| Authors | Year | Attractive term | U | w |
|---|---|---|---|---|
| Two parameters equations | | | | |
| Van Der Waals(VDW) | 1873 | $\frac{a}{V^2}$ | 0 | 0 |
| Soave-Redlich-Kwong(SRK) | 1972 | $\frac{a(T)}{V(V+b)}$ | 1 | 0 |
| Peng-Robinson (PR) | 1976 | $\frac{a(T)}{V(V+b)+b(V-b)}$ | 2 | -1 |
| Three parameters equations | | | | |
| Schmidt-Wenzel(SW) | 1980 | $\frac{a(T)}{V^2+(1+3\omega)bV-3\omega b^2}$ | 1+3ω | -3ω |
| Patel-Teja(PT) | 1982 | $\frac{a(T)}{V(V+b)+c(V-b)}$ | (b+c)/b | -c/b |
| Four parameters equations | | | | |
| Adachi-Lu-Sugie(ALS) | 1983 | $\frac{a(T)}{(V-b_2)(V+b_3)}$ | $(b_2-b_1)/b$ | $-b_1b_2/b^2$ |
| Lawal-Lake-Silberberg (LLS) | 1983 | $\frac{a\alpha(T)}{(V^2+\alpha bV-\beta b^2)}$ | A | -β |

## 2. Property Models

The calculation of the vapor pressure of a pure component through an equation of state usually is made by an algorithm; the same algorithm is used to calculate the saturated phase (liquid and vapor) volumes.

Equation (1) had been applied as a basis to calculate saturated properties for pure components.

Z-Form of equation (1) is as follows.

$$\Phi_3 Z^3 + \Phi_2 Z^2 + \Phi_1 Z + \Phi_0 = 0 \qquad (2)$$

Where

$\Phi_3$=1 , $\Phi_2$= - [1+ (1-u) B]

$\Phi_1$= [A- uB + (w-u) $B^2$] , $\Phi_0$= - [AB+w ($B^2$+$B^3$)]

$$A = \frac{a\alpha(T)P}{R^2T^2} \quad , \quad B = \frac{bP}{RT}$$

The initial guess pressure can be obtained from Antoine equation

$$\ln P = C_1 - C_2 /(T + C_3) \qquad (3)$$

Where C1, C2, C3 are Antoine constants.

The fugacity coefficient can be calculated from

$$\ln \frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{B(u^2 - 4w)^{0.5}} \ln \left( \frac{Z + (u + (u^2 - 4w)^{0.5}) \frac{B}{2}}{Z + (u - (u^2 - 4w)^{0.5}) \frac{B}{2}} \right)$$

(4)

The saturated volumes can be obtained from the following equation as

$$Z = \frac{PV}{RT} \Rightarrow V = \frac{ZRT}{P} \qquad (5)$$

The absolute average percent deviation(AAPD) for each property (P)

calculates from

$$AAPD = \frac{1}{N} \left| \frac{(P_{\exp} - P_{cal}) * 100}{P_{\exp}} \right| \qquad (6)$$

Where N is the Number of data points.

