

A New Four-Parameter Cubic Equation of State for Predicting Fluids Phase Behavior

*ZhiRen He**

Science and Technology Research Institute, China University of Petroleum (Beijing), Beijing
102249, China

ABSTRACT: A new four-parameter cubic equation of state (EoS) is generated by incorporating the critical compressibility factor (Z_c) apart from the critical pressure (P_c) and temperature (T_c). One free parameter in the denominator of the attractive term and two parameters in the alpha function are adjusted using the experimental data of saturated liquid density, vapor pressure, and isobaric liquid heat capacity of 48 components including hydrocarbons and non-hydrocarbons. Applying this equation of state, saturated liquid density, saturated vapor density, and vapor pressure of pure components are accurately reproduced compared with experimental values. Furthermore, the predicted properties including derivatives of alpha function, such as enthalpy of vaporization, entropy of vaporization and isobaric heat capacity of liquid, also have decent accuracy. The global average absolute relative deviation (AAD) of saturated liquid density, saturated vapor density, saturated vapor pressure, enthalpy of vaporization, entropy of vaporization, and isobaric heat capacity of liquid in a wide reduced temperature (T_r) range of subcritical region reproduced by this work are 4.33%, 4.18%, 3.19%, 2.26%, 2.27%, and 5.82%,

1 respectively. Substantial improvement has been achieved for the isobaric liquid heat capacity
2 calculation.

3 Keywords: cubic equation of state, critical compressibility factor, isobaric heat capacity
4

5 1. INTRODUCTION

6 Equation of state is of fundamental instrument for thermodynamic properties prediction of both
7 pure substance and mixtures as well as simulating fluids phase behavior for practical application.
8 Cubic EoS is an outstanding member of the EoS family equipped with balanced feature of
9 simplicity, accuracy, and computational speed. Therefore, cubic EoSs are widely applied in
10 reservoir modelling, petrochemical industries, chemical design, and separation processes.

11 Since the time van der Waals proposed the first cubic equation of state, numerous equation of
12 state have been deduced by either revising the repulsive term[1] or modifying the attractive
13 term[2] in order to improve its predictive capability. Among them, Soave[3] (SRK EoS) and
14 Peng and Robinson[4] (PR EoS) developed probably the most successful cubic equations of state
15 for vapor liquid equilibrium calculation. However, both of these two generic cubic EoSs
16 assumed a particular critical compressibility factor for all substances, 0.333 and 0.307,
17 respectively, which violates the facts of component dependent critical compressibility. Therefore,
18 the predicted densities differ significantly from their experimental values, so do some related
19 properties. Many attempts have been made to counter this weakness. Equations of state proposed
20 by Schmit and Wenzel[5], Patel and Teja[6], and Trebble and Bishnoi[7] introduced a
21 component dependent empirical critical compressibility. While this parameter, in general, does
22 not equal to the experimental value of critical compressibility of fluids, the new free parameter
23 made the deviation of the thermodynamic properties to be adjustable, and subsequently improved

1 the accuracy of the EoSs. On the other hand, the work conducted by Guennec and Privat[8]
 2 recently showed the volume translated-consistent Peng-Robinson (tc-PR) and the volume
 3 translated-consistent Redlich-Kwong (tc-RK) EoSs could noticeably eliminate the apparent
 4 discrepancy of the saturated densities reproduced by the original PR and RK EoSs.

5 Instead of using an empirical critical compressibility factor as those three parameter cubic
 6 EoSs, the present work integrate the experimental critical compressibility factor, and introduce a
 7 fourth parameter as a free one to be determined by minimizing the deviation of the saturated
 8 liquid density. Moreover, the Melhem[9] type of alpha function is found to be suitable for the
 9 attractive term of the new EoS,

10

11 2. THE NEW CUBIC EQUATION OF STATE

12 The equation of state proposed in this work has the following form:

13

$$14 \quad P = \frac{RT}{V-b} - \frac{a(T)}{V^2+ubV+wb^2} \quad (1)$$

15

16 Where R is the universal gas constant, a(T) is function of temperature, while b, w, and u are
 17 temperature independent constant for particular component.

18 The arrangement of the cubic equation chosen here is not fresh, identical forms having been
 19 chosen earlier by Schmit and Wenzel[5], Adachi et al.[10], Jan et al.[11]. By imposing the van
 20 der Waals constraints at the critical point, the following set of equations are obtained:

21

$$22 \quad a(T) = a_c \alpha(T) \quad (2)$$

$$23 \quad a_c = \Omega_a \frac{R^2 T_c^2}{P_c} \quad (3)$$

$$24 \quad b = \Omega_b \frac{RT_c}{P_c} \quad (4)$$

1
$$w = \frac{(u+2)^3 Z_c^3 - 3(2u+1)^2 Z_c^2 + 3u(2u+1)Z_c - u^2}{(u-1)(3Z_c-1)^2} \quad (5)$$

2 where

3
$$\Omega_a = \left(\frac{u-2Z_c-uZ_c}{u-1}\right)^3 \quad (6)$$

4
$$\Omega_b = -\frac{3Z_c-1}{u-1} \quad (7)$$

5

6 In this particular work, the following Melhem[9] type of alpha function is employed for the
7 proposed EoS:

8
$$\alpha(T) = \exp[m(1 - T_r) + n(1 - \sqrt{T_r})^2] \quad (8)$$

9 Equations (1) - (8) complete the description of the new cubic EoS.

10 48 pure components including hydrocarbons and non-hydrocarbons are selected to adjust the
11 undetermined parameters in the new EoS. Table 1 presents the pure fluids, which were used to
12 correlate the physical properties, with the number of data points (NDP), critical properties, and
13 ranges of reduced temperature and pressure, together with acentric factor (ω) for each
14 component.

