



Comparative Study of Equations of State

S. A. Abdul-Aziz¹, A. A. Rabah²

¹Department of Chemical Engineering, University of Khartoum,

²Department of Chemical Engineering, University of Khartoum,
 Khartoum, Sudan (E-mail: rabahssr@uofk.edu)

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	$\frac{a(T)}{V^2 + (1 + 3\omega)bV - 3\omega b^2}$	$1 + 3\omega$	-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	$\frac{a(T)}{(V - b_2)(V + b_3)}$	$(b_2 - b_1)/b$	$-b_1 b_2 / b^2$
Lawal-Lake-Silberberg (LLS)	1983	$\frac{a\alpha(T)}{(V^2 + \alpha bV - \beta b^2)}$	A	$-\beta$

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.

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

Where

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

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

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

The initial guess pressure can be obtained from Antoine equation

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

Where C1, C2, C3 are Antoine constants.

The fugacity coefficient can be calculated from

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

(4)

The saturated volumes can be obtained from the following equation as

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

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

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

Where N is the Number of data points.

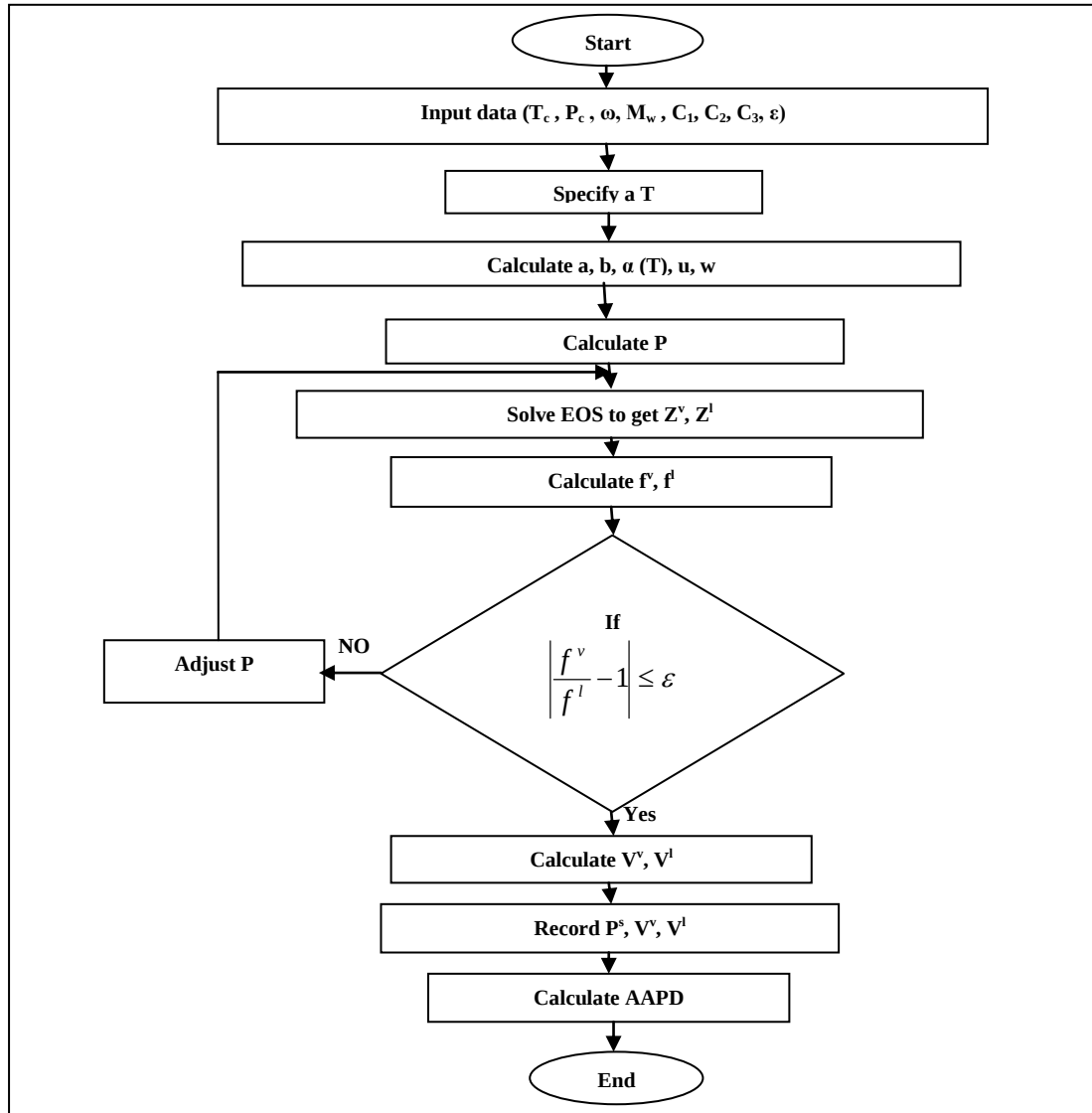


Figure (1). systematic algorithm to calculate phase volumes and vapor pressure

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 ₂ O	0.03	0.01	0.01	0.02	0.03	0.02	10	0.5872	0.9735	Perry.1997
H ₂ S	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	Tr range		Data source
								T _{r,min}	T _{r,max}	
H ₂ O	5.55	3.55	3.47	3.21	3.17	12.39	10	0.5872	0.9735	[5]
H ₂ S	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 ₂ O	44.06	25.72	24.37	24.16	76.62	24.73	10	0.5872	0.9735	Perry.1997
H ₂ S	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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