



Density calculation of liquid organic compounds using a simple equation of state up to high pressures

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ABSTRACT

Experimental densities of three groups of liquid organic substances (acids, esters, alcohols) have been correlated using Goharshadi–Morsali–Abbaspour (GMA) equation of state and then the values calculated from the equation of state have been compared with the experimental data. The paper reports new correlation for the density of 20 organic liquids (7 acids, 7 esters and 6 alcohols) at temperatures between 293.15 K and 393.15 K and pressures between 0.1 MPa and 35 MPa. A comparison with experimental data in the specified range of temperature from low to high pressures has been made. Some generalized correlations are also used for comparison with GMA equation of state and experimental data. The results show that the equation of state reproduces the experimental $P\rho T$ data of liquid organic compounds with good accuracy. The excellent agreement with experimental data indicates that this equation of state can be used to calculate the density of liquid organic compounds with a high degree of certainty. The comparison with other correlations shows that the GMA equation of state is better to some extent and reliable in the given temperature and pressure range.

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1. Introduction

To design chemical reactors and separation equipment efficiently, it is necessary to have data on fluid properties over a wide range of temperatures and pressures. Liquid densities are needed in many engineering problems such as process calculations, simulations, equipment and pipeline design, and liquid metering calculations. Liquid densities are usually calculated using correlations. A good liquid density correlation must be simple and accurate. It must also be predictive so that it can be used when experimental data are not available.

Straight chain organic acids (e.g. acetic acid, propanoic acid, etc.) are useful reagents and synthetic precursors. Annual production of acetic acid in the United States alone exceeds 2 million tons. It is used to manufacture monomers for polymerization, as well as, pharmaceuticals, dyes and pesticides. Another large scale produced acid in chemical productions is hexanoic acid, which is used in the manufacture of nylon. Esters and their widespread occurrence in nature and many practical uses make them perhaps the most important carboxylic acid derivative. Thermophysical properties of

aliphatic esters are particularly important in the pharmaceutical, food, and flavor industries. The importance of alcohols to manufactures is undoubted; and in view of this, producing alcohol at large scales has been given great attention. A question that may tend to become important in the near future is the use of alcohol either as a fuel in internal combustion engines or in fuel cells [1–3].

Several thermodynamic correlations have been developed to predict the thermodynamic properties of liquid compounds up to high pressures. A new equation of state (EoS) for liquids has been recently introduced by Goharshadi et al. [4] (Goharshadi–Morsali–Abbaspour “GMA EoS”) which has been found to be valid for polar, nonpolar, and hydrogen bonding fluids [5–7]. The GMA EoS is based on the average potential energy and implies that a linear regularity exists between $(2Z - 1)V_m^3$ and ρ_m for the liquids at all temperatures in which V_m is molar volume, $\rho_m = 1/V_m$ is molar density and Z is compressibility factor. GMA EoS has some substance specific parameters which will be more described in the next section. Hankinson et al. proposed one of the most successful saturated liquid density models which is Hankinson–Thomson (HT), often called COSTALD [8]. HT was developed originally for hydrocarbons and other organic compounds, but it has been improved for many other types of compounds [9]. A good discussion of saturated and compressed liquid density calculation methods can be found in Poling et al. [10]. Hankinson–Brobst–Thomson model (HBT) was proposed by Thomson et al. [11] to calculate liquid density at pressures above saturation which we denote it by compressed liquid density for convenience in

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this paper. This model first calculates the saturated liquid density. The effect of pressure is then taken into account using the generalized Tait equation. This method needs component's vapor and critical pressure. Aalto et al. [12–14] have presented a compressed liquid density calculation method that first calculates saturated liquid density using HT model, and then the effect of pressure is taken into account by a modification of equation of Chang and Zhao [15]. The Aalto et al. model uses the same parameters as the HT model. This model is accurate for density prediction as discussed by Poling et al. [10]. However, the drawback of this model is that data used in the general model parameter fitting was limited to 20 MPa. The model has been found to have large errors in pressures higher than 25 MPa and it is recommended only for the pressure range it was originally fitted. Later, Aalto and Keskinen (AK) [17,18] improved the model of Aalto et al. [12–14] to overcome this defect. The data used in fitting the general model parameters extended up to 800 MPa. A lot of data points were also located near the critical temperature. Thus the AK model can be used with excellent accuracy up to extremely high pressures. The AK model also applies with good accuracy to the critical region giving also the liquid compression at the critical temperature when pressure is higher than critical pressure. Nasrifar et al. [16] has also proposed a compressed liquid density calculation model (named NM) that is also based on the HT saturated liquid density. They have published the necessary general model parameters. The prediction of compressed liquid density with this method has also given reliable results with less deviation from experimental data.

The purpose of this work is using the GMA EoS [4] to calculate the densities of 20 liquid organic compounds in three groups which are straight chain organic acids, esters and alcohols in extended ranges of temperature and up to high pressures. GMA is an EoS with substance specific adjustable parameters for the correlation of experimental density data. The accuracy of an EoS is a feature that most efforts are focused on it and, therefore, by having such EoS calculations in the specified range of temperature and pressure can be done with more confidence. Thus, a wide comparison between results reproduced by GMA EoS and experimental data was made. The accuracy of GMA EoS in prediction of volumetric properties of liquid organic compounds has been determined by the statistical parameters, i.e. the average absolute deviation (AAD), deviation plots, pressure–density diagrams and parity graphs. To assess and compare the performance of GMA EoS with other models in density prediction of liquid organic compounds, the calculated densities were compared with AK and

NM compressed liquid correlation and Peng Robinson (PR) EoS [4,16,20]. Section describes the theoretical basis of GMA EoS, AK and NM correlation and PR EoS. It should be noted that these comparisons are not quite fair as the generalized methods (AK and NM) are more generalized and require much less parameters with physical meanings to characterize a substance in spite of GMA EoS which has substance specific parameters. Their ability for density calculation of specific compounds selected in this study should be investigated and the results may be useful in the field. Density values calculated from generalized methods selected for a comparison can be regarded as predicted. However, general parameters are averages over large number of substances; moreover it is not sure whether the substances considered here have been included in the input data set used for evaluation of generalized parameters. On the other hand, the GMA EoS is a correlation method representing smoothed data for particular substance in particular temperature and pressure range. Thus GMA EoS calculations do not concern to predicted densities but to smoothed values calculated from the fits.

Table 1(a)

The intercept (A), slope (B), square of correlation coefficient (R^2) of Eq. (1), and pressure range of the data for straight chain organic acids.

