

An Accurate Correlation to Estimate Saturated Molar Volume of Liquids

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There are a number of techniques available to estimate saturated-liquid molar or specific volumes or densities of liquids. In this study, a new empirical correlation is presented to calculate volume of saturated liquids as a function of critical volume, reduced temperature and acentric factor. An optimization algorithm is utilized to obtain unknown parameters of this correlation by fitting them with the data bank. The accuracy of presented correlation is evaluated vs. mostly used methods and the result indicates the priority of new equation than other methods used in this work with average absolute relative deviation 1.7%.

Keywords: Liquid, Empirical, Equation, Specific volume

INTRODUCTION

Correct liquid molar volume estimation is one of the fundamentals to develop equations of state to evaluate, optimize, simulate, and petrochemical processes. The accuracy of molar volume calculations is essential because it is used as a basis to estimate other equilibrium properties. Correct molar volume data are of key factors in designing process. Most petrochemical processing operations require molar volume or density data to calculate phase equilibrium. In combustion modeling, vapor pressure also plays an important role. When the number of computations is massive, an accurate equation can be useful. In this condition, the large volumes of values are required and it is common to calculate each value using an adequate equation [1]. Some researchers have used different molar volume correlations to estimate parameters in equations of state [2-6].

Numerous empirical molar volume equations have been published and the best known are Rackett equation [7], Yamada and Gunn equation [8] and Hankinson and Thomson equation [9]. The most common of all is

Hankinson and Thomson equation [9].

In this work, new simple substance-dependent equation is developed based on liquid-vapor equilibrium data bank which accurately reproduces the molar volume behavior over an acceptable range of the liquid-vapor region. Based on this model an accurate correlation is presented. The source of molar volume data utilized in this study is National Institute of Standards and Technology (NIST) Chemistry WebBook [10].

MOLAR VOLUME CORRELATIONS

There are a number of techniques available to predict pure saturated-liquid molar or specific volumes or densities as a function of temperature. Here, one group contribution technique and several corresponding state methods are presented to estimate saturated-liquid densities [11].

Rackett Equation

Rackett (1970) [7] proposed that saturated liquid volumes could be calculated by:

$$V_s = V_c Z_c^{(1-T/T_c)^{2/7}} \quad (1)$$

where V_s = saturated liquid volume, V_c = critical volume, Z_c

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= critical compressibility factor, and T_c = critical temperature. Eq. (1) is often written in the equivalent form:

$$V_s = \frac{RT_c}{P_c} Z_c^{[1+(1-T/T_c)^{2/7}]} \quad (2)$$

while Eqs. (1) and (2) are not remarkably accurate for many substances.

Yamada and Gunn equation (YG)

Yamada and Gunn (1973) [8] proposed that Z_c in Eq. (3) can be correlated with the acentric factor:

$$V_s = \frac{RT_c}{P_c} \left[(0.29056 - 0.08775\omega)^{[1+(1-T/T_c)^{2/7}]} \right] \quad (3)$$

Hankinson and Thomson Correlation (HT)

Another liquid volume correlation was proposed by Hankinson and Thomson (1979) [9] and further developed by Thomson, *et al.* (1982) [12]. This correlation, called HT correlation here, is:

$$V_s = V^* V^{(0)} [1 - \omega_{SRK} V^\delta] \quad (4)$$

$$V^{(0)} = 1 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + c(1-T_r) + d(1-T_r)^{4/3} \quad (5)$$

$$V^\delta = \frac{e + f T_r + g T_r^2 + h T_r^3}{T_r - 1.00001} \quad (6)$$

Equation (5) may be used in the range $0.25 < T_r < 0.95$ and Eq. (6) may be used when $0.25 < T_r < 1.0$. Constants a through h are given by:

In Equation (4), ω_{SRK} is the value of acentric factor that causes the Soave equation of state gives the best fit to pure component of vapor pressure, and V^* is a parameter whose value is close to the critical volume.