15

16 Table 1. Pure Components, Number of Experimental Data Points, Critical Constant, Range of
17 Reduced Temperature, Pressure Range, and Acentric Factor Used in This Work.

component	NDP	Tc / K	Pc / MPa	Tr range	P range / MPa	ω^c
methane ^a	11	190.56	4.599	0.476 - 0.997	0.0117 - 4.519	0.011
ethane ^a	12	305.32	4.872	0.296 - 0.983	1.10E-06 - 4.357	0.0995
propane ^a	15	369.89	4.251	0.231 - 0.973	1.70E-10 - 3.555	0.1523
butane ^a	14	425.13	3.796	0.317 - 0.988	6.66E-07 - 3.49	0.2002
isobutane ^a	13	407.81	3.629	0.279 - 0.981	2.29E-08 - 3.186	0.1808

pentane ^b	23	469.7	3.371	0.305 - 0.990	7.63E-08 - 3.1355	0.2515
neopentane ^b	19	433.74	3.1963	0.592 - 0.991	0.035401 - 3.0111	0.1957
hexane ^b	23	507.82	3.0429	0.350 - 0.975	1.28E-06 - 2.5196	0.3013
heptane ^b	19	540.13	2.7311	0.338 - 0.972	1.75E-07 - 2.207	0.3495
octane ^b	19	569.32	2.4978	0.380 - 0.984	1.99E-06 - 2.1958	0.3996
nonane ^b	19	594.55	2.282	0.370 - 0.942	4.44E-07 - 1.4023	0.4435
decane ^b	20	617.7	2.1014	0.394 - 0.988	1.40E-06 - 1.8918	0.4923
dodecane ^b	21	658.1	1.8176	0.401 - 0.988	6.26E-07 - 1.6298	0.5764
ethylene ^a	13	282.35	5.042	0.368 - 0.992	0.000122 - 4.784	0.0865
propylene ^a	12	364.21	4.555	0.241 - 0.988	7.47E-10 - 4.219	0.142
1-butene ^b	19	419.29	4.0057	0.209 - 0.966	5.95E-13 - 3.1556	0.1845
cis-2-butene ^b	21	435.75	4.236	0.308 - 0.975	2.64E-07 - 3.5654	0.2019
trans-2-butene ^b	19	428.61	4.0191	0.391 - 0.992	7.48E-05 - 3.7851	0.2176
cyclohexane ^b	28	553.64	4.075	0.505 - 0.993	0.0052538 - 3.8928	0.2081
methanol ^b	24	513.38	8.2159	0.342 - 0.993	1.86E-07 - 7.7496	0.5658
ethanol ^a	18	514.71	6.268	0.311 - 0.971	9.02E-10 - 4.872	0.6451
benzene ^a	11	562.02	4.906	0.496 - 0.979	0.004784 - 4.223	0.2103
toluene ^a	16	591.75	4.126	0.301 - 0.929	3.94E-08 - 2.428	0.264
acetone ^b	23	508.1	4.6924	0.351 - 0.974	2.33E-06 - 3.8632	0.3065
R-23 ^b	19	299.29	4.8317	0.394 - 0.969	5.80E-05 - 3.8516	0.2641
R-22 ^b	18	369.3	4.99	0.313 - 0.975	3.79E-07 - 4.1837	0.2192
R-12 ^b	19	385.12	4.1362	0.301 - 0.974	2.43E-07 - 3.4527	0.1797
R-11 ^b	22	471.11	4.4076	0.345 - 0.987	6.51E-06 - 4.0318	0.1894
R-152a ^b	24	386.41	4.5168	0.400 - 0.983	6.41E-05 - 3.9966	0.2751
R-143a ^b	19	345.86	3.7618	0.466 - 0.983	0.0010749 - 3.325	0.2614
R-141b ^b	22	477.5	4.2117	0.355 - 0.995	6.49E-06 - 4.0574	0.2211
R-134a ^a	11	374.21	4.059	0.454 - 0.962	0.0003896 - 3.04	0.326

R-218 ^b	23	345.02	2.6402	0.364 - 0.985	2.02E-06 - 2.3634	0.328
neon ^b	21	44.492	2.6786	0.552 - 0.989	0.043464 - 2.5168	-0.0396
argon ^a	8	150.69	4.863	0.556 - 0.995	0.06889 - 4.735	-0.002
krypton ^b	19	209.48	5.5255	0.553 - 0.979	0.073503 - 4.869	0
xenon ^b	25	289.73	5.842	0.557 - 0.984	0.081748 - 5.3025	0
hydrogen ^a	11	32.94	1.286	0.419 - 0.971	0.007041 - 1.12	-0.216
hydrogen sulfide ^a	15	373.1	9.00	0.503 - 0.992	0.02326 - 8.529	0.0942
water ^a	25	647.1	22.064	0.422 - 0.978	0.000612 - 18.666	0.3449
ammonia ^a	12	405.4	11.33	0.482 - 0.987	0.006091 - 10.3	0.2526
fluorine ^b	19	144.41	5.2394	0.370 - 0.969	0.00023881 - 4.3357	0.053
nitrogen ^a	7	126.19	3.396	0.500 - 0.951	0.01252 - 2.511	0.0377
oxygen ^a	11	154.58	5.043	0.352 - 0.970	0.0001463 - 4.219	0.0222
carbon monoxide ^a	8	132.86	3.494	0.513 - 0.978	0.01554 - 3.065	0.0916
carbon dioxide ^a	10	304.13	7.377	0.712 - 0.986	0.518 - 6.713	0.2236
sulfur dioxide ^a	13	430.64	7.884	0.459 - 0.975	0.00166 - 6.59	0.2441
nitrous oxide ^b	26	309.52	7.2447	0.589 - 0.985	0.087837 - 6.5663	0.1409