Substance	T/(K)	B/(m ¹² ·mol ⁻⁴)	A/(m ⁹ ·mol ⁻³)	R ²	ΔP/(MPa)
Acetic acid [18]	293.15	-1.13E-11	6.36E-16	0.9963	0.1–25
	298.15	-1.09E-11	6.19E-16	0.9969	
	303.15	-1.06E-11	6.03E-16	0.9973	
	308.15	-1.03E-11	5.89E-16	0.9976	
	313.15	-1.00E-11	5.76E-16	0.9982	
	318.15	-9.76E-12	5.63E-16	0.9986	
	323.15	-9.49E-12	5.49E-16	0.9987	
Propanoic acid [18]	293.15	-2.97E-11	2.19E-15	0.9997	0.1–25
	298.15	-2.87E-11	2.12E-15	0.9999	
	303.15	-2.78E-11	2.06E-15	1.0000	
	308.15	-2.70E-11	2.01E-15	0.9999	
	313.15	-2.62E-11	1.96E-15	1.0000	
	318.15	-2.54E-11	1.91E-15	1.0000	
	323.15	-2.48E-11	1.87E-15	1.0000	
Butanoic acid [18]	293.15	-6.60E-11	6.01E-15	0.9995	0.1–25
	298.15	-6.44E-11	5.88E-15	0.9997	
	303.15	-6.19E-11	5.68E-15	0.9996	
	308.15	-6.06E-11	5.59E-15	0.9996	
	313.15	-5.88E-11	5.44E-15	0.9995	
	318.15	-5.71E-11	5.31E-15	0.9995	
	323.15	-5.53E-11	5.17E-15	0.9995	
Pentanoic acid [18]	293.15	-1.31E-10	1.41E-14	0.9982	0.1–25
	298.15	-1.27E-10	1.37E-14	0.9984	
	303.15	-1.23E-10	1.34E-14	0.9984	
	308.15	-1.20E-10	1.31E-14	0.9984	
	313.15	-1.17E-10	1.28E-14	0.9987	
	318.15	-1.13E-10	1.25E-14	0.9984	
	323.15	-1.11E-10	1.22E-14	0.9987	
Hexanoic acid [18]	293.15	-2.35E-10	2.93E-14	0.9967	0.1–25
	298.15	-2.14E-10	2.62E-14	0.9970	
	303.15	-2.07E-10	2.55E-14	0.9973	
	308.15	-2.01E-10	2.49E-14	0.9974	
	313.15	-1.96E-10	2.44E-14	0.9974	
	318.15	-1.91E-10	2.38E-14	0.9975	
	323.15	-1.85E-10	2.33E-14	0.9976	
Heptanoic acid [18]	293.15	-3.89E-10	5.49E-14	0.9950	0.1–25
	298.15	-3.78E-10	5.35E-14	0.9957	
	303.15	-3.66E-10	5.20E-14	0.9963	
	308.15	-3.57E-10	5.10E-14	0.9965	
	313.15	-3.47E-10	4.91E-14	0.9969	
	318.15	-3.39E-10	4.88E-14	0.9967	
	323.15	-3.30E-10	4.78E-14	0.9969	
Octanoic acid [18]	293.15	-6.13E-10	9.64E-14	0.9939	0.1–25
	298.15	-5.92E-10	9.35E-14	0.9950	
	303.15	-5.75E-10	9.12E-14	0.9950	
	308.15	-5.60E-10	8.92E-14	0.9955	
	313.15	-5.46E-10	8.73E-14	0.9958	
	318.15	-5.30E-10	8.51E-14	0.9961	
	323.15	-5.18E-10	8.35E-14	0.9963	

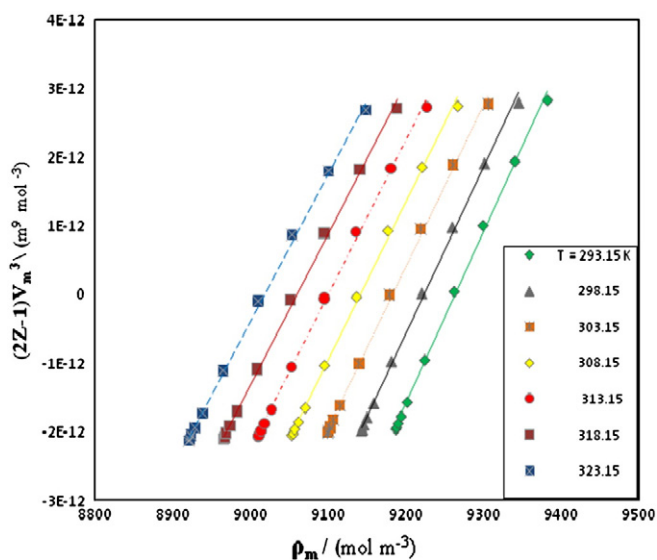


Fig. 1. Isotherms of $(Z-1)V_m^3$ versus ρ_m for pentanoic acid.

Table 1(b)

The intercept (A), slope (B), square of correlation coefficient (R^2) of Eq. (1), and pressure range of the data for esters.

Substance	T/(K)	B/(m ¹² •mol ⁻⁴)	A/(m ⁹ •mol ⁻³)	R ²	ΔP/(MPa)		
Ethyl acetate ^[20]	298.15	-6.91E-11	6.72E-15	0.9976	0.1–35		
	303.15	-6.67E-11	6.53E-15	0.9976			
	308.15	-6.45E-11	6.35E-15	0.9978			
	313.15	-6.30E-11	6.24E-15	0.9979			
	318.15	-6.09E-11	6.07E-15	0.9980			
	323.15	-5.94E-11	5.96E-15	0.9978			
	328.15	-5.75E-11	5.80E-15	0.9975			
	333.15	-5.57E-11	5.65E-15	0.9979			
	338.15	-5.37E-11	5.48E-15	0.9979			
	343.15	-5.23E-11	5.38E-15	0.9980			
	348.15	-4.79E-11	4.96E-15	0.9988			
	353.15	-5.03E-11	5.26E-15	0.9986			
	358.15	-4.87E-11	5.12E-15	0.9987			
	363.15	-4.71E-11	4.99E-15	0.9985			
	368.15	-4.53E-11	4.83E-15	0.9986			
	373.15	-4.43E-11	4.76E-15	0.9988			
	378.15	-4.26E-11	4.60E-15	0.9986			
	383.15	-4.16E-11	4.52E-15	0.9986			
	388.15	-3.99E-11	4.37E-15	0.9985			
Ethyl butyrate ^[19]	298.15	-1.55E-10	1.80E-14	0.9978	0.1–35		
	303.15	-1.51E-10	1.76E-14	0.9977			
	308.15	-1.45E-10	1.70E-14	0.9979			
	313.15	-1.41E-10	1.66E-14	0.9976			
	318.15	-1.35E-10	1.59E-14	0.9978			
	323.15	-1.31E-10	1.56E-14	0.9981			
	328.15	-2.12E-10	2.90E-14	0.9979			
	333.15	-2.07E-10	2.84E-14	0.9978			
	338.15	-2.00E-10	2.76E-14	0.9979			
	343.15	-2.00E-10	2.78E-14	0.9975			
	348.15	-1.91E-10	2.67E-14	0.9979			
	353.15	-1.83E-10	2.57E-14	0.9979			
	363.15	-1.68E-10	2.39E-14	0.9998			
	373.15	-1.58E-10	2.29E-14	0.9999			
	383.15	-1.50E-10	2.20E-14	0.9999			
	393.15	-1.42E-10	2.11E-14	0.9998			
	Ethyl pentanoate ^[19]	298.15	-4.06E-10	6.03E-14		0.9999	0.1–35
		303.15	-3.95E-10	5.89E-14		0.9999	
		308.15	-3.85E-10	5.77E-14		0.9999	
313.15		-3.76E-10	5.68E-14	0.9999			
318.15		-3.67E-10	5.56E-14	1.0000			
323.15		-3.57E-10	5.45E-14	0.9999			
328.15		-3.48E-10	5.34E-14	0.9999			
333.15		-3.35E-10	5.18E-14	0.9999			
338.15		-3.28E-10	5.10E-14	0.9999			
343.15		-3.19E-10	4.99E-14	0.9999			
348.15		-3.11E-10	4.88E-14	0.9999			
353.15		-3.03E-10	4.79E-14	0.9999			
363.15		-2.84E-10	4.55E-14	0.9998			
373.15		-2.72E-10	4.40E-14	0.9999			
383.15		-2.58E-10	4.22E-14	0.9999			
393.15		-2.56E-10	4.24E-14	0.9994			
Ethyl propionate ^[19]		298.15	-1.41E-10	1.62E-14	0.9981	0.1–35	
		303.15	-1.36E-10	1.57E-14	0.9982		
		308.15	-1.31E-10	1.52E-14	0.9980		
	313.15	-1.27E-10	1.48E-14	0.9979			
	318.15	-1.24E-10	1.46E-14	0.9985			
	323.15	-1.21E-10	1.42E-14	0.9982			
	328.15	-1.18E-10	1.39E-14	0.9983			
	333.15	-1.12E-10	1.34E-14	0.9981			
	338.15	-1.09E-10	1.31E-14	0.9977			
	343.15	-1.06E-10	1.28E-14	0.9984			
	348.15	-1.02E-10	1.25E-14	0.9984			
	353.15	-9.91E-11	1.21E-14	0.9983			
	363.15	-9.04E-11	1.12E-14	0.9998			
	373.15	-8.57E-11	1.08E-14	0.9998			
	383.15	-8.18E-11	1.04E-14	0.9998			
	393.15	-7.88E-11	1.02E-14	0.9994			
	Propyl acetate ^[20]	298.15	-1.40E-10	1.61E-14	0.9984		0.1–35
		303.15	-1.36E-10	1.57E-14	0.9983		
		308.15	-1.32E-10	1.53E-14	0.9981		
313.15		-1.27E-10	1.48E-14	0.9984			
318.15		-1.12E-10	1.31E-14	0.9739			
323.15		-1.20E-10	1.42E-14	0.9978			