New Predictive Method for Molar Volume

This study tried to find a new simple equation for the molar volume of pure liquids. It is an eight-constant non-linear equation which developed the vapor-liquid equilibrium data with high accuracy, even at low temperatures. After multiple analyses of regression, an

Table 1. Coefficients of Hankinson and Thomson Correlation

Constant	Value
a	-1.52816
b	1.43907
c	-0.81446
d	0.190454
e	-0.296123
f	0.386914
g	-0.0427258
h	-0.0480645

Table 2. Tuned Coefficients of the New Proposed Model

Coeff.	Value	Standard deviation (%)
a	1.5816	0.0207
b	0.711	0.0042
c	0.1906	0.0134
d	-1.2668	0.0193
e	0.0745	0.0116
f	1.7454	0.0097
g	-0.4914	0.0338
h	-1.5227	0.0431

empirical correlation was presented as follow:

$$V_s = V_c \frac{A(\omega)^{1+(1-T_r)^y}}{B(\omega)^{1+T_r}} \quad (7)$$

$$A = b + c\omega + d\omega^2 + e\omega^4 \quad (8)$$

$$B = f + g\omega + h\omega^2 \quad (9)$$

where V_s is saturated molar volume, V_c is critical molar volume, $T_r = T/T_c$, is the reduced temperature, ω is acentric factor, and the parameters $a-h$ are constant coefficients obtained by using Levenberg-Marquardt algorithm which minimize the sum of the squared differences between observed and predicted values of the dependent variables [13]. The tuned coefficients are presented in Table 2.

RESULTS AND DISCUSSION

First, calculations were carried out for 65 pure liquids. The values of molar volume, temperature, critical pressure, critical temperature, critical volume, and acentric factor were taken from data bank [10].

To prove the high accuracy of the presented empirical model, calculated molar volume of all substances *vs.* corresponded values of experimental data is presented in Fig. 1.

In Fig. 1, if a solid circle is standing on the diagonal line, the deviation of this point is equal to zero. Also the deviation of each data point is increased by the increase of

distance from the diagonal line [14]. Therefore, Fig. 1 shows that the most of data points are close to the line and has low deviation from experimental values.

In Table 3, average absolute relative deviation (AARD%) of molar volumes calculated from the new proposed correlation and literature models for all 65 pure liquids against the values given by experimental data are presented. It showed that new presented model is more accurate than other methods approximately for all types of pure substances considered in this work. Table 4 presents the statistical parameters including average absolute relative deviation (AARD%) and root mean square deviation (RMSD) of the considered models and new developed correlation.

Figure 2 shows the cumulative frequency of the developed method and the literature correlations *vs.* average absolute relative deviations. As shown in Fig. 2, developed equation is more accurate than other two commonly used models in molar volume prediction. The new correlation has successfully predicted 97% of all experimental data with AARD% less than 5, and 99.2% with AARD% less than

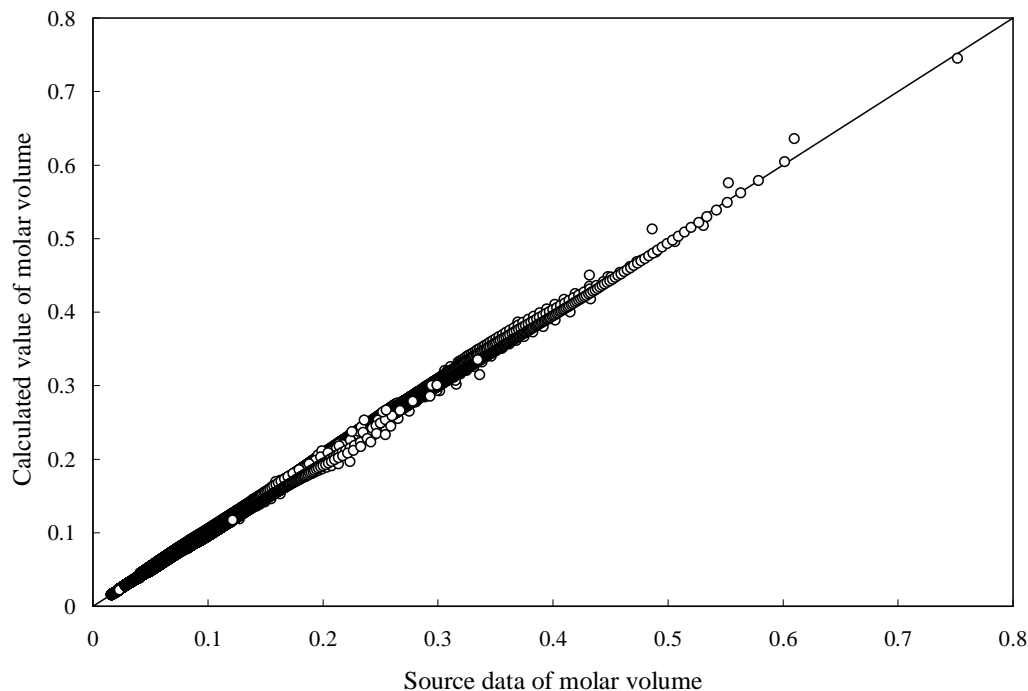


Fig. 1. Values of the calculated data *vs.* source data of the molar volume.