1 ^adata source from CRC Handbook of Chemistry and Physics, 95th Edition.[12]

2 ^bdata source from Perry's Chemical Engineers' Handbook, Eighth Edition.[13]

3 ^cdata source from Guennec and Privat.[8]

4

5 3. OBJECTIVE FUNCTION FOR IDENTIFYING OPTIMAL u , m AND n

6 A proper objective function is indispensable for obtaining the optimal value of those
7 undetermined parameters. The common form of the objective functions usually took the vapor
8 pressure and saturated liquid density into consideration, and different weighting factor set (w_1 ,
9 w_2) were used for authors, such as Dashtizadeh et al.[14], Nasrifar et al. [15], Bonyadi et al. [16]
10 set (0.8, 0.2), while Haghtalab et al. [17] sets (0.7, 0.3), for vapor pressure term and saturated

1 liquid density term, respectively. In contrast, in the literature of Guennec et al.[8], the properties,
 2 for instance enthalpy of vaporization and heat capacity, were incorporated into the objective
 3 function due to the enthalpy and heat capacity calculation involve the first and second derivatives
 4 of the alpha function with respect to temperature, while the vapor pressure and density
 5 calculation only involve the alpha function itself. Therefore, if the derivatives of alpha are not
 6 involved in the objective function, it may lead to parameters in the alpha function unsuitable for
 7 reproducing properties containing alpha derivatives.

8 In this work, objective function is also applied in order to acquire optimal value for those
 9 undetermined parameters in the new EoS, but the form of the objective functions used here are
 10 slightly different from those aforementioned, and details are described below. An interesting
 11 feature of the EoS proposed in this work is that the deviation of the saturated liquid density has
 12 weak correlation with the alpha value as long as the value belongs to the neighborhood of
 13 optimal alpha value, while strongly depend on the value of parameter u. Therefore, the procedure
 14 for identifying optimal u is decoupled from the procedure for identifying parameters in the alpha
 15 function.

16 In the present work, the following objective function one (OF₁), eq 10, is chosen to optimize
 17 the value of u, while the discrete alpha value derived from the phase equilibrium condition when
 18 experimental value of pressure is used as input parameter at each data point. The calculation is
 19 confined by the principle of iso-fugacities of two phases in equilibrium condition, eq 9. The
 20 principle denotes as below:

21

$$f^l = f^v \quad (9)$$

22

23

$$OF_1 = \frac{100}{NDP} \sum_{i=1}^{NDP} \left| \frac{\rho_{cal,i}^{sat,l} - \rho_{exp,i}^{sat,l}}{\rho_{exp,i}^{sat,l}} \right| \quad (10)$$

1
2
3
4
5
6
7
8
9
10

Instead of integrate the enthalpy of vaporization and isobaric heat capacity simultaneously, objective function two (OF₂), eq 11, which is used for optimizing m and n in the alpha function, include the isobaric heat capacity only in addition to the vapor pressure. The reason for this option is that the first derivative of alpha function with respect to temperature which involved in the enthalpy of vaporization calculation is also contained in the heat capacity calculation. Therefore, OF₂ include two terms, the pressure term and the heat capacity term. The weighting factors are 0.7 and 0.3 for w₁ and w₂, respectively. Phase equilibrium condition is also satisfied during the optimization. And the generalized form for parameter u was employed in this procedure.

$$OF_2 = \frac{100}{NDP} \left(w_1 \sum_{i=1}^{NDP} \left| \frac{P_{cal,i}^{sat} - P_{exp,i}^{sat}}{P_{exp,i}^{sat}} \right| + w_2 \sum_{i=1}^{NDP} \left| \frac{C_{p,i}^{sat,l,cal} - C_{p,i}^{sat,l,exp}}{C_{p,i}^{sat,l,exp}} \right| \right) \quad (11)$$

11
12
13
14
15
16

For the present work, the Genetic Algorithm in MATLAB toolbox has been utilized to optimize the regulable parameters. With this technique, the optimal values of u, m and n can be acquired respectively.

The generalized form of u denotes as eq 12:

$$u = 3.2475/Z_c - 8.8820 \quad (12)$$

17
18
19
20
21
22

For the nonpolar and slightly polar substance pool, where methanol, ethanol, water, acetone, and ammonia were excluded, the following generalized form, eq 13 and 14, could be used for the parameters m and n in the alpha function. And the relationship between m and n was elaborated in literature by Forero G. et al.[18].

$$m = 76.8570(\omega Z_c^2)^2 + 10.8880\omega Z_c^2 + 0.1486 \quad (13)$$

23

1
$$n = 2(3.2254\omega^3 - 2.7450\omega^2 + 1.8404\omega + 0.2319 - m^2) \quad (14)$$

2 In the case of polar substances (methanol, ethanol, water, acetone, and ammonia) included in
 3 Table 1, particular values for m and n are recommended in Table 2.

4 Table 2. Values of m and n for Particular Polar Components.

Component	m	n
Methanol	0.5818	0.3134
Ethanol	0.8249	0.2099
Acetone	0.3114	0.9019
Water	0.3474	0.7042
Ammonia	0.3533	0.6587

5

6 4. RESULTS AND DISCUSSION

7

8 In order to assess the performance of the newly proposed cubic EoS, calculation of some
 9 thermodynamic properties, including saturated liquid density, saturated vapor density, vapor
 10 pressure, enthalpy of vaporization, entropy of vaporization, and isobaric heat capacity of liquid,
 11 of pure substances are carried out. The thermodynamic relations for using eq 1 are provided in
 12 Appendix. Results are compared with the Jan et al.[11] (JT) EoS, the Adachi et al.[19] (ALS)
 13 EoS, the generalized tc-PR[8] EoS with Twu88 alpha function, and the generalized tc-RK[8]
 14 EoS with Twu88 alpha function. While addressing those substances listed in Table 2 with tc-PR
 15 and tc-RK EoS, the Twu91 alpha function is incorporated instead of Twu88 alpha function. The
 16 JT and ALS EoSs are selected as comparison is because they have the same form as the EoS
 17 proposed in this work, while developed with different methodology. The generalized tc-PR and
 18 tc-RK EoSs are involved due to their accuracy and the significance of original PR and RK EoSs.
 19 Results are categorized in Tables 3-5. The calculated average absolute relative deviations (AAD)

1 for each component presented in Table 1 and the global average absolute relative deviation are
 2 reported.