Table 1(b) (continued)

Substance	T/(K)	B/(m ¹² •mol ⁻⁴)	A/(m ⁹ •mol ⁻³)	R ²	ΔP/(MPa)		
Propyl acetate ^[20]	328.15	-1.15E-10	1.36E-14	0.9982	0.1–35		
	333.15	-1.12E-10	1.34E-14	0.9980			
	338.15	-1.09E-10	1.31E-14	0.9982			
	343.15	-9.67E-11	1.17E-14	0.9554			
	348.15	-1.03E-10	1.25E-14	0.9984			
	353.15	-1.01E-10	1.23E-14	0.9982			
	358.15	-1.04E-10	1.28E-14	0.9994			
	363.15	-9.77E-11	1.21E-14	0.9995			
	368.15	-9.58E-11	1.20E-14	0.9999			
	373.15	-6.85E-11	1.17E-14	0.9673			
	378.15	-8.43E-11	1.07E-14	0.9961			
	383.15	-8.27E-11	1.05E-14	0.9959			
	388.15	-8.27E-11	1.06E-14	0.9994			
	393.15	-7.91E-11	1.02E-14	0.9964			
	N-Butyl acetate ^[20]	298.15	-4.02E-10	5.93E-14		0.9980	0.1–35
		303.15	-3.92E-10	5.82E-14		0.9982	
		308.15	-3.79E-10	5.66E-14		0.9983	
		313.15	-3.68E-10	5.52E-14		0.9982	
		318.15	-3.58E-10	5.40E-14		0.9980	
323.15		-3.46E-10	5.25E-14	0.9975			
328.15		-3.40E-10	5.19E-14	0.9986			
333.15		-3.27E-10	5.01E-14	0.9986			
338.15		-3.15E-10	4.85E-14	0.9985			
343.15		-3.04E-10	4.71E-14	0.9981			
348.15		-2.94E-10	4.58E-14	0.9982			
353.15		-2.86E-10	4.48E-14	0.9983			
358.15		-3.06E-10	4.85E-14	0.9832			
363.15		-2.54E-10	4.04E-14	0.9937			
368.15		-2.81E-10	4.50E-14	0.9992			
373.15		-2.54E-10	4.08E-14	0.9945			
378.15		-1.96E-10	3.17E-14	0.9522			
383.15		-2.45E-10	3.99E-14	0.9924			
388.15		-2.63E-10	4.31E-14	0.9995			
393.15	-2.33E-10	3.85E-14	0.9934				
N-Pentyl acetate ^[20]	298.15	-4.29E-10	6.37E-14	0.9982	0.1–35		
	303.15	-4.17E-10	6.22E-14	0.9977			
	308.15	-4.05E-10	6.06E-14	0.9979			
	313.15	-3.95E-10	5.95E-14	0.9979			
	318.15	-3.81E-10	5.77E-14	0.9977			
	323.15	-3.70E-10	5.63E-14	0.9980			
	328.15	-3.60E-10	5.51E-14	0.9975			
	333.15	-3.50E-10	5.38E-14	0.9978			
	338.15	-3.37E-10	5.22E-14	0.9979			
	343.15	-3.29E-10	5.11E-14	0.9978			
	348.15	-3.20E-10	5.00E-14	0.9979			
	353.15	-3.08E-10	4.83E-14	0.9982			
	358.15	-2.94E-10	4.65E-14	0.9969			
	363.15	-2.88E-10	4.59E-14	0.9975			
	368.15	-2.81E-10	4.50E-14	0.9980			
	373.15	-2.84E-10	4.58E-14	0.9940			
	378.15	-3.25E-10	5.28E-14	0.9917			
	383.15	-2.65E-10	4.31E-14	0.9971			
	388.15	-2.58E-10	4.23E-14	0.9989			
393.15	-2.54E-10	4.18E-14	0.9991				

2. Theoretical basis

The content of this section of the paper is divided in two parts. In the first part a great effort is applied to support hypothesis proposed by Goharshadi et al. [4] for liquids which will be described in Section 2.1. The second part contains brief description of AK and NM generalized correlations and PR EoS which were used in this study for comparison. Detailed description of the correlations and PR EoS are given in Appendix A.