Table 3. Properties and AARD% of New and Literature Models for Each Pure Liquid

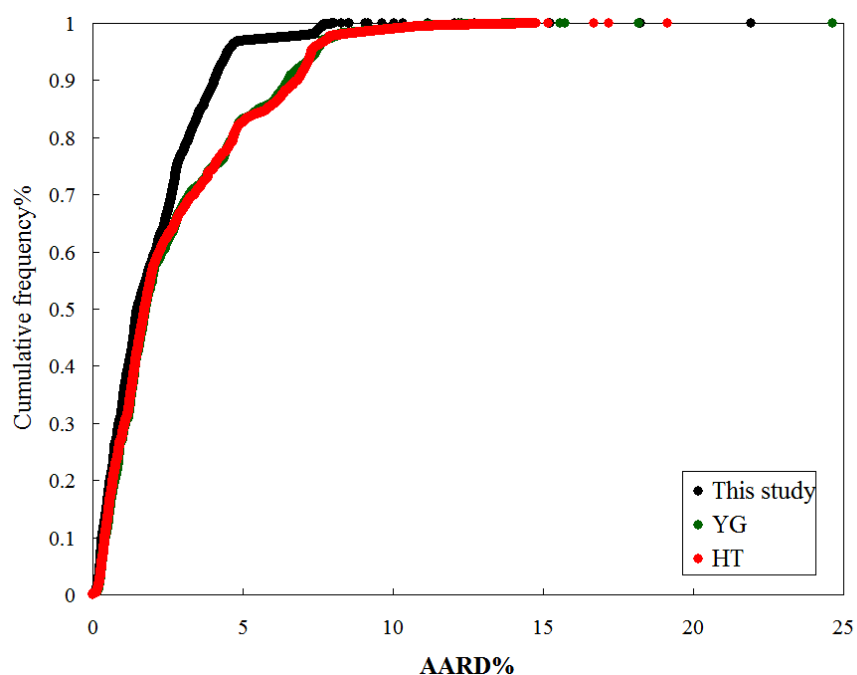
Substance	T _c (K)	P _c (bar)	ω	V _c (M ⁻¹)	AARD (%)		
					YG	HT	This study
Deuterium	38.3	16.65	-0.175	0.1914	3.22	3.16	0.78
H ₂	33.1	12.96	-0.219	0.2126	4.25	4.18	0.50
O ₂	154.6	50.43	0.022	0.2548	0.47	0.47	0.56
Flourine	144.4	51.72	0.045	0.2321	0.43	0.46	0.72
CO	132.9	34.94	0.050	0.3162	1.73	1.70	2.00
CO ₂	304.1	73.77	0.224	0.3427	0.90	1.02	0.29
N ₂ O	309.5	72.45	0.162	0.3552	1.04	1.02	1.18
C1	190.6	45.99	0.011	0.3445	0.29	0.21	0.28
C2	305.3	48.72	0.099	0.5211	0.63	0.52	0.15
Ethene	282.4	50.42	0.087	0.4656	0.82	0.70	0.35
C3	369.8	42.48	0.152	0.7239	0.47	0.34	0.29
Propene	365.6	46.65	0.141	0.6516	1.08	1.06	1.25
Propyne	402.4	56.26	0.204	0.5946	1.59	1.51	2.23
Cyc-propane	398.3	55.80	0.131	0.5935	2.65	2.66	2.66
n-C4	425.1	37.96	0.201	0.9311	0.19	0.15	0.47
i-C4	407.8	36.29	0.184	0.9343	0.19	0.17	0.38
n-C5	469.7	33.70	0.251	1.1588	0.27	0.19	1.19
2-Meth-butane	460.4	33.96	0.230	1.1271	1.29	1.37	0.90
2,2-Dimethyl propane	433.7	31.96	0.196	1.1283	1.34	1.39	0.82
n-C6	507.8	30.34	0.299	1.3916	0.45	0.32	1.89
2-Methyl pentane	497.7	30.40	0.280	1.3611	1.33	1.39	0.60
Cyc-Hexane	553.6	40.75	0.209	1.1296	0.74	0.78	0.39
C7	540.1	27.36	0.349	1.6413	0.66	0.56	2.66
C8	569.3	24.97	0.393	1.8956	1.02	1.02	2.98
C9	594.6	22.81	0.443	2.1671	1.39	1.26	3.33
C10	617.7	21.03	0.488	2.4420	2.27	2.23	2.66
C12	658.1	18.17	0.574	3.0113	4.18	4.06	0.47
He	5.2	2.27	-0.382	0.1899	6.88	7.19	1.07
Ne	44.5	26.79	-0.039	0.1381	3.70	3.79	3.95
Ar	150.7	48.63	-0.002	0.2576	0.59	0.49	0.51
Kr	209.5	55.25	-0.001	0.3152	0.40	0.24	0.47
Xe	289.7	58.42	0.004	0.4123	1.13	1.18	1.15