3 In Table 3, the predicted saturated liquid density and saturated vapor density of 48 pure
 4 substances are compared with experimental data, as well as the predictions given by the JT, ALS,
 5 tc-PR and tc-RK EoSs. In regard to Table 3, among the five EoSs, the JT EoS predicts the
 6 saturated liquid density better than the other four cubic EoSs package in terms of global AAD,
 7 while the results of this work ranking next to the JT EoS. The global AAD of the predicted
 8 saturated liquid density with the JT and this work EoSs are 3.52% and 4.33% respectively,
 9 whereas this value for ALS, tc-PR, and tc-RK EoSs are 4.41%, 4.76%, and 6.59%, respectively.
 10 However, the global representation of saturated vapor density shows that the tc-PR and tc-RK
 11 EoSs, which have very similar results of global AAD, 3.23% and 3.46% respectively, forecast
 12 more precise result than the JT, ALS and this work EoSs, 6.89% 5.32%, and 4.18% respectively.

13
 14 Table 3 The Percent of Average Absolute Relative Deviation in Correlation of the Saturated
 15 Liquid Density and Vapor Density Using Various Cubic EoSs for the Pure Components.

component	AAD (%)									
	liquid density					vapor density				
	JT	ALS	tc-PR	tc-RK	this work	JT	ALS	tc-PR	tc-RK	this work
Methane	3.12	4.41	5.46	7.58	3.18	2.30	1.29	2.30	2.46	2.89
Ethane	2.92	3.92	3.59	6.95	4.22	10.18	3.57	7.41	7.96	4.69
Propane	3.03 ^a	3.63	2.94	6.07	4.99	11.98 ^a	9.67	12.28	12.80	5.67
Butane	3.10	3.64	3.55	6.37	4.26	8.53	4.50	3.14	3.75	2.62
Isobutane	2.96	3.53	3.39	6.16	4.12	8.29	7.09	2.78	2.80	3.45

Pentane	3.57	3.75	3.16	5.71	4.85	12.05	6.92	3.41	4.47	2.58
Neopentane	3.52	3.77	4.57	6.47	6.26	2.21	0.83	0.82	0.54	2.79
Hexane	3.52	3.03	2.86	5.06	4.73	9.72	5.33	2.93	4.05	1.93
Heptane	4.43	3.53	3.69	4.37	5.22	9.98	9.42	1.48	2.57	4.03
Octane	3.42	3.02	3.95	4.81	5.25	7.11	7.00	1.43	2.84	2.87
Nonane	4.32	2.60	4.26	3.31	5.59	8.42	9.02	0.68	1.86	3.55
Decane	3.93	3.17	5.51	4.82	5.74	7.03	6.98	1.94	3.78	3.01
Dodecane	5.76	3.13	5.96	4.83	5.95	5.05	8.78	1.56	2.34	3.73
Ethylene	3.51	6.45	5.33	8.40	3.35	2.94	3.12	1.17	0.85	4.25
Propylene	3.79	5.70	3.74	5.89	5.16	11.12	11.60	2.95	2.60	3.64
1-Butene	3.04	4.26	2.67	4.88	4.92	11.59	10.56	5.04	4.34	3.10
cis-2-Butene	3.96	3.90	2.69	5.14	4.92	5.35	9.09	1.55	0.69	5.45
trans-2-Butene	3.01	5.13	3.37	5.72	4.37	8.93	2.25	6.30	7.00	8.99
Cyclohexane	2.01	2.95	3.63	5.89	3.71	1.79	3.84	3.01	2.96	2.23
Methanol	3.73	-	7.18	11.24	8.28	15.79	-	4.71	11.18	7.66
Ethanol	1.93 ^b	-	5.01	8.69	5.44	18.35 ^b	-	6.02	3.47	7.12
Benzene	2.19	3.81	2.51	5.31	3.01	2.10	3.48	1.97	1.63	2.90
Toluene	4.41	4.47	2.75	3.09	5.44	13.34	13.55	1.71	2.86	1.48
Acetone	4.74	-	4.42	7.81	6.08	8.14	-	6.75	3.05	3.12
R-23	4.04	9.07	7.66	5.85	4.75	6.72	2.91	4.44	5.25	10.31
R-22	3.62	5.20	3.04	4.51	5.01	6.51	8.72	1.32	1.24	2.11
R-12	3.02	2.69	2.99	6.15	4.67	8.09	8.05	1.74	2.34	3.34
R-11	3.02	2.62	3.31	6.37	4.27	4.80	5.66	0.84	1.11	4.91
R-152a	4.35	11.83	10.67	9.10	4.69	5.34	2.57	3.67	4.43	12.97
R-143a	3.14	10.52	9.23	8.28	4.19	2.86	1.98	2.37	2.78	8.91
R-141b	3.42	4.36	3.31	5.89	4.50	2.21	7.43	3.02	2.21	4.95