2.1. Goharshadi–Morsali–Abbaspour (GMA) equation of state

A simple general EoS has been recently derived by Goharshadi et al. which has been found to be valid for polar, nonpolar, and hydrogen bonding liquids [4,21]. This EoS is named GMA. The GMA EoS is based on the average potential energy. The average potential energy is approximately equal to the summation of contribution from nearest neighbors

only, assuming single inverse powers for the effective repulsion and attraction and the final result is given in the form of following regularity:

$$(2Z-1)V_m^3 = A(T) + B(T)\rho_m \quad (1)$$

Coefficients of linear dependency are functions of temperature where Z , V_m , and ρ_m ($\rho_m = 1/V_m$) are compressibility factor, molar volume, and molar density, respectively. GMA EoS can be used for high density regions (liquid state) since it does not give correct low pressure limit (zero pressure limiting compressibility factor issuing from Eq. (1) is 0.5, not 1). The intercept and the slope of this equation both depend on temperature via the following equations:

$$A(T) = A_0 \frac{2A_1}{RT} + \frac{2A_2 \ln T}{R} \quad (2)$$

$$B(T) = B_0 \frac{2B_1}{RT} + \frac{2B_2 \ln T}{R} \quad (3)$$

where A_0 to A_2 and B_0 to B_2 are substance dependent constants (not generalized).

To use the GMA EoS for a liquid, the A and B parameters must be known. To find these parameters, we plot $(2Z-1)V_m^3$ against ρ_m for different isotherms. The slope and intercept of the straight lines can be fitted to Eqs. (2) and (3) from which A_0 to A_2 and B_0 to B_2 can be found, respectively. The constants A_0 – A_2 and B_0 – B_2 can be used to calculate the density of these organic compounds at specified ranges of temperature and pressure.

Another EoS that has previously been derived for liquids is linear isotherm regularity (LIR EoS) [19] which is written as $(Z-1)V_m^2 = A'(T) + B'(T)\rho^2$. Goharshadi et al. [4] have tested $(Z-1)V_m^2 = A'(T) + B'(T)\rho^2$ for a number of different liquids using experimental data and found that there is not a complete linear relation between $(Z-1)V_m^2$ and ρ^2 and also the slope and intercept of $(Z-1)V_m^2 = A'(T) + B'(T)\rho^2$ are not the same for different temperatures. Hence, the temperature dependence of the coefficients of LIR EoS is also revised in GMA EoS. We do not intend to use LIR EoS for density calculation of liquid organic compounds here, instead we want to use the new EoS (GMA) which has been improved for liquid density calculation and gives more reliable results.

In Sections 2.2–2.4 the theoretical basis of three other models in which the performance of GMA EoS will be compared with, is briefly given. The results of these comparisons will be discussed in Section 4.

2.2. Aalto–Keskinen model

Aalto and Keskinen [22] (AK) improved the model of Aalto et al. [17,18] in which the data used in fitting the general model parameters extended up to 800 MPa. A lot of data points were also located near the critical temperature. Thus the AK correlation can be used with excellent accuracy up to extremely high pressures. The AK correlation also applies with good accuracy to the critical temperature giving also the liquid compression at the critical temperature when pressure is higher than critical pressure. The Aalto et al. model was compared with AK and it was found to have nearly the same accuracy in the pressure range from saturation pressure to only 20 MPa. Therefore the AK correlation is recommended over the model of Aalto et al. The AK correlation uses V_s (saturated liquid molar volume) from the HT model. The detailed description of equations needed for calculation of saturated and compressed liquid density by AK model is given in Appendix A.

2.3. Nasrifar–Moshfeghian correlation for compressed liquid density

A new correlation is developed for calculation of the compressed liquid density of compounds by Nasrifar et al. [16] which is named NM in this paper. This correlation is used together with the HT (COSTALD)

correlation of saturated liquid density and the Riedel equation for the calculation of vapor pressures. The range of application of this correlation is quite wide; from freezing point temperature to critical point temperature and from saturation pressure to 500 MPa [16].

The pure component parameters which are needed are T_c , P_c and ω_{SRK} . The parameter V^* is also required which has been assumed equal to V^* in HT model. The compound's vapor pressure is also required. Detail of equations needed for density calculation by NM is given in the Appendix A.

Table 1(c)

The intercept (A), slope (B), square of correlation coefficient (R^2) of Eq. (1), and pressure range of the data for alcohols.

Substance	$T(K)$	$B/(m^{12} \cdot mol^{-4})$	$A/(m^9 \cdot mol^{-3})$	R^2	$\Delta P/(MPa)$
1-Pentanol [21]	323.15	−1.20E-10	1.32E-14	0.9993	0.1–10
	328.15	−1.20E-10	1.33E-14	0.9974	
	333.15	−1.15E-10	1.27E-14	0.9993	
	338.15	−1.16E-10	1.30E-14	0.9994	
	343.15	−1.10E-10	1.24E-14	0.9991	
	348.15	−1.04E-10	1.17E-14	0.9996	
	353.15	−1.04E-10	1.18E-14	0.9989	
	358.15	−1.00E-10	1.14E-14	0.9996	
	363.15	−9.83E-11	1.12E-14	0.9994	
	373.15	−9.50E-11	1.10E-14	0.9998	
1-Hexanol [21]	323.15	−2.25E-10	2.86E-14	0.9996	0.1–10
	328.15	−2.21E-10	2.81E-14	0.9978	
	333.15	−2.11E-10	2.70E-14	0.9997	
	338.15	−2.08E-10	2.68E-14	0.9998	
	343.15	−1.97E-10	2.54E-14	0.9991	
	348.15	−1.92E-10	2.50E-14	0.9991	
	353.15	−1.91E-10	2.49E-14	0.9998	
	358.15	−1.86E-10	2.44E-14	0.9991	
	363.15	−1.81E-10	2.38E-14	0.9994	
	373.15	−1.77E-10	2.35E-14	0.9995	
1-Heptanol [21]	323.15	−3.74E-10	5.38E-14	0.9993	0.1–10
	328.15	−3.68E-10	5.31E-14	0.9976	
	333.15	−3.60E-10	5.22E-14	0.9997	
	338.15	−3.65E-10	5.32E-14	0.9997	
	343.15	−3.33E-10	4.87E-14	0.9984	
	348.15	−3.29E-10	4.84E-14	0.9996	
	353.15	−3.28E-10	4.84E-14	0.9996	
	358.15	−3.15E-10	4.67E-14	0.9998	
	363.15	−3.10E-10	4.62E-14	0.9994	
	373.15	−3.04E-10	4.57E-14	0.9998	
1-Octanol [21]	323.15	−6.08E-10	9.77E-14	0.9997	0.1–10
	328.15	−6.06E-10	9.79E-14	0.9964	
	333.15	−5.77E-10	9.36E-14	0.9997	
	338.15	−5.86E-10	9.54E-14	0.9995	
	343.15	−5.33E-10	8.71E-14	0.9993	
	348.15	−5.25E-10	8.64E-14	0.9983	
	353.15	−5.23E-10	8.64E-14	0.9997	
	358.15	−5.01E-10	8.30E-14	0.9997	
	363.15	−4.99E-10	8.32E-14	0.9997	
	373.15	−4.78E-10	8.05E-14	0.9997	
1-Nonanol [21]	323.15	−9.16E-10	1.63E-13	0.9992	0.1–10
	328.15	−9.16E-10	1.63E-13	0.9958	
	333.15	−8.84E-10	1.58E-13	0.9989	
	338.15	−8.98E-10	1.62E-13	0.9997	
	343.15	−8.00E-10	1.45E-13	0.9985	
	348.15	−7.94E-10	1.44E-13	0.9993	
	353.15	−7.95E-10	1.45E-13	0.9993	
	358.15	−7.67E-10	1.41E-13	0.9945	
	363.15	−7.61E-10	1.40E-13	0.9991	
	373.15	−7.33E-10	1.36E-13	0.9998	
1-Dodecanol [21]	323.15	−2.64E-09	6.02E-13	0.9996	0.1–10
	328.15	−2.63E-09	6.02E-13	0.9967	
	333.15	−2.53E-09	5.82E-13	0.9997	
	338.15	−2.54E-09	5.87E-13	0.9998	
	343.15	−2.33E-09	5.40E-13	0.9985	
	348.15	−2.26E-09	5.26E-13	0.9996	
	353.15	−2.32E-09	5.42E-13	0.9998	
	358.15	−2.19E-09	5.16E-13	0.9997	
	363.15	−2.16E-09	5.10E-13	0.9997	
	373.15	−2.10E-09	5.00E-13	0.9987	

