Application of a simple cubic regularity for liquid density predictions and comparison with GMA EOS

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Abstract

Based on a cubic regularity, (2Z-1)*v* is nearly linear versus molar density at isothermal condition for each liquids, where Z and *v* is compressibility factor and molar volume, respectively. Using the regularity, a cubic equation of state can be obtained. The temperature-dependent parameters of the cubic EOS are obtained through correlation of pu..re liquid density of several substances at various pressures and temperatures. The results of the cubic EOS are in good agreement with the experimental data. In addition, the results of the cubic EOS are compared with the Goharshadi-Morsali-Abbaspour (GMA) EOS.

Keyword: regularity, liquid density, cubic

1. Introduction

Finding the density of liquids in different pressures and temperatures has become one of the considerable issues in thermodynamics from past to present because of the importance of it in buoyant force, floating objects and etc. So, a lot of experimental studies were done to measure various liquid densities in the wide ranges of pressures and temperatures.
Simultaneously with the experimental studies, research to find the regularities which relate density of liquids to pressure and temperature was started. Because of the complex

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behavior of liquids on molecular scale, the earlier regularities such as Tait-Murnaghan relation have been applied for years without any theoretical foundation.

In 1993 Parsafar and Mason [2] have proposed a model for density of liquid which $(Z-1)v^2$ varies linearly with respect to ρ^2 on statistical-mechanical theory but do not predict as great a range of linearity as is suggested by experiment. In 2005 Goharshadi and et al. [3] have introduced regularities for liquids based on average potential energy that known as GMA EOS. The GMA EOS suggests that $(2Z-1)v^3 = a(T) + b(T)\rho$ where a and b are temperature dependence parameters for each component. The agreements of the results of the GMA equation with experimental data have been shown to be acceptable with minor errors, however density calculations is rather difficult due to the order of ρ in this equation.

The purpose of this work is to evaluate the accuracy of a simple cubic regularity, suggested by Moosavi and Sabzevari [4], for density calculations of liquids and compare the results with GMA EOS.

2. Theory

To obtain the cubic EOS for calculating density of liquids, assumptions and principles of LIR and GMA EOS were used. Approximately, the average potential energy is summation of effects of nearest neighbors only, therefore [3, 4],

$$U = \frac{N}{2} Z(\rho)\left[\frac{C_n}{r^n} - \frac{C_m}{r^m}\right] \qquad (1)$$

and we can write U as:

$$\frac{U}{N} = \frac{K_n}{V^{\frac{n}{3}+1}} - \frac{K_m}{V^{\frac{m}{3}+1}} \qquad (2)$$

Where K_n and K_m are the corresponding parameters. since:

$$P_i = \left(\frac{\partial E}{\partial V}\right)_T \approx \left(\frac{\partial (\frac{U}{N})}{\partial V}\right)_T \qquad (3)$$

By carrying out the derivative, internal pressure may be obtained as,

$$P_i = \left(\frac{m}{3}+1\right) K_m \rho^{\frac{m}{3}+2} - n\left(\frac{n}{3}+1\right) K_n \rho^{\frac{n}{3}+2} \qquad (4)$$

In order to obtain the cubic EOS, it is needed to assume m=0 and n=3. It means that $P_i {v_i}^2$ versus ρ is linear in each isotherm, thus [4],

$$P_i {v_i}^2 = a(T) + b(T)\rho \qquad (5)$$

a and b are temperature dependence parameters. To find the dependence, GMA EOS assumptions for the parameters was used [4],

$$a(T) = A_1 + A_2 T \qquad (6)$$

$$b(T) = B_1 + B_2 T \qquad (7)$$

Using $d\left(\frac{P}{T}\right) = \frac{P_i}{T^2} dT$ and eq. (5) and integration, the regularity can be obtained [4],

$$B(T)\rho^3 + A(T)\rho^2 + \rho - \frac{2P}{RT} = 0 \qquad (8)$$

or,

$$(2Z-1)\, v = a(T) + b(T)\rho \qquad (9)$$

Where:

Z and v are the compressibility factor and molar volume and,

$$A(T) = A_0 + \frac{2A_2 lnT}{R} - \frac{2A_1}{RT} \qquad (10)$$

$$B(T) = B_0 + \frac{2B_2 lnT}{R} - \frac{2B_1}{RT} \qquad (11)$$

Which A_0, A_1, A_2, B_0, B_1 and B_2 are constants and they just depends on the component.