R-134a	2.82	4.51	4.37	4.52	4.41	2.36	3.44	0.73	1.33	2.29
R-218	3.01	4.93	5.35	8.08	4.54	10.37	4.52	4.66	5.73	4.94
Neon	2.99	3.79	7.37	8.47	1.35	3.19	1.44	2.09	1.90	2.49
Argon	3.42	4.39	5.88	7.57	2.86	2.67	0.82	1.79	1.56	2.39
Krypton	1.97	3.25	4.60	6.16	1.67	1.69	1.68	1.57	1.25	1.78
Xenon	2.09	4.93	4.05	5.73	1.86	1.78	1.31	1.16	0.83	2.04
Hydrogen	7.45	5.63	10.15	12.05	3.93	7.50	13.40	17.35	17.64	3.45
Hydrogen sulfide	1.92	3.52	3.83	5.67	3.05	3.29	1.83	1.41	1.34	3.55
Water	6.70	-	8.98	12.81	3.02	8.04	-	1.56	1.53	2.65
Ammonia	9.97	-	5.36	8.53	4.97	20.66	-	3.37	3.00	3.98
Fluorine	4.18	2.35	5.50	7.99	5.66	2.38	1.81	3.22	3.49	4.40
Nitrogen	2.06	2.60	5.26	7.02	2.39	2.60	0.88	1.53	1.47	2.65
Oxygen	2.16	2.65	4.93	7.66	3.19	3.79	1.08	4.57	4.92	2.90
Carbon monoxide	2.08	3.88	5.38	7.58	2.70	10.54	11.44	1.46	0.95	8.99
Carbon dioxide	2.27	4.27	4.27	5.96	3.93	1.87	0.93	0.92	0.47	2.43
Sulfur dioxide	3.29	5.20	3.53	4.68	3.74	3.58	5.37	3.23	2.81	4.79
Nitrous Oxide	1.87	5.85	3.34	5.28	3.65	5.42	3.63	3.68	3.53	3.59
Global	3.52	4.41	4.76	6.59	4.33	6.89	5.32	3.23	3.46	4.18

^aTr range 0.270 – 0.973. ^bTr range 0.466 – 0.971. “-”: blank.

2

3 Table 4 shows the predicted AAD of vapor pressure and enthalpy of vaporization for the 48
4 substances with selected and the new EoSs. In this comparison, the global AAD of vapor
5 pressure is 5.25%, 6.94%, 2.32%, 2.74%, and 3.19% using the JT, ALS, tc-PR, tc-RK and this

1 work EoSs, respectively. With the outcome of tc-PR EoS ranking first, while the results of this
 2 work ranking in the middle. In regarding to the enthalpy of vaporization, the global AAD of this
 3 work is 2.26%, slightly superior to the rest of EoSs. This value delivered by the JT ALS, tc-PR,
 4 and tc-RK EoSs are 3.46%, 2.80%, 2.33%, and 2.56%, respectively. Nevertheless, the
 5 differences are not obvious except the JT EoS,

6
 7 Table 4 The Percent of Average Absolute Relative Deviation in Correlation of the Vapor
 8 Pressure and Enthalpy of Vaporization Using Various Cubic EoSs for the Pure Components.

component	AAD (%)									
	vapor pressure					enthalpy of vaporization				
	JT	ALS	tc-PR	tc-RK	this work	JT	ALS	tc-PR	tc-RK	this work
Methane	1.01	0.77	1.56	1.91	1.60	5.02	4.12	4.77	4.96	3.84
Ethane	6.56	4.20	5.28	6.02	3.19	3.92	2.20	2.97	3.23	2.32
Propane	7.41 ^a	15.32	7.21	7.95	4.03	3.30 ^a	2.40	2.39	2.62	1.87
Butane	5.50	5.54	2.44	3.29	1.49	3.69	2.58	2.43	2.74	2.37
Isobutane	5.09	11.03	2.01	2.37	2.60	3.21	2.70	1.86	2.09	2.63
Pentane	7.68	9.17	2.79	3.95	1.82	3.54	2.61	1.99	2.33	1.80
Neopentane	0.59	0.59	0.41	0.69	1.68	3.05	2.20	2.05	2.13	2.82
Hexane	6.78	6.17	2.43	3.70	1.55	3.00	1.96	1.59	2.00	1.19
Heptane	7.05	12.70	0.97	2.27	4.25	2.40	2.52	0.90	1.31	0.87
Octane	5.38	8.10	0.81	2.34	2.63	2.21	2.36	1.00	1.50	0.68
Nonane	6.29	12.53	1.02	2.30	3.76	2.18	2.55	0.66	1.14	0.81
Decane	5.29	7.60	1.19	3.26	2.62	2.23	2.50	1.27	1.86	0.67
Dodecane	4.42	10.98	1.31	2.39	2.95	2.29	3.51	1.66	2.09	1.27