2.4. Peng–Robinson equation of state

The Peng–Robinson (PR) EoS was introduced in 1976 [20]. The PR EoS provides results similar to the SRK EoS, though it is generally superior in estimating the liquid densities of many compounds, especially the nonpolar ones. The details of PR EoS are given in Appendix A.

3. Method of parameter determination

To obtain the coefficient estimates, the least-squares method was employed. This method minimizes the summed square of residuals. The residual for the i th data point r_i is defined as the difference between the observed response value y_i and the fitted response value \hat{y}_i , and is identified as the error associated with the data.

$$r_i = y_i - \hat{y}_i \quad (4)$$

The summed square of residuals is given by:

$$S = \sum_{i=1}^n r_i^2 = \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (5)$$

where n is the number of data points included in the fit and S is the sum of square error estimate.

It is usually assumed that the response data is of equal quality and, therefore, has constant variance. If this assumption is violated, the fit might be unduly influenced by data of poor quality. To improve the fit, we used weighted least-squares regression where an additional scale factor (the weight) is included in the fitting process. Weighted least-squares regression minimizes the error estimate, and that is:

$$S = \sum_{i=1}^n w_i (y_i - \hat{y}_i)^2 \quad (6)$$

where w_i are the weights. The weights determine how much each response value influences the final parameter estimates. A high-quality data point influences the fit more than a low-quality data point.

4. Results and discussion

Experimental density data of 20 organic compounds (7 acids, 7 esters and 6 alcohols C_5 – C_{10}) in the temperature region of 293.15–393.15 K and wide pressure region were used. The experimental $P\rho T$ data of acids, alcohols and esters [22–25] at various temperatures and pressures are used to examine the linearity of $(2Z - 1)V_m^3$ versus ρ_m (Eq. (1)). Fig. 1 presents the isotherms of $(2Z - 1)V_m^3$ versus the density for pentanoic acid. Obtained results support the GMA EoS hypothesis. As Fig. 1 shows, the linearity holds very well and the slope and intercept depend on temperature. The results are summarized in Table 1(a, b, and c), including the slope and intercept of the fitted straight line (Eq. (1)) at each temperature, the square of correlation coefficient (R^2), and the pressure range of the experimental data which is composed of 20 pure organic compounds including acids, esters and alcohols. Table 2 shows the values of the constants and the square of the correlation coefficients of Eqs. (2) and (3). The ranges of pressure and temperature of experimental points in this table are the same as in Table 1(a, b, and c). To evaluate the GMA EoS, a more sensible test would be performed to calculate density at the different temperatures and pressures and compare with the corresponding experimental data.

Fig. 2 illustrates the pressure–density diagram for 1-hexanol. In this diagram pressure is plotted versus calculated density by GMA EoS and experimental densities. There is a good agreement between calculated densities and experimental data. It can be seen from the pressure–density diagram that as pressure increases, density increases as well which is expected. The density of the liquid organic compounds in a wide range of temperature and pressure has been calculated using the GMA EoS and the results were compared with corresponding experimental data.

The ability of GMA EoS in the calculation of density at different temperatures and pressures for all 20 pure organic compounds may be evaluated by statistical parameters such as percent of deviations (% Dev) and the average absolute deviation (% AAD). These parameters are defined as:

$$\%Dev = 100 \times \left(\frac{\rho_{exp} - \rho_{cal}}{\rho_{exp}} \right) \quad (7)$$

$$\%AAD = \frac{1}{N} \sum_{i=1}^N 100 \left| \frac{\rho_{exp} - \rho_{cal}}{\rho_{exp}} \right| \quad (8)$$

Table 2
The values of constants and the square of the correlation coefficients (R^2) of Eqs. (2) and (3).

Substance	$A_0/(\text{m}^3 \text{mol}^{-3})$	$A_1/(\text{m}^6 \text{Pa mol}^{-4})$	$A_2/(\text{m}^6 \text{Pa mol}^{-4} \text{K}^{-2})$	R^2	$B_0/(\text{m}^{12} \text{mol}^{-4})$	$B_1/(\text{m}^{15} \text{Pa mol}^{-5})$	$B_2/(\text{m}^{15} \text{Pa mol}^{-2} \text{K}^{-2})$	R^2
<i>Acids</i>								
Acetic acid	−8.19E−15	−2.63E−12	4.88E−15	0.9995	3.44E−10	8.73E−08	−2.08E−10	0.9994
Propanoic acid	−7.97E−14	−1.91E−11	4.84E−14	0.9996	8.64E−10	2.24E−07	−5.19E−10	0.9997
Butanoic acid	8.54E−16	−1.02E−11	−2.38E−15	0.9965	−1.88E−10	9.51E−08	1.46E−10	0.9972
Pentanoic acid	−6.01E−14	−3.48E−11	3.34E−14	0.9992	3.38E−09	8.90E−07	−2.03E−09	0.9979
Hexanoic acid	1.16E−12	−1.55E−09	4.82E−12	0.9452	4.82E−08	9.70E−06	−2.96E−08	0.9712
Heptanoic acid	4.06E−13	−6.14E−10	1.69E−12	0.9908	9.21E−09	2.48E−06	−5.54E−09	0.9995
Octanoic acid	3.96E−13	−6.73E−10	1.64E−12	0.9989	1.93E−08	4.83E−06	−1.17E−08	0.9992
<i>Esters</i>								
Ethyl acetate	−2.72E−14	−1.72E−11	1.46E−14	0.9878	4.44E−10	2.33E−07	−2.37E−10	0.9932
Ethyl propionate	−7.18E−14	−4.48E−11	3.78E−14	0.9952	7.46E−10	−7.47E−06	2.18E−08	0.9965
Ethyl butyrate	5.65E−12	1.20E−09	−3.41E−12	0.9897	−3.60E−08	1.29E−06	−1.41E−09	0.9743
Ethyl pentanoate	−2.48E−13	−1.46E−10	1.39E−13	0.9949	2.56E−09	4.57E−07	−3.78E−10	0.9970
Propyl acetate	−1.55E−13	−5.84E−11	8.99E−14	0.9226	1.32E−09	5.64E−07	−7.33E−10	0.9089
N-Butyl acetate	−3.89E−13	−1.87E−10	2.18E−13	0.9796	3.07E−09	1.47E−06	−1.67E−09	0.9912
N-Pentyl acetate	−1.13E−12	−3.37E−10	6.72E−13	0.9858	7.72E−09	2.42E−06	−4.52E−09	0.9812
<i>Alcohols</i>								
1-Pentanol	−3.20E−14	−3.13E−11	1.59E−14	0.9997	6.63E−10	4.03E−07	−3.49E−10	0.9922
1-Hexanol	−1.92E−12	−4.54E−10	1.16E−12	0.9827	1.55E−08	3.73E−06	−9.30E−09	0.9879
1-Heptanol	−1.32E−12	−3.68E−10	7.94E−13	0.9874	9.16E−09	2.67E−06	−5.43E−09	0.9876
1-Octanol	−3.86E−12	−9.96E−10	2.32E−12	0.9861	2.33E−08	6.24E−06	−1.39E−08	0.9986
1-Nonanol	−6.03E−12	−1.56E−09	3.62E−12	0.9816	3.67E−08	9.66E−06	−2.19E−08	0.9948
1-Dodecanol	−2.32E−11	−5.98E−09	1.39E−11	0.9959	1.01E−07	2.70E−05	−6.04E−08	0.9904