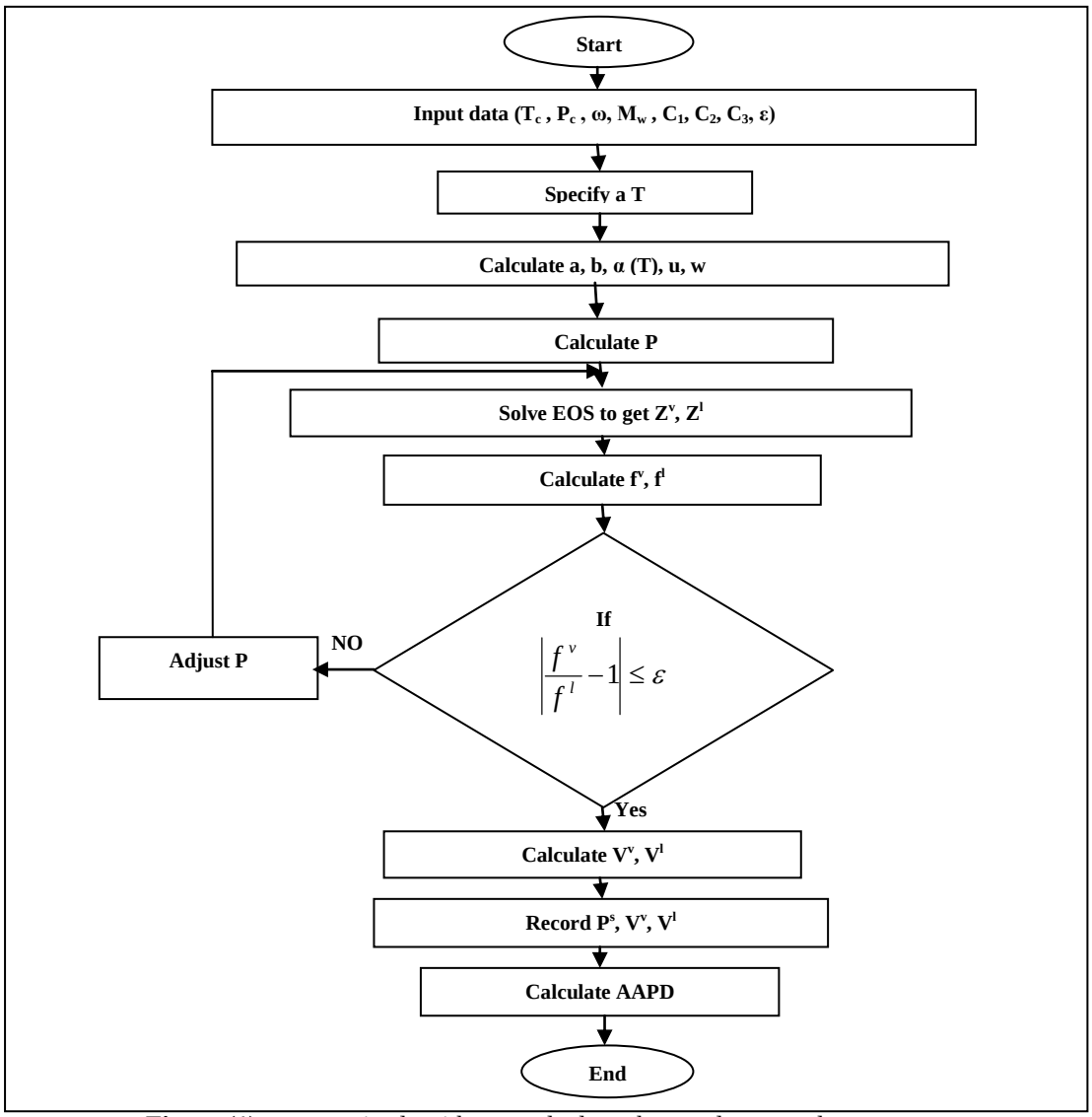


**Figure (1).** systematic algorithm to calculate phase volumes and vapor pressure

## 3. Results

For comparison between calculated and Experimental data, the average absolute percent deviation (AAPD) as computed. A flow diagram is presented in figure (1) to illustrate the procedure of calculating Vapor pressure and saturated phase volumes. A computer code using MATLAB was written to facilitate the calculations.

**Table (2).** Average Absolute Percent Deviation of six Equations of state in predicting vapor pressure of pure hydrocarbon compounds