Ethylene	1.08	3.20	0.39	0.68	1.96	4.85	4.22	3.55	3.69	4.35
Propylene	6.83	25.13	2.86	2.86	2.70	3.83	3.73	2.72	2.49	2.62
1-Butene	5.56	33.05	4.85	4.48	2.63	2.00	2.75	1.26	1.27	1.28
cis-2-Butene	4.30	13.47	1.55	1.09	5.58	2.20	2.85	1.12	1.27	1.77
trans-2-Butene	6.45	1.60	5.06	5.62	7.02	4.11	2.42	3.40	3.78	3.09
Cyclohexane	1.34	1.79	1.11	1.28	2.09	0.94	2.81	2.24	2.28	1.74
Methanol	36.78	-	0.88	6.08	4.41	9.19	-	4.16	5.39	3.57
Ethanol	10.03 ^b	-	6.15	3.03	6.16	7.49 ^b	-	1.50	1.20	1.53
Benzene	1.70	3.73	2.05	1.85	2.25	1.73	2.77	1.89	1.81	2.15
Toluene	9.50	21.47	1.60	2.73	1.27	2.45	3.16	0.82	1.13	0.26
Acetone	9.47	-	4.75	0.73	1.99	2.67	-	3.35	2.85	1.48
R-23	4.82	1.77	3.00	3.98	8.18	2.85	1.84	2.43	2.85	2.73
R-22	4.84	12.19	1.11	1.45	1.50	2.37	2.70	1.24	1.53	0.94
R-12	5.67	11.13	1.30	2.18	2.77	2.74	2.60	1.21	1.49	1.71
R-11	3.56	6.96	0.57	1.00	4.53	2.82	2.41	1.25	1.58	2.45
R-152a	3.74	1.44	2.48	3.48	9.99	2.83	2.10	2.61	3.04	3.51
R-143a	1.61	0.71	1.19	1.95	7.00	2.53	2.06	2.52	2.97	3.13
R-141b	1.11	9.62	2.79	2.03	4.33	2.95	3.93	2.53	2.57	3.27
R-134a	1.64	3.15	0.26	1.25	1.69	1.85	1.97	1.29	1.77	0.67
R-218	7.05	4.70	3.91	4.79	4.77	3.47	2.20	1.95	2.39	2.02
Neon	2.32	1.04	1.23	1.51	0.94	3.28	2.24	2.58	2.72	2.93
Argon	1.19	0.34	0.95	1.10	1.02	5.19	4.21	4.67	4.83	5.00
Krypton	0.64	1.23	0.82	1.05	0.79	2.45	2.28	2.19	2.46	2.49
Xenon	0.49	0.84	0.58	0.90	0.93	2.65	2.30	2.17	2.29	2.95
Hydrogen	5.29	9.56	11.22	11.62	3.24	6.53	9.26	11.39	11.56	2.46
Hydrogen	2.45	1.99	1.34	1.64	1.91	3.17	2.03	1.70	1.73	3.51

sulfide

Water	9.72	-	0.50	0.31	2.06	4.10	-	1.32	1.61	0.72
Ammonia	11.78	-	1.83	1.24	2.45	10.96	-	2.34	2.90	2.12
Fluorine	1.31	1.44	2.36	2.82	3.65	2.02	1.38	1.86	2.15	1.11
Nitrogen	1.38	0.49	0.73	1.04	1.63	2.29	1.34	1.48	1.71	2.72
Oxygen	2.56	0.83	3.54	4.15	2.20	2.90	1.53	2.47	2.69	2.19
Carbon monoxide	8.37	9.32	0.57	0.63	7.42	5.04	4.89	2.27	2.03	3.33
Carbon dioxide	0.38	0.44	0.34	0.46	1.16	3.38	2.08	2.14	2.37	3.58
Sulfur dioxide	3.60	6.93	4.18	4.04	4.59	1.73	2.49	1.50	1.52	2.18
Nitrous oxide	4.26	3.95	3.69	4.18	1.88	4.67	3.57	3.38	2.95	4.05
Global	5.25	6.94	2.32	2.74	3.19	3.46	2.80	2.33	2.56	2.26

^aTr range 0.270 – 0.973. ^bTr range 0.466 – 0.971. “-”: blank.

2

3 Results of the entropy of vaporization and isobaric liquid heat capacity for the same pure

4 substances listed in Table 1 are presented in Table 5. It is found that the global AAD of the

5 predicted entropy of vaporization are very close to the outcomes of the enthalpy of vaporization.

6 Actually, this result parallels well with the thermodynamic theory of the relationship between

7 enthalpy of vaporization and entropy of vaporization at the condition of constant temperature and

8 saturated vapor pressure. In the final step of predictability investigation of the new EoS, global

9 AAD of isobaric liquid heat capacity are compared. The results are 16.41%, 11.06%, 10.61% and

10 11.22% for JT, ALS, tc-PR and tc-RK EoSs, respectively, which has been reduced down to 5.82%

11 by the new equation of state proposed in this work. As one can see a significant improvement is

12 achieved in the calculation of isobaric liquid heat capacity of pure components using the newly

13 proposed model.

1
2 Table 5 The Percent of Average Absolute Relative Deviation in Correlation of the Entropy of
3 Vaporization and Isobaric Liquid Heat Capacity Using Various Cubic EoSs for the Pure
4 Components.

component	AAD %									
	entropy of vaporization					liquid isobaric heat capacity				
	JT	ALS	tc-PR	tc-RK	this work	JT	ALS	tc-PR	tc-RK	this work
Methane	5.02	4.12	4.77	4.97	3.85	12.44	8.80	13.17	14.00	6.45
Ethane	3.92	2.21	2.97	3.22	2.32	16.95	9.69	14.83	14.89	8.74
Propane	3.31 ^a	2.42	2.41	2.64	1.87	14.20 ^a	9.44	14.21	13.87	7.81
Butane	3.68	2.58	2.43	2.74	2.35	10.74	8.28	8.11	8.38	5.63
Isobutane	3.22	2.68	1.85	2.10	2.64	10.69	8.39	8.39	8.65	5.03
Pentane	3.55	2.61	1.99	2.33	1.80	10.03	8.09	6.99	7.01	4.63
Neopentane	3.05	2.20	2.04	2.13	2.82	5.81	6.64	5.79	6.63	3.89
Hexane	3.00	1.96	1.59	2.00	1.19	8.94	5.64	5.61	5.65	4.05
Heptane	2.40	2.52	0.90	1.32	0.87	6.88	6.28	3.70	3.61	1.86
Octane	2.21	2.35	1.00	1.50	0.68	5.52	5.72	3.15	3.24	1.80
Nonane	2.17	2.55	0.66	1.14	0.81	5.53	5.10	2.64	2.55	1.72
Decane	2.23	2.50	1.27	1.86	0.67	5.54	5.37	3.64	3.78	2.81
Dodecane	2.29	3.51	1.66	2.09	1.27	4.78	6.15	3.46	3.66	2.75
Ethylene	4.85	4.22	3.55	3.69	4.35	14.35	16.73	14.26	15.65	9.15
Propylene	3.81	3.71	2.70	2.47	2.61	13.47	12.54	11.60	12.02	5.84
1-Butene	2.00	2.75	1.26	1.27	1.28	9.86	9.20	7.45	7.53	4.16
cis-2-Butene	2.20	2.85	1.12	1.27	1.77	13.56	9.79	9.66	9.64	7.00
trans-2-butene	4.11	2.42	3.40	3.78	3.09	6.82	10.48	6.66	7.03	3.99