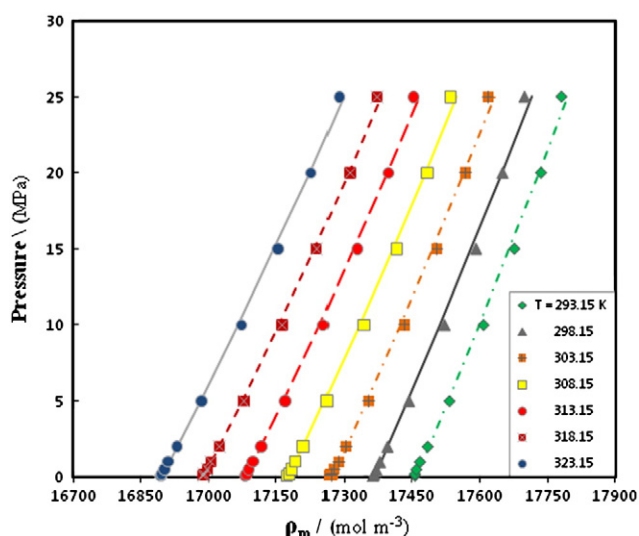


Fig. 2. Pressure–density diagram for 1-hexanol; calculated values by GMA EoS (markers) and experimental data (dashed line).

Fig. 3 depicts the liquid density deviations of GMA EoS for esters at constant temperature and extended range of pressure. The esters have the most percent of deviation range which is $-2.29 < \% \text{Dev} < 0.82$, while alcohols have the least %Dev one ($-0.02 < \% \text{Dev} < 0.04$).

Fig. 4 presents the % Dev for calculating the liquid density of ethyl pentanoate, 1-octanol and butanoic acid (ester, alcohol and acid) at $T = 323.15 \text{ K}$ at different pressures. From this figure it is more sensible to understand that the ability of the GMA EoS for density calculation of alcohols in the considered pressure range is better than esters and acids. Generally, the GMA EoS reproduces experimental data within 0.01%, 0.1% and 0.01% for acids, esters and alcohols, respectively, while some of data points scatter with rather positive deviation. These values confirm the ability of GMA EoS in density calculation of organic liquids from low to high pressures.

The parity graph of GMA EoS calculations was also considered to assess the ability of GMA EoS to reproduce experimental data. Fig. 5 presents parity graph of calculated densities of GMA EoS versus experimental data at different temperatures for pentanoic acid. GMA EoS reveals a good sparseness around angle bisector line for pentanoic acid.

Although the studied compounds cover components including polar and hydrogen bonding, the results in calculation of density show good agreement with experimental data. The excellent results have been obtained since the size and the strength of intermolecular forces of compounds are very similar. Our results show that the effect of size is more important than the strength of intermolecular forces. Since the strength of hydrogen bonding is very high, the agreement of calculated

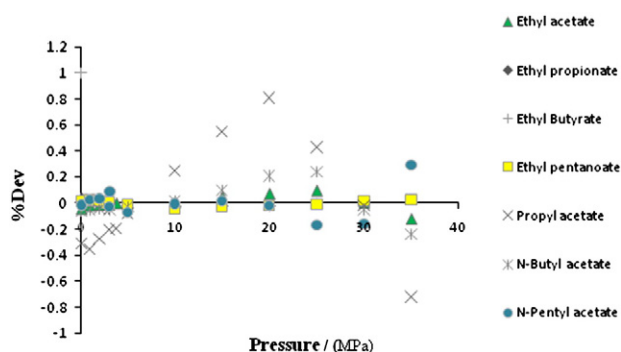


Fig. 3. Percent of deviations for calculating the liquid density of esters at $T = 273.15 \text{ K}$.

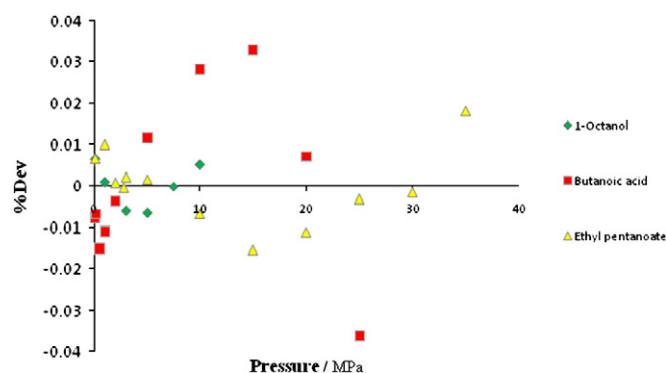


Fig. 4. Percent of deviations for calculating the liquid density of ethyl pentanoate, 1-octanol and butanoic acid at $T = 323.15 \text{ K}$ and different pressures.

densities with the corresponding experimental values is interesting since the average absolute deviations are much better than 1%.

To show the ability of this EoS in calculation of density, the computed densities of the liquid organic compounds have been compared with two generalized correlations and PR EoS. The generalized correlations are AK and NM.

The %AAD characterizes that the calculated values are more or less close to experimental data. Table 3 presents these comparisons for 20 considered compounds. The temperature and pressure range for this table is the same as in Table 1 (a, b, and c). This table presents %AAD for generalized correlations and EoSs for calculated liquid densities. Table 3 indicates that GMA EoS results are better than the other correlations. According to this table the average %AAD for GMA EoS is 0.0266, 0.0265 and 0.0101 for acids, esters and alcohols, respectively. The comparison is from low to high pressures and the total number of experimental points is 2332. Again this comparison supports the ability of this EoS for accurate density calculation of organic liquids up to high pressures.