Table 3. Continud

NF ₃	234.0	44.61	0.126	0.4361	0.27	0.17	0.33
R11	471.1	44.08	0.189	0.8886	1.11	1.16	0.97
R12	385.1	41.36	0.179	0.7741	0.78	0.83	0.78
R13	302.0	38.79	0.172	0.6473	1.17	1.23	1.26
R14	227.5	37.50	0.179	0.5044	3.69	3.72	3.56
R21	451.5	51.81	0.206	0.7245	0.87	0.84	1.37
R22	369.3	49.90	0.221	0.6153	1.81	1.76	2.37
R23	299.3	48.32	0.263	0.5150	5.94	5.90	7.39
R113	487.2	33.92	0.253	1.1941	1.83	1.88	0.61
R114	418.8	32.57	0.252	1.0691	2.56	2.66	1.18
R115	353.1	31.20	0.252	0.9409	2.98	3.03	1.77
R116	293.0	30.48	0.257	0.7993	4.65	4.73	3.24
R123	456.8	36.62	0.282	1.0372	0.71	0.74	0.99
R124	395.4	36.24	0.288	0.9071	1.77	1.81	0.44
R125	339.2	36.18	0.305	0.7795	2.08	2.14	0.47
R134a	374.2	40.59	0.327	0.7664	1.30	1.31	4.01
R141b	477.5	42.12	0.220	0.9425	0.80	0.76	1.40
R142b	410.3	40.55	0.232	0.8412	2.02	1.98	2.82
R218	345.0	26.40	0.317	1.0866	6.12	6.14	3.85
R227ea	376.0	29.99	0.354	1.0422	7.02	7.03	4.04
R236ea	412.4	35.02	0.379	0.9792	7.08	7.14	3.88
R236fa	398.1	32.00	0.377	1.0342	4.56	4.58	1.07
R245ca	447.6	39.25	0.354	0.9481	5.36	5.37	2.32
R245fa	427.2	36.40	0.372	0.9758	3.75	3.78	0.69
RC318	388.4	27.78	0.355	1.1626	7.07	7.19	4.00
Benzene	562.1	48.94	0.209	0.9548	1.43	1.39	2.01
Toluene	591.8	41.26	0.266	1.1923	1.43	1.40	2.77
C ₄ F ₁₀	386.3	23.23	0.374	1.3824	8.38	8.42	5.07
C ₅ H ₁₂	420.6	20.45	0.423	1.7098	7.14	7.17	3.06
SO ₂	430.6	78.84	0.256	0.4541	1.38	1.38	2.65
H ₂ S	373.1	90.00	0.100	0.3447	1.07	1.04	1.36
SF ₆	318.7	37.55	0.210	0.7058	2.97	3.06	2.13
COS	378.8	63.70	0.098	0.4944	1.83	1.78	1.37

Table 4. Statistical parameters of Considered Models

	AARD	RMSD
HT	2.343	3.308
YG	2.349	3.283
This study	1.734	1.317

**Fig. 2.** Cumulative frequency of the new method over other literature models.

7.5. Only 0.001% of the molar volume data were predicted with AARD% of more than 10 by the new method. Hankinson and Thomson equation, that is the second accurate method, predicted 82% of the data with AARD% less than 5, and 96% with AARD% less than 7.5. Hence, the superiority of the new method over the other corresponding states has been verified for approximately all data existed in data bank. To estimate the applicability of the presented method for calculating molar volume of pure liquids, deviations AARD% of 602 data points of *para*-H₂ in the range of 85 K ≤ T ≤ 234 K are presented in Fig. 3. It should be noted that data points of this substance were not employed in regression analysis of the new proposed

equation.