3. Result and discussion

To consider the precision of this EOS and compare its result to GMA EOS and experimental data, we did the calculations for 11 components with both EOSs.

First, we plot isotherms $(2Z-1)\,v$ versus ρ for 11 liquids in different temperatures and pressures by the cubic EOS using available experimental data [5-10]. Figs. 1 to show these isotherms for 2-Butyne, Krypton, Mercury, Argon and 2,3-Dimethyl butane.

Then, we calculate the densities of these components by cubic EOS and GMA in ranges of temperature and pressure of available experimental data and compare them together.

In table 1, we summarize the calculations for all studying components and show the value of R-square and error (=100 $|\rho_{cal} - \rho_{exp}|/\rho_{exp}$) for both EOSs.

The result of table 1 clearly shows that isotherms $(2Z-1)\,v$ versus ρ are linear and the experimental data confirm this linearity. The cubic EOS could predict the density with average error 0.75% and average error of GMA EOS is 0.73%.

By compare the result of cubic EOS to GMA EOS, it is obvious that the cubic EOS results for most of the component are almost near to GMA EOS and for some cases have better results, so we can use this cubic EOS as the same as GMA EOS with acceptable errors. The advantage of this equation is that cubic EOSs are more common and they can solve easily as the same as RK or another cubic equation of state.

The constants of the cubic can calculate easily in desire temperature and pressure for different components. Table 2 shows these values for each components that we studied in this work. The procedure of determining the parameters are first plotting $(2Z-1)v$ versus ρ for various isotherms. The slopes and intercepts of the straight lines can be used to obtain A_0 to A_2 and B_0 to B_2, respectively. This was done by Matlab software.
The fair results for some components may be attributed to fact that this cubic EOS has no co-volume that affect results at lower temperatures and higher pressures.

4. Conclusion

From the result we can find that:

1- Isotherm (2Z-1)v versus ρ are linear and the experimental data support this linearity.
2- The cubic EOS could predict the density of liquids with acceptable errors.
3- The results of the cubic EOS were near to GMA EOS results for most of the component.

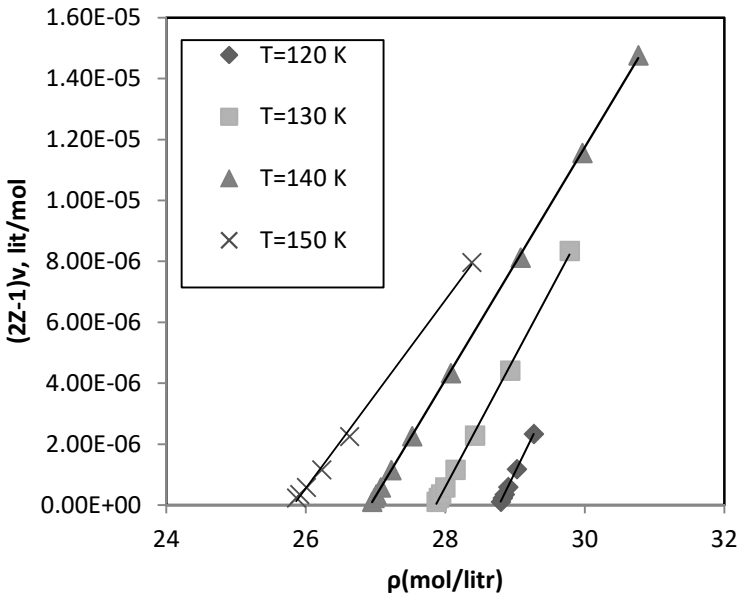

Fig 1. Isotherms $(2Z-1)\,v$ versus ρ for Krypton [5].