| Comp. | SRK | PR | SW | PT | LLS | ALS | No. of data points | $T_r$ range | | Data source |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $T_{r,min}$ | $T_{r,max}$ | |
| C1 | 0.13 | 0.03 | 0.31 | 0.10 | 0.06 | 0.05 | 10 | 0.5248 | 0.9971 | Perry.1997 |
| C2 | 0.09 | 0.05 | 0.08 | 0.13 | 0.04 | 0.05 | 10 | 0.3275 | 0.9826 | Perry.1997 |
| C3 | 0.18 | 0.05 | 0.09 | 0.06 | 0.04 | 0.06 | 9 | 0.3245 | 0.9734 | Perry.1997 |
| C4 | 0.21 | 0.10 | 0.12 | 0.14 | 0.12 | 0.05 | 10 | 0.3293 | 0.9880 | Perry.1997 |
| i-C4 | 0.20 | 0.02 | 0.07 | 0.07 | 0.06 | 0.03 | 9 | 0.3920 | 0.9801 | Perry.1997 |
| C5 | 0.06 | 0.02 | 0.02 | 0.03 | 0.02 | 0.03 | 8 | 0.7132 | 0.9368 | VDI, 2007 |
| C6 | 0.11 | 0.04 | 0.03 | 0.06 | 0.07 | 0.06 | 8 | 0.7289 | 0.9358 | VDI, 2007 |
| C7 | 0.06 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 10 | 0.5553 | 0.9256 | Perry.1997 |
| C8 | 0.16 | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 | 9 | 0.4924 | 0.9847 | Perry.1997 |
| C9 | 0.09 | 0.01 | 0.00 | 0.02 | 0.01 | 0.04 | 10 | 0.5045 | 0.9754 | Perry.1997 |
| C10 | 0.06 | 0.00 | 0.01 | 0.02 | 0.01 | 0.03 | 9 | 0.4533 | 0.9713 | Perry.1997 |
| $AAPD_{grand}$ | 0.12 | 0.03 | 0.07 | 0.06 | 0.04 | 0.04 | 102 | | | |
| $AAPD_{min}$ | 0.06 | 0.00 | 0.00 | 0.02 | 0.01 | 0.01 | | | | |
| $AAPD_{max}$ | 0.21 | 0.10 | 0.31 | 0.14 | 0.12 | 0.06 | | | | |

**Table (3).** Average Absolute Percent Deviation of six Equations of state in predicting vapor pressure of pure non-hydrocarbon compounds

| Comp. | SRK | PR | SW | PT | LLS | ALS | No. of data points | Tr range | | Data source |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Tr,min | Tr,max | |
| $H_2O$ | 0.03 | 0.01 | 0.01 | 0.02 | 0.03 | 0.02 | 10 | 0.5872 | 0.9735 | Perry.1997 |
| $H_2S$ | 0.10 | 0.02 | 0.04 | 0.04 | 0.03 | 0.03 | 8 | 0.5890 | 0.9638 | VDI,2007 |
| $CO_2$ | 0.29 | 0.07 | 0.07 | 0.10 | 0.27 | 0.10 | 10 | 0.7232 | 0.9862 | Perry.1997 |
| $N_2$ | 0.14 | 0.02 | 0.12 | 0.11 | 0.07 | 0.05 | 10 | 0.5155 | 0.9913 | Perry.1997 |
| $AAPD_{grand}$ | 0.14 | 0.03 | 0.06 | 0.07 | 0.10 | 0.05 | 38 | | | |
| $AAPD_{min}$ | 0.03 | 0.01 | 0.01 | 0.02 | 0.03 | 0.02 | | | | |
| $AAPD_{max}$ | 0.29 | 0.07 | 0.12 | 0.11 | 0.27 | 0.10 | | | | |

**Table (4).** Average Absolute Percentage Deviation of six Equations of state in predicting Saturated vapor volume of pure hydrocarbon compounds

| Comp. | SRK | PR | SW | PT | LLS | ALS | No. of data points | Tr range | | Data source |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $T_{r,min}$ | $T_{r,max}$ | |
| C1 | 2.40 | 1.03 | 1.71 | 1.56 | 6.40 | 1.09 | 10 | 0.5248 | 0.9971 | [5] |
| C2 | 1.45 | 0.38 | 0.55 | 0.61 | 2.41 | 0.32 | 10 | 0.3275 | 0.9826 | [5] |
| C3 | 1.64 | 0.57 | 0.58 | 0.54 | 2.05 | 0.45 | 9 | 0.3245 | 0.9734 | [5] |
| C4 | 2.08 | 0.43 | 0.57 | 0.71 | 4.87 | 0.48 | 10 | 0.3293 | 0.9880 | [5] |
| i-C4 | 1.91 | 0.55 | 0.66 | 0.66 | 2.88 | 0.53 | 9 | 0.3920 | 0.9801 | [5] |
| C5 | 3.39 | 1.19 | 1.52 | 1.41 | 0.85 | 1.24 | 8 | 0.7132 | 0.9368 | [15] |
| C6 | 3.19 | 1.39 | 1.53 | 1.36 | 6.26 | 1.39 | 8 | 0.7289 | 0.9358 | [15] |
| C7 | 4.13 | 2.86 | 2.82 | 2.75 | 2.98 | 2.71 | 10 | 0.5553 | 0.9256 | [5] |
| C8 | 4.90 | 3.05 | 2.89 | 2.65 | 4.1 | 2.58 | 9 | 0.4924 | 0.9847 | [5] |
| C9 | 10.37 | 8.85 | 8.43 | 8.43 | 7.72 | 8.62 | 10 | 0.5045 | 0.9754 | [5] |
| C10 | 8.78 | 7.33 | 6.88 | 6.79 | 6.49 | 6.76 | 9 | 0.4533 | 0.9713 | [5] |
| $AAPD_{grand}$ | 4.02 | 2.51 | 2.56 | 2.50 | 4.27 | 2.38 | 102 | | | |
| $AAPD_{min}$ | 1.45 | 0.38 | 0.55 | 0.61 | 2.41 | 0.32 | | | | |
| $AAPD_{max}$ | 10.37 | 8.85 | 8.43 | 8.43 | 7.72 | 8.62 | | | | |