Cyclohexane	0.94	2.81	2.24	2.28	1.74	4.05	6.38	5.19	5.68	3.49
Methanol	9.19	-	4.16	5.39	3.57	89.16	-	7.64	12.97	6.22
Ethanol	7.49 ^b	-	1.50	1.21	1.54	48.66 ^b	-	6.81	6.62	6.37
Benzene	1.74	2.76	1.88	1.81	2.16	3.15	10.34	6.59	7.24	4.77
Toluene	2.45	3.17	0.83	1.14	0.26	8.60	9.77	4.82	4.26	1.90
Acetone	2.67	-	3.35	2.85	1.48	10.25	-	7.35	8.07	5.54
R-23	2.85	1.84	2.43	2.85	2.73	15.88	9.51	11.66	12.05	11.23
R-22	2.36	2.70	1.24	1.53	0.95	13.22	11.75	8.94	8.97	6.16
R-12	2.74	2.60	1.21	1.49	1.71	10.55	10.74	6.86	6.83	3.50
R-11	2.82	2.42	1.25	1.58	2.45	9.98	8.67	6.61	6.82	3.80
R-152a	2.83	2.10	2.61	3.05	3.51	13.31	9.74	10.87	11.37	10.77
R-143a	2.54	2.06	2.52	2.97	3.13	11.51	8.99	9.64	10.44	9.44
R-141b	2.95	3.93	2.53	2.57	3.27	6.64	11.70	6.08	7.20	5.06
R-134a	1.83	1.97	1.29	1.76	0.67	10.66	8.77	6.87	7.46	5.82
R-218	3.47	2.21	1.95	2.39	2.02	10.13	7.32	5.57	5.79	2.79
Neon	3.28	2.24	2.58	2.72	2.93	14.76	12.46	15.07	16.08	5.22
Argon	5.18	4.24	4.70	4.85	4.99	12.15	11.29	13.27	14.45	6.80
Krypton	2.45	2.28	2.19	2.46	2.49	14.80	11.66	13.72	14.85	6.34
Xenon	2.65	2.30	2.17	2.29	2.95	14.19	12.49	13.32	14.60	7.22
Hydrogen	6.53	9.27	11.40	11.57	2.47	63.27	77.19	96.07	96.98	8.78
Hydrogen sulfide	3.16	2.02	1.70	1.72	3.50	8.88	10.22	7.82	9.40	4.90
Water	4.10	-	1.32	1.61	0.72	38.94	-	8.82	9.72	9.56
Ammonia	10.96	-	2.33	2.89	2.12	93.02	-	11.43	12.44	7.69
Fluorine	2.02	1.38	1.86	2.15	1.11	11.36	8.54	10.63	10.91	5.17
Nitrogen	2.30	1.35	1.49	1.72	2.73	11.17	9.08	9.57	10.27	4.70
Oxygen	2.90	1.52	2.46	2.68	2.19	14.99	8.67	14.57	14.90	5.49

Carbon monoxide	5.02	4.88	2.27	2.04	3.33	18.44	11.98	9.31	10.18	11.00
Carbon dioxide	3.39	2.09	2.15	2.38	3.58	9.84	12.73	12.27	13.68	7.97
Sulfur dioxide	1.73	2.47	1.49	1.50	2.18	13.25	11.30	8.97	9.71	7.51
Nitrous oxide	4.68	3.57	3.38	2.95	4.05	6.86	11.78	9.83	10.98	6.68
Global	3.46	2.80	2.33	2.56	2.27	16.41	11.06	10.61	11.22	5.82

^aTr range 0.270 – 0.973. ^bTr range 0.466 – 0.971. “–”: blank.

4. CONCLUSION

A new four-parameter cubic equation of state is presented by integrating the critical compressibility factor apart from the critical pressure and temperature to predict accurately the pure compounds thermodynamic properties in subcritical region. Method had been outlined to calculate the component dependent parameters of the obtained EoS. Thereafter, parameter u is correlated with critical compressibility, and parameters belong to nonpolar and slightly polar substances in the alpha function are also fitted against acentric factors and critical compressibility factors. In most instances, the new equation of state yields comparable results to the equations of state selected in this work. However, for those thermodynamic properties including enthalpy of vaporization, entropy of vaporization, and isobaric liquid heat capacity, this work has better performance. The most significant improvement is observed for the isobaric liquid heat capacity of pure substance.

APPENDIX

1. Fugacity coefficient of pure fluid:

$$\ln \frac{f}{P} = Z - 1 - \ln \frac{P(V-b)}{RT} + \frac{a}{RT(r_1-r_2)} \ln \frac{V-r_1}{V-r_2} \quad (\text{A.1})$$

2. Enthalpy departure:

$$\frac{H-H^0}{RT} = Z - 1 + \frac{a-Tda/dT}{RT(r_1-r_2)} \ln \frac{V-r_1}{V-r_2} \quad (\text{A.2})$$

3. Entropy departure:

$$\frac{S-S^0}{R} = -\ln \frac{P}{P_0} + \ln \frac{Z(V-b)}{V} - \frac{da/dT}{R(r_1-r_2)} \ln \frac{V-r_1}{V-r_2} \quad (\text{A.3})$$