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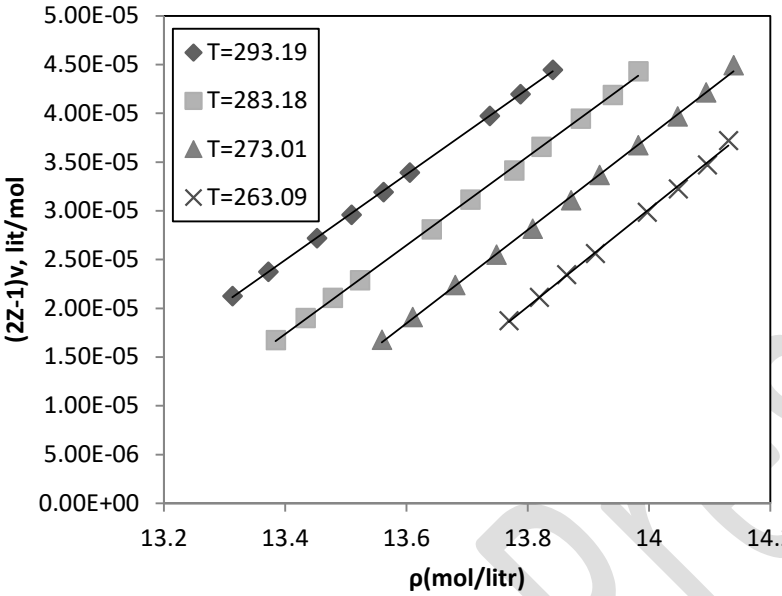

Fig 2. Isotherms $(2Z-1)\,v$ versus ρ for 2-Butyne [6].

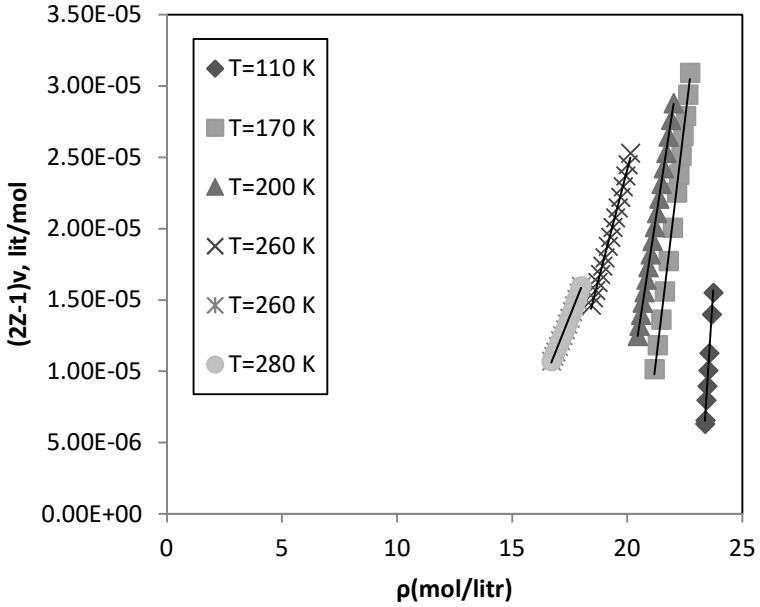

Fig 3. Isotherms $(2Z-1)\,v$ versus ρ for Ethylene [7].