**Table (5).** Average Absolute Percentage Deviation of six Equations of state in predicting Saturated vapor volume of pure non- hydrocarbon compounds

| Comp. | SRK | PR | SW | PT | LLS | ALS | No. of data points | $T_r$ range | | Data source |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $T_{r,min}$ | $T_{r,max}$ | |
| $H_2O$ | 5.55 | 3.55 | 3.47 | 3.21 | 3.17 | 12.39 | 10 | 0.5872 | 0.9735 | [5] |
| $H_2S$ | 6.18 | 4.54 | 5.17 | 5.15 | 5.72 | 4.93 | 8 | 0.5890 | 0.9638 | [15] |
| $CO_2$ | 3.12 | 0.69 | 0.61 | 0.54 | 3.75 | 0.65 | 10 | 0.7232 | 0.9862 | [5] |
| $N_2$ | 1.16 | 1.10 | 0.56 | 0.46 | 3.50 | 0.59 | 10 | 0.5155 | 0.9913 | [5] |
| $AAPD_{grand}$ | 4.00 | 2.47 | 2.45 | 2.34 | 4.04 | 4.64 | 38 | | | |
| $AAPD_{min}$ | 1.16 | 0.69 | 0.56 | 0.46 | 3.17 | 0.59 | | | | |
| $AAPD_{max}$ | 5.55 | 4.54 | 5.17 | 5.15 | 5.72 | 12.39 | | | | |

**Table (6**). Average Absolute Percentage Deviation of six Equations of state in predicting Saturated liquid volume of pure hydrocarbon compounds

| Comp. | SRK | PR | SW | PT | LLS | ALS | No. of data points | $T_r$ range | | Data source |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $T_{r,min}$ | $T_{r,max}$ | |
| C1 | 21.46 | 8.86 | 6.45 | 5.83 | 46.47 | 4.87 | 10 | 0.5248 | 0.9971 | [5] |
| C2 | 9.17 | 7.04 | 3.44 | 3.51 | 35.82 | 3.78 | 10 | 0.3275 | 0.9826 | [5] |
| C3 | 11.21 | 5.46 | 3.40 | 3.46 | 35.39 | 3.69 | 9 | 0.3245 | 0.9734 | [5] |
| C4 | 13.46 | 5.34 | 4.41 | 4.5 | 32.44 | 4.49 | 10 | 0.3293 | 0.9880 | [5] |
| i-C4 | 12.59 | 5.67 | 3.91 | 4.11 | 41.75 | 3.75 | 9 | 0.3920 | 0.9801 | [5] |
| C5 | 16.11 | 2.96 | 3.65 | 3.3 | 52.08 | 3.51 | 8 | 0.7132 | 0.9368 | [15] |
| C6 | 18.04 | 3.09 | 3.42 | 3.18 | 49.98 | 3.40 | 8 | 0.7289 | 0.9358 | [15] |
| C7 | 17.53 | 2.58 | 1.85 | 1.94 | 37.02 | 1.82 | 10 | 0.5553 | 0.9256 | [5] |
| C8 | 23.37 | 7.92 | 4.62 | 4.95 | 38.78 | 4.97 | 9 | 0.4924 | 0.9847 | [5] |
| C9 | 21.58 | 6.38 | 2.44 | 2.74 | 29.22 | 2.63 | 10 | 0.5045 | 0.9754 | [5] |
| C10 | 24.59 | 9.23 | 3.23 | 3.57 | 31.16 | 3.49 | 9 | 0.4533 | 0.9713 | [5] |
| $AAPD_{grand}$ | 17.19 | 5.87 | 3.71 | 3.74 | 39.10 | 3.67 | 102 | | | |
| $AAPD_{min}$ | 9.17 | 2.58 | 1.85 | 1.94 | 29.22 | 1.82 | | | | |
| $AAPD_{max}$ | 24.59 | 9.23 | 6.45 | 5.83 | 52.08 | 4.97 | | | | |