GMA is an EoS with six substance specific parameters while the methods selected from the literature for a comparison are generalized methods with parameters generally valid for any substance which are non-adjustable with particular physical meaning (critical temperature, critical pressure, characteristic volume and acentric factor). Naturally, the GMA EoS as a purely empirical correlation method gives better results than those generalized methods and in this work we are more concerned on the accuracy of EoS. Therefore, the selected methods for comparison might not give more accurate results than GMA EoS in the high density region. General parameters are averages over a large number of substances; moreover it is not sure whether

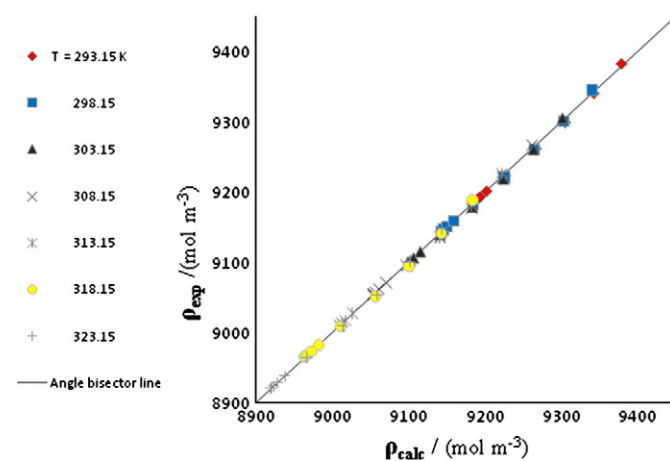


Fig. 5. Parity graph of calculated densities by GMA EoS versus experimental densities at different temperatures for pentanoic acid.

Table 3

The % AAD values between experimental density data and calculated values by GMA EoS, NM, AK and PR EoS.

Substance	nps	GMA	NM	AK	PR	$\Delta T/(K)$	$\Delta P/(MPa)$
<i>Acids</i>							
Acetic acid	70	2.79E-02	11.43	1.69	23.34	293.15–323.15	0.1–25
Propanoic acid	70	4.87E-03	9.54	0.26	8.27		
Butanoic acid	70	1.25E-02	8.21	0.52	9.43		
Pentanoic acid	70	2.44E-02	7.18	0.62	9.49		
Hexanoic acid	70	3.53E-02	9.70	0.30	9.89		
Heptanoic acid	70	4.09E-02	5.26	6.93	8.15		
Octanoic acid	70	4.05E-02	2.02	13.07	8.45		
Total	490	2.66E-02	7.62	3.34	11.01		
<i>Esters</i>							
Ethyl acetate	231	2.03E-02	11.32	0.20	4.39	298.15–393.15	0.1–35
Ethyl propionate	190	2.09E-02	10.48	0.49	2.63		
Ethyl butyrate	192	1.00E-02	11.89	0.19	0.12		
Ethyl pentanoate	192	1.35E-02	10.61	0.34	0.15		
Propyl acetate	221	1.09E-02	11.35	1.27	5.25		
N-Butyl acetate	216	9.49E-02	10.06	0.30	1.00		
N-Pentyl acetate	240	1.51E-02	10.48	0.18	5.56		
Total	1482	2.65E-02	10.88	0.42	2.73		
<i>Alcohols</i>							
1-Pentanol	60	9.49E-03	13.43	0.56	0.18	323.15–373.15	0.1–10
1-Hexanol	60	9.42E-03	9.87	0.81	1.00		
1-Heptanol	60	1.20E-02	10.82	0.74	0.48		
1-Octanol	60	7.97E-03	9.32	0.87	0.76		
1-Nonanol	60	1.17E-02	9.40	0.57	0.55		
1-Dodecanol	60	1.00E-02	15.76	6.01	1.39		
Total	360	1.01E-02	11.43	1.59	0.72		

the substances considered here have been included in the input data set used for evaluation of generalized parameters. In other words, generalized methods are obtained by wide experimental data of many groups of substances which might make them less accurate than GMA EoS for three groups of substances. The parameters in Table 2 do not have any physical meaning and they could not be derived from other properties of compound as, e.g., the coordinates of the critical point. However, this is the lack of GMA EoS in all papers [4,21] relating to it and this is the subject of our upcoming paper to overcome this problem for improving it.

Generalized methods give density values that are predicted while GMA EoS is a correlation method representing smoothed data for particular substance in particular (T, P) range. Since no extrapolation abilities of the GMA EoS have been examined, the reliability of values calculated from the GMA EoS for the temperature and pressure outside of the considered (T, P) regions of input experimental data is highly uncertain and thus the extrapolation cannot be recommended.

In other respects, the saturate liquid density calculated from PR EoS differs always significantly from the experimental one, therefore, the so called volume shift (proposed by Peneloux et al. [26]) has to be used. Therefore, PR EoS is not suitable choice for calculation of temperature and pressure dependence of the liquid density. Therefore, greater deviations are observed between calculated and experimental values.

Linear dependency $(2Z-1)V_m^3 = A(T) + B(T)\rho_m$ holds also for liquid mixtures and it is possible to use quadratic dependence of parameters A and B on composition; however this is the subject of an upcoming work.

5. Conclusion

In the present work GMA EoS was used to calculate the density of 20 liquid organic compounds in extended ranges of temperature up to high pressures. The excellent agreement with experimental data proves that this EoS can be used with a very high degree of certainty to calculate the density of these compounds up to high pressure. However, the extension of EoS predictions to (T, P) region outside

experimental data is not recommended. The comparisons of GMA EoS with important generalized correlations proved the superiority of this EoS in the considered range of temperature and pressure. The GMA EoS can be a good alternative for complex models in simulations, process designs and calculation of the thermodynamic properties due to its accuracy together with simplicity with restriction to some specific compounds.

Nomenclature

List of symbols

A	a function given by in Eq. (A.5) and defined in Eq. (A.6)
$A(T)$	intercept of Eq. (1) ($m^9 mol^{-3}$)
A_0	constant in Eq. (2) ($m^3 mol^{-3}$)
A_1	constant in Eq. (2) ($m^6 Pa mol^{-4}$)
A_2	constant in Eq. (2) ($m^6 Pa mol^{-4} K^{-2}$)
a	constant in Eqs. (A.2) and (A.14)
a_0, a_1, a_2, a_3, a_4	constants in Eq. (A.4)
B	a function given by Eq. (A.4) defined in Eq. (A.6)
$B(T)$	slope of Eq. (1) ($m^{12} mol^{-4}$)
B_0	constants in Eq. (3) ($m^{12} mol^{-4}$)
B_1	constant in Eq. (3) ($m^{15} Pa mol^{-5}$)
B_2	constant in Eq. (3) ($m^{15} Pa mol^{-2} K^{-2}$)
b	constant in Eq. (A.2) and a constant in Eq. (A.14) defined in Eq. (A.16)
b_0, b_1, b_2	constants in Eq. (A.6)
C	a function given by Eqs. (A.4) and (A.8) define in Eqs. (A.7) and (A.11)
c_1, c_2, c_3, c_4	constants in Eq. (A.7)
c_0, c_1	global constants in Eq. (A.11)
D, E	constant in Eq. (A.4)
d	constant in Eq. (A.2)
e, f, g, h	constant in Eq. (A.3)
F	a function of reduced temperature given by Eq. (A.10)
f_0	global constant of Eq. (A.10)
G, I	global constant of Eq. (A.8)
J	a function of temperature as defined by Eq. (A.9)
j_0, j_1, j_2	global constants of Eq. (A.9)