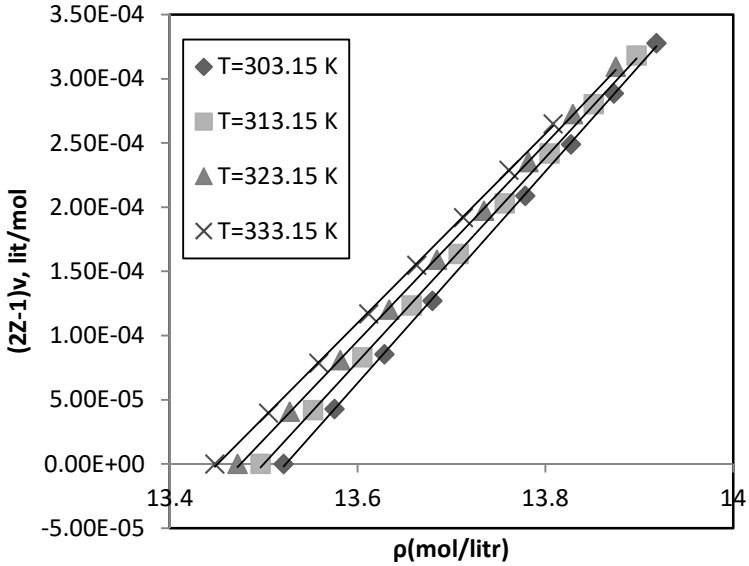

Fig 4. Isotherms $(2Z-1)\,v$ versus ρ for Mercury [8].

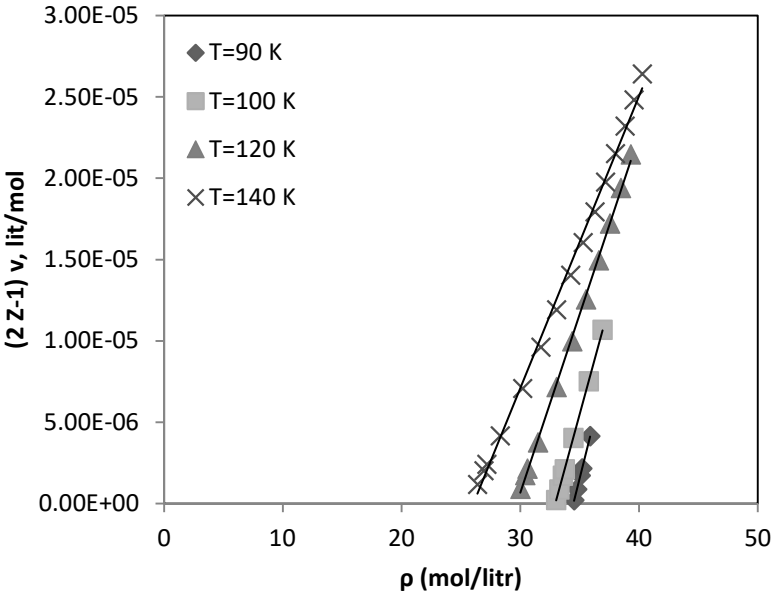

Fig 5. Isotherms $(2Z-1)\,v$ versus ρ for Argon [9].

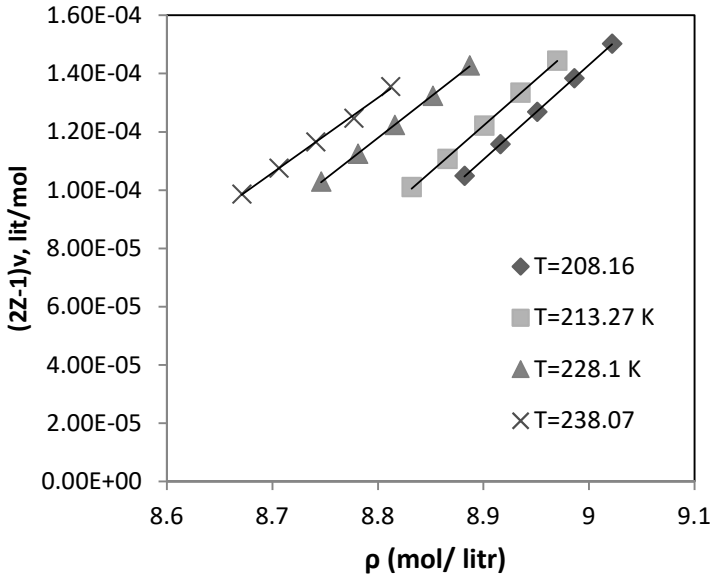

Fig 6. Isotherms $(2Z-1)\,v$ versus ρ for 2,3-Dimethyl butane [10].