The new correlation has successfully predicted 94% of this new set of experimental data with AARD% less than 1, and 97% with AARD% less than 2. Hankinson and Thomson (HT) equation, that is the second accurate method, predicted 13% of the new data set with AARD% less than 1, and 25% with AARD% less than 2. Figure 3 showed the superiority of this new method over the other corresponding states for data set not participating in regression analysis. To further estimate the applicability of the new method for calculating molar volume of the liquids, deviations (AARD%) of 895 experimental measurement data points of 18 binary mixtures from literatures [15-20] are calculated

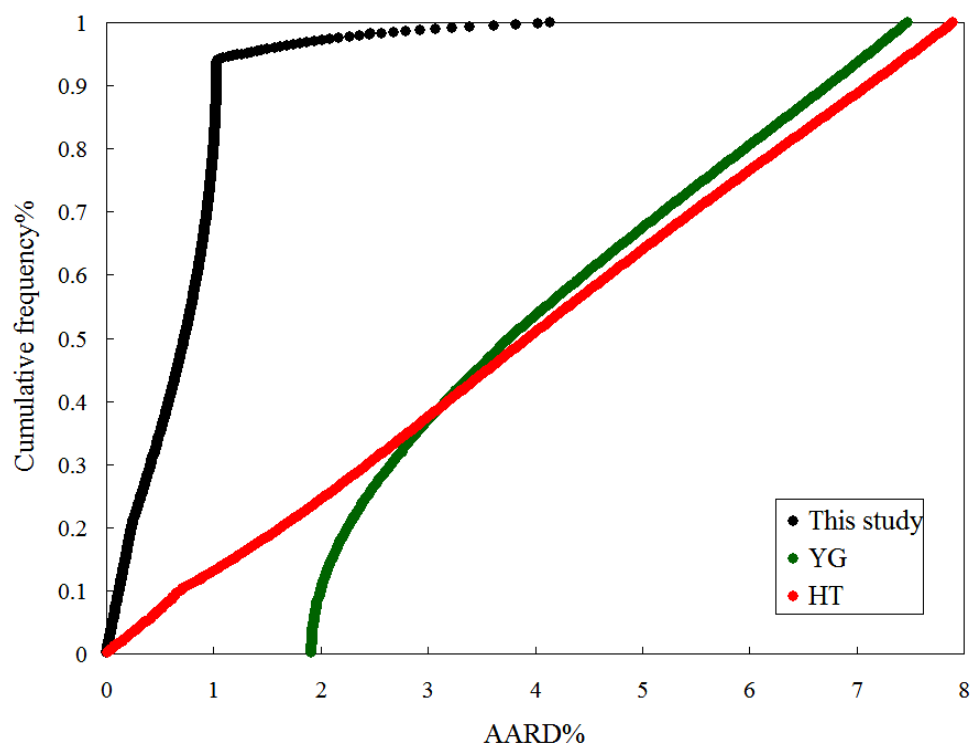


Fig. 3. Deviation of 602 data points for *para*-H₂ calculated by the new general model.