4. Heat capacity:

$$C_v = C_v^0 - T \frac{d^2a/dT^2}{(r_1-r_2)} \ln \frac{V-r_1}{V-r_2} \quad (\text{A.4})$$

$$C_p = C_p^0 - T \frac{d^2a/dT^2}{(r_1-r_2)} \ln \frac{V-r_1}{V-r_2} - T \frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T} - R \quad (\text{A.5})$$

$$C_p^0 - C_v^0 = R \quad (\text{A.6})$$

$$C_p^0/R = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 \quad (\text{A.7})$$

Parameters a_0 , a_1 , a_2 , a_3 , and a_4 are available from Poling and Prausnitz.[20]

where

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} - \frac{da/dT}{(V-r_1)(V-r_2)} \quad (\text{A.8})$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{a}{(r_1-r_2)} \left(\frac{1}{(V-r_1)^2} - \frac{1}{(V-r_2)^2} \right) \quad (\text{A.9})$$

$$r_1 = \frac{b(\sqrt{u^2-4w-u})}{2} \quad (\text{A.10})$$

$$r_2 = \frac{b(-\sqrt{u^2-4w-u})}{2} \quad (\text{A.11})$$

AUTHOR INFORMATION

Corresponding Author

*E-mail: heh zr@163.com.

1 REFERENCES

- 2 [1] N.F. Carnahan, K.E. Starling, Equation of State for Nonattracting Rigid Spheres, *Journal of*
3 *Chemical Physics*, 51 (1969) 635-636.
- 4 [2] O. Redlich, J.N.S. Kwong, On the Thermodynamics of Solutions. V. An Equation of State.
5 Fugacities of Gaseous Solutions, *Chemical Reviews*, 44 (1949) 233.
- 6 [3] G. Soave, Equilibrium constants from a modified Redlich-Kwong equation of state, *Chemical*
7 *Engineering Science*, 27 (1972) 1197-1203.
- 8 [4] D.-Y. Peng, D.B. Robinson, A New Two-Constant Equation of State, *Industrial &*
9 *Engineering Chemistry Fundamentals*, 15 (1976) 59-64.
- 10 [5] G. Schmidt, H. Wenzel, A modified van der Waals type equation of state, *Chemical*
11 *Engineering Science*, 35 (1980) 1503-1512.
- 12 [6] N.C. Patel, A.S. Teja, A new cubic equation of state for fluids and fluid mixtures, *Chemical*
13 *Engineering Science*, 37 (1982) 463-473.
- 14 [7] M.A. Trebble, P.R. Bishnoi, Development of a new four-parameter cubic equation of state,
15 *Fluid Phase Equilibria*, 35 (1987) 1-18.
- 16 [8] Y. Le Guennec, R. Privat, J.-N. Jaubert, Development of the translated-consistent tc-PR and
17 tc-RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and
18 saturation properties of pure compounds in the sub- and super-critical domains, *Fluid Phase*
19 *Equilibria*, 429 (2016) 301-312.
- 20 [9] G.A. Melhem, R. Saini, B.M. Goodwin, A modified Peng-Robinson equation of state, *Fluid*
21 *Phase Equilibria*, 47 (1989) 189-237.
- 22 [10] Y. Adachi, H. Sugie, B.C.Y. Lu, DEVELOPMENT OF VAN DER WAALS TYPE OF
23 EQUATION OF STATE, *Journal of Chemical Engineering of Japan*, 18 (1985) 20-26.
- 24 [11] D.-S. Jan, F.-N. Tsai, A new four-parameter cubic equation of state for fluids, *The Canadian*
25 *Journal of Chemical Engineering*, 69 (1991) 992-996.
- 26 [12] W.M. Haynes, *CRC Handbook of Chemistry and Physics*, 95th Edition, in: CRC Press,
27 Boca Raton, FL, 2015, pp. 6-21-26-46.
- 28 [13] D.W. Green, R.H. Perry, *Perry's Chemical Engineers' Handbook*, Eighth Edition, in,
29 McGraw-Hill: New York, Chicago, San Francisco, Lisbon, London, Madrid, Mexico City, Milan,
30 New Delhi, San Juan, Seoul, Singapore, Sydney, Toronto, 2007, pp. 2-209-202-417.
- 31 [14] A. Dashtizadeh, G.R. Pazuki, V. Taghikhani, C. Ghotbi, A new two-parameter cubic
32 equation of state for predicting phase behavior of pure compounds and mixtures, *Fluid Phase*
33 *Equilibria*, 242 (2006) 19-28.
- 34 [15] K. Nasrifar, M. Moshfeghian, A new cubic equation of state for simple fluids: pure and
35 mixture, *Fluid Phase Equilibria*, 190 (2001) 73-88.
- 36 [16] M. Bonyadi, F. Esmaeilzadeh, A modification of the alpha function (α), and the critical
37 compressibility factor (ζ_c) in ER (Esmaeilzadeh–Roshanfekar) equation of state, *Fluid Phase*
38 *Equilibria*, 273 (2008) 31-37.
- 39 [17] A. Haghtalab, M.J. Kamali, S.H. Mazloumi, P. Mahmoodi, A new three-parameter cubic
40 equation of state for calculation physical properties and vapor–liquid equilibria, *Fluid Phase*
41 *Equilibria*, 293 (2010) 209-218.
- 42 [18] L.A. Forero G, J.A. Velásquez J, The Patel–Teja and the Peng–Robinson EoSs performance
43 when Soave alpha function is replaced by an exponential function, *Fluid Phase Equilibria*, 332
44 (2012) 55-76.
- 45 [19] Y. Adachi, C.Y. Lu, H. Sugie, A four-parameter equation of state, *Fluid Phase Equilibria*,
46 11 (1983) 29-48.

- 1 [20] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gases and Liquids, in,
- 2 McGraw-Hill Book, 2004, pp. 753-764.