Table1. The experimental range of data, the minimum and maximum square of correlation coefficient (R^2) for Cubic EOS and GMA. Experimental data were taken from [5-10].

			Model used in this work		GMA EOS	
Component	T(min)-T(max), K	P(min)-P(max), bar	R^2(min-max)	Error %	R^2(min-max)	Error %
Argon	90-150	10-2400	0.996-0.999	1.294	0.993-1	0.378
2-Butyne	263.09-293.19	349.6-1038.1	0.998-0.999	0.022	0.996-0.999	0.595
Dimethyl butane	208.16-238.07	715.9-1069.1	0.997-0.999	0.068	0.997-1	0.415
Ethylene	110-280	158.46-1150.25	0.997-1	0.483	0.996-1	0.101
krypton	120-150	5-800	0.998-0.999	0.167	0.997-1	0.186
Mercury	303.15-333.15	0-8000	0.999	1.244	1	1.357
methanol	298.15-353.15	1-1000	0.999	3.491	0.999	2.34
1-ethyl-3-methylimidazoliumethylsulfate	283.14-293.14	40-139.485	0.999-1	0.0131	1	0.005
Tetramethylsilane	198.16-257.91	732.8-1016.9	0.995-0.999	0.0357	0.995-1	0.0384
water	303.15-333.15	200-1600	0.975-0.994	0.149	0.971-0.994	0.199
xenon	170-220	5-200	0.998-0.999	1.365	0.999-1	2.451

Table 2. The values of constant parameters for each component for studied systems.

Component	$A_0(\mathrm{L}\,mol^{-1})$	$A_1(L^2 bar\,mol^{-2})$	$A_2(L^2 bar\,K^{-1}mol^{-2})$	$B_0(L^2 mol^{-2})$	$B_1(L^4 bar\,mol^{-3})$	$B_2(L^3 bar\,K^{-1}mol^{-3})$
Argon	-1.52E+01	-6.95E+00	1.14E-01	4.29E-01	2.28E-01	-3.13E-03
2-Butyne	6.26E-01	1.09E+02	1.84E-02	2.02E-01	-6.01E+00	-1.84E-03
Dimethyl butane	-2.37E+04	-3.36E+04	1.54E+02	2.87E+03	4.09E+03	-1.87E+01
Ethylene	-3.49E+00	3.06E+01	3.98E-02	4.71E-01	-8.73E-01	-3.69E-03
krypton	-1.64E+01	-3.84E+00	1.23E-01	9.57E-01	5.69E-01	-6.90E-03
mercury	-2.97E+03	-5.79E+03	1.83E+01	2.17E+02	4.23E+02	-1.33E+00
methanol	1.22E+06	-1.37E+07	-1.22E+04	-3.93E+07	3.23E+08	3.63E+05
1-ethyl-3-methylimidazoliumethylsulfate	3.33E+02	4.49E+03	-4.34E-01	-6.66E+02	-1.90E+03	3.87E+00
Tetramethylsilane	-1.01E+03	-1.15E+03	6.60E+00	1.22E+02	1.45E+02	-8.00E-01
water	2.35E+05	4.24E+05	-1.45E+03	-2.50E+05	-4.48E+05	1.54E+03
xenon	4.13E+02	5.41E+02	-2.73E+00	-1.96E+01	-2.55E+01	1.30E-01

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