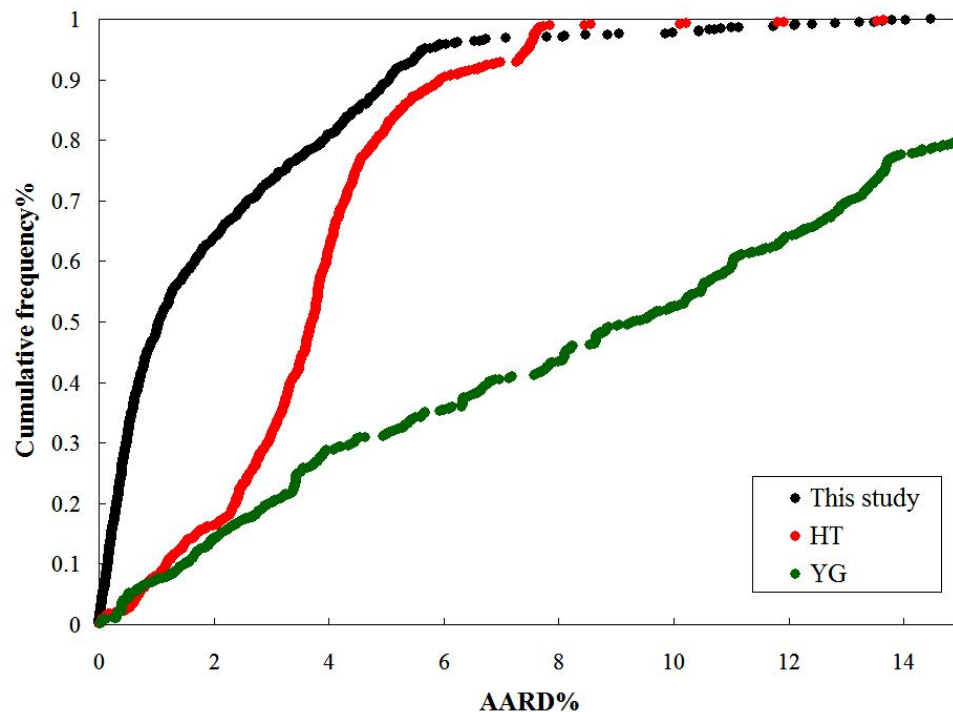


Fig. 4. Deviation of 895 data points for 18 binary mixtures calculated by the new general model.

Table 5. AARD% of the New and Literature Models for Each Binary Mixtures

Mixture	No of data	YG	HT	This study	Ref.
Methanol+Water	24	7.43	3.36	4.53	[15]
Ethanol+Water	24	15.98	2.71	4.75	[15]
Propanol+Water	24	23.04	2.5	4.95	[15]
Methanol+cyclohexylamin	42	14.15	2.57	4.38	[16]
Phenetol+1-Pentanol	44	7.62	4.45	1.3	[16]
Phenetol+1-Hexanol	44	6.48	3.37	0.33	[17]
Phenetol+1-Heptanol	44	5.61	3.88	0.9	[17]
Phenetol+1-Octanol	44	5.97	3.12	0.87	[17]
Phenetol+1-Nonanol	44	6.31	1.25	1.77	[17]
Phenetol+1-Decanol	44	6.97	1.06	2.93	[17]
3-Picoline+Water	90	21.56	5.57	2.91	[18]
Decane+1-Pentanol	154	13.26	4.3	0.57	[19]
Decane+1-Hexanol	143	10.85	3.78	0.51	[19]
Aniline+chlorobenzene	26	1.36	3.04	4.85	[20]
Aniline+bromobenzene	26	1.49	6.99	5.15	[20]
Aniline+1,2-dichlorobenzene	26	4.39	3.03	4.02	[20]
Aniline+1,3-dichlorobenzene	26	2.21	3.74	3.98	[20]
Aniline+1,2,4-trichlorobenzene	26	2.69	4.27	2.66	[20]
Total	895	10.36	3.71	2.05	

with new and two previous correlations and results are presented in Table 5. Calculated values are compared against other previous methods and indicated in Table 5. Estimation was made with simple mixing rules for acentric factor, critical volume, critical pressure, critical temperature and molecular weight.

$$\omega_{mix} = \sum_{i=1}^2 x_i \omega_i \quad (10)$$

$$V_{c,mix} = \sum_{i=1}^2 x_i V_{ci} \quad (11)$$

$$T_{c,mix} = \sum_{i=1}^2 x_i T_{ci} \quad (12)$$

$$P_{c,mix} = \sum_{i=1}^2 x_i P_{ci} \quad (13)$$

$$Mw_{mix} = \sum_{i=1}^2 x_i Mw_i \quad (14)$$

The results showed applicability of the new equation to predict molar volume of hydrocarbon mixtures indicated in first column of Table 5. Cumulative frequency of 895 data

points of 18 binary mixtures versus AARD% are presented in Fig. 4.

The new equation has successfully predicted 51% of this new set of experimental data with AARD% less than 1, and 64% with AARD% less than 2. Yamada and Gunn (YG) equation, that is the second accurate method in mixture molar volume prediction, predicted 9% of the new data set with AARD% less than 1, and 16% with AARD% less than 2.

CONCLUSIONS

In this study, a new method was presented to estimate the molar volume of pure liquids in wide temperature range. To estimate the accuracy of this correlation, the comparisons were made for the presented model and two commonly used empirical methods including Yamada & Gunn method and Hankinson and Thomson method. The results indicated that the new proposed equation is the best model for overall 65 pure liquids. The result indicates the superiority of the new presented method over the other methods used to calculate molar volume of the pure liquids with average absolute relative deviation (AARD%) of 1.73. Also new correlation was examined for estimation molar volume of 18 binary mixtures. It showed that the presented equation has successfully predicted molar volume of mixtures with AARD% of 2.05 which is lower than that for other two methods.

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