L, M	global constants of Eq. (A.8)
nps	number of points
p	pressure (MPa)
P_c	critical pressure (MPa)
P_r	reduced pressure
$P_{r,s}$	saturated liquid reduced pressure
R	gas constant ($8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$)
T	temperature (K)
T_c	critical temperature (K)
T_r	reduced temperature
V_m	molar volume ($\text{m}^3 \text{ mol}^{-1}$)
V_s	Saturated liquid molar volume ($\text{m}^3 \text{ mol}^{-1}$)
V^*	characteristic volume ($\text{m}^3 \text{ mol}^{-1}$)
V_R^0	a function reduced temperature given by Eq. (A.2)
$V_R^{(6)}$	a function of reduced temperature given by Eq. (A.3)
v	molar volume ($\text{m}^3 \text{ mol}^{-1}$)
v_s	saturated molar volume ($\text{m}^3 \text{ mol}^{-1}$)
v_∞	molar volume at infinite pressure ($\text{m}^3 \text{ mol}^{-1}$)
Z	compressibility factor

Greek letters

α	a function given by Eq. (A.17)
κ	a function given by Eq. (A.18)
ρ_m	molar density (mol m^{-3})
ω_{SRK}	SRK-acentric factor
ω	acentric factor
Ω_0, Ω_1	global constants of Eq. (A.13)
Ω	a function of ω_{SRK} as defined by Eq. (A.13)

Subscripts

c	critical
cal	calculated value
exp	experimental value
r	reduced
s	saturated

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Appendix A

A.1. Aalto–Keskinen model

The saturated liquid molar volume, V_s , is computed in the HT model from [8]:

$$\frac{V_s}{V^*} = V_R^{(0)} [1 - \omega_{SRK} V_R^{(6)}] \quad (\text{A.1})$$

$$V_R^0 = 1 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + c(1-T_r) + d(1-T_r)^{4/3} \quad \text{when } 0.25 < T_r < 0.95 \quad (\text{A.2})$$

$$V_R^{(6)} = \frac{(e + fT_r + gT_r^2 + hT_r^3)}{T_r - 1.00001} \quad \text{when } 0.25 < T_r < 1.0 \quad (\text{A.3})$$

where $T_r = T/T_c$.

For Eqs. (5) and (6) the general parameters are the following:

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

The pure component specific parameters are the following: characteristic volume V^* , slightly adjusted critical temperature $T_{c,HBT}$ and the SRK acentric factor ω_{SRK} . ω_{SRK} is named SRK (Soave–Redlich–Kwong) acentric factor by Aalto and Keskinen [18] which was correlated to all data using the SRK EoS, while usually it is calculated from the saturated pressure at 0.7 of the critical pressure.

Once the saturated molar volume V_s and saturation pressure P_s have been calculated at a chosen temperature T , one can use the equation to calculate molar volume V at the actual pressure P of the liquid. The pressure dependence of liquid density is as follows:

$$\frac{V}{V_s} = \frac{A + C^{(D-T_r)^B} (P_r - P_{s,r})^E}{A + C(P_r - P_{s,r})^E} \quad (\text{A.4})$$

$$A = a_0 + a_1 T_r + a_2 T_r^2 + a_3 T_r^6 + a_4 / T_r \quad (\text{A.5})$$

$$B = b_0 + \frac{b_1}{b_2 + \omega_{SRK}} \quad (\text{A.6})$$

$$C = c_1(1-T_r)^{c_2} + [1 - (1-T_r)^{c_2}] \exp[c_3 + c_4(P_r - P_{s,r})] \quad (\text{A.7})$$

where $P_r = P/P_c$ and $P_{s,r} = P_s/P_c$.

The general equation parameters for Eqs. (A.8) through (A.11) are:

$a_0 = 482.85416$	$a_1 = -1154.2977$	$a_2 = 790.09727$	$a_3 = -212.14413$
$a_4 = 93.4904$	$b_0 = 0.0264002$	$b_1 = 0.42711522$	$b_2 = 0.5$
$c_1 = 9.2892236$	$c_2 = 2.5103968$	$c_3 = 0.5939722$	$c_4 = 0.0010895002$
$D = 1.00001$	$E = 0.80329503$		

A.2. Nasrifar–Moshfeghian correlation for compressed liquid density

Nasrifar et al. presented their correlation as follows:

$$\frac{v - v_s}{v_\infty - v_s} = C \frac{J + L(P_r - P_{r,s}) + M(P_r - P_{r,s})^3}{F + G(P_r - P_{r,s}) + I(P_r - P_{r,s})^3} \quad (\text{A.8})$$

where

$$J = j_0 + j_1(1-T_r)^{1/3} + j_2(1-T_r)^{2/3} \quad (\text{A.9})$$

$$F = f_0(1-T_r) \quad (\text{A.10})$$

$$C = c_0 + c_1 \omega_{SRK} \quad (\text{A.11})$$

$$v_\infty = \Omega \frac{RT_c}{P_c} \quad (\text{A.12})$$

$$\Omega = \Omega_0 + \Omega_1 \omega_{SRK} \quad (\text{A.13})$$

The parameters $j_0, j_1, j_2, L, M, f_0, G, I, c_0, c_1, \Omega_0$ and Ω_1 are global constants. Eq. (A.11) together with Eqs. (A.12)–(A.16) are the

working equations for calculation of the compressed liquid density for pure compounds. The final values of global constants are as follows:

$j_0 = 1.3168 \times 10^{-3}$	$j_1 = 3.4448 \times 10^{-2}$	$j_2 = 5.4131 \times 10^{-2}$	$L = 9.6840 \times 10^{-2}$
$M = 8.6761 \times 10^{-6}$	$f_0 = 48.8756$	$G = 0.7185$	$I = 3.4031 \times 10^{-5}$
$c_0 = 5.5526$	$c_1 = -2.7659$	$\Omega_0 = 7.9019 \times 10^{-2}$	$\Omega_1 = -2.8431 \times 10^{-2}$

A.3. Peng–Robinson equation of state

The general form of the PR equation is as follows:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \quad (\text{A.14})$$

The constants a and b can be obtained by using the pure fluid critical properties.

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha \quad (\text{A.15})$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (\text{A.16})$$

$$\alpha = \left\{ 1 + \kappa \left(1 - \sqrt{T/T_c} \right) \right\}^2 \quad (\text{A.17})$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (\text{A.18})$$

where T_c and P_c are the critical temperature and pressure, respectively, and ω is the acentric factor.

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