**Table (7).** Average Absolute Percent Deviation of six Equations of state in predicting Saturated liquid volume of pure non- hydrocarbon compounds

| Comp. | SRK | PR | SW | PT | LLS | ALS | No. of data points | $T_r$ range | | Data source |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $T_{r,min}$ | $T_{r,max}$ | |
| $H_2O$ | 44.06 | 25.72 | 24.37 | 24.16 | 76.62 | 24.73 | 10 | 0.5872 | 0.9735 | Perry.1997 |
| $H_2S$ | 11.67 | 5.06 | 5.88 | 4.68 | 38.9 | 5.28 | 8 | 0.5890 | 0.9638 | VDI, 2007 |
| $CO_2$ | 16.21 | 4.36 | 4.58 | 4.48 | 63.88 | 4.21 | 10 | 0.7232 | 0.9862 | Perry.1997 |
| $N_2$ | 7.14 | 10.3 | 5.21 | 6.24 | 30.41 | 4.65 | 10 | 0.5155 | 0.9913 | Perry.1997 |
| $AAPD_{grand}$ | 19.77 | 11.36 | 10.01 | 9.89 | 52.45 | 9.72 | 38 | | | |
| $AAPD_{min}$ | 7.14 | 4.36 | 4.58 | 4.48 | 30.41 | 4.21 | | | | |
| $AAPD_{max}$ | 44.06 | 25.72 | 24.37 | 24.16 | 76.62 | 24.73 | | | | |

The tables (2 through 7) show a summary of AAPD for eleven hydrocarbon compounds using 102 data points and four non- hydrocarbon compounds using 38 data points from literature.

## 4. Discussion

**Vapor pressure:** Pure hydrocarbon compounds: Table (2) shows that All EOSs produced results with a grand AAPD ≤0.12. Although the six EOSs yielded good results, PR EOS is superior to other five EOSs. For Pure non-hydrocarbon compounds: Table (3) shows that All EOSs produced results with a grand AAPD ≤ 0.14. The six EOSs yielded good results, while PR EOS is superior to other five EOSs.

**Saturated vapor volume:** Pure hydrocarbon compounds: Table (4) shows that the six EOSs produced results with a grand AAPD exceed 2.0. The maximum AAPD for six EOSs is more than 6.0. Although PR, SW, PT and ALS EOS yield good results, ALS EOS is superior to other EOSs. For Pure non-hydrocarbon compounds: Table (5) shows that the six EOSs produced results with a grand AAPD between 2.0 and 5.0. Although all EOSs yielded good results, PT EOS is superior to other EOSs.

**Saturated liquid volume:** Pure hydrocarbon compounds: Table (6) shows that All EOSs except SRK and LLS EOS

produced results with a grand AAPD between 3.0 and 6.0.. Although the four EOSs yield good results, ALS EOS is superior to other EOSs. For Pure non-hydrocarbon compounds: Table (7) shows that All EOSs except LLS EOS produced results with a grand AAPD more than 9.0 . Although all EOSs except SRK EOS yield good results, ALS EOS is superior to other EOSs.

**Nomenclature**

| | |
|---|---|
| A | Coefficient of Equation of state |
| A | Dimensionless constant |
| B | Coefficient of Equation of state |
| B | Dimensionless constant |
| C | Parameter of Equation of state |
| F | Fugacity |
| P | Pressure |
| R | Universal Gas Constant |
| T | Temperature |
| U | Parameter of Equation of state |
| V | Volume |
| w | Parameter of Equation of state |
| Z | Compressibility factor |

**Greek symbols**

| | |
|---|---|
| A | Parameter of Equation of state |
| B | Parameter of Equation of state |
| ω | Acentric factor |

**Subscripts and Superscripts**

| | |
|---|---|
| C | critical property |
| cal | calculated |
| exp | Experimental |
| max | Maximum |
| min | Minimum |
| L | Liquid |
| R | Reduced |
| V | vapor |

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