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## Comparative Analysis of the Performance of Mixing Rules for Density Prediction of Simple Chemical Mixtures

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**Abstract.** Four different mixing rules (MRs) in three equations of state (EOSs) have been used to account for the intermolecular forces of attraction between dissimilar molecules of different substances that form simple mixtures. The combined effects of the co-volumes of all constituent species of the mixtures were also considered, and the densities of these simple mixtures were predicted. Thereafter, the density results obtained were compared with accurately simulated experimental density values, and the effectiveness of these MRs was determined and compared. The four MRs compared are geometric mean average (GMA), whole square root average (SRA), Expanded geometric average (EGA), and simple average (SA) of attractive force parameter. They were all used in Van der Waals, Redlich Kwong, and Peng Robinson EOSs for two simple mixtures: a binary system (Ammonia – Water system) and a ternary mixture (methyl acetate – water – toluene system). It was found that GMA and EGA gave reasonably accurate estimates of the mixture attractive force parameter ( $a_m$ ) and hence good density prediction for both Ammonia – Water and Methyl acetate – Water – Toluene systems. SRA gave unrealistic values of mixture densities for both systems and was discarded. SA gave a somewhat good result with Peng Robinson EOS for the ammonia-water system, but not that good in Redlich Kwong EOS and very poor in Van der Waals EOS. SA does not give reasonable estimates of the mixture densities with the three EOSs considered for the methyl acetate – water – toluene system.

**Keywords:** equation of state, mixing rule, density predictions, chemical mixtures, thermodynamics, models.

## 1 Introduction

Many industrial processes involve multicomponent systems consisting of more than one liquid mixture. One of the fundamental properties of aqueous solutions commonly used in process industries is density; other properties are solubility, viscosity, vapor pressure, thermal conductivity, and many others. The physical and transport properties of liquid mixtures are essential in understanding the nature of molecular interactions between molecules of liquid mixtures and various transport and process equipment designs. In conjunction with other thermodynamic properties, volumetric properties of aqueous solutions provide helpful information about molecular interactions between liquid mixtures.

Cubic equations of state (EOS) were developed to describe property relationships in pure systems. Usually explicit in pressure (P), an equation of state (EOS) relates other measurable properties such as volume (V) and

temperature (T) of a pure system to its pressure. The attractive forces between the molecules of a pure system, which contribute significantly to these measurable properties, are accounted for by an attractive force parameter called parameter “a.” The volume of the system molecules at infinite pressure is accounted for by the inclusion of a constant called parameter “b” and known as the co-volume. Mixing rules (MR) are employed when an equation of state is applied to mixtures. EOS parameters represent the attractive and repulsive forces between the molecules; hence, mixing rules are used to describe the dominant forces between dissimilar molecules of different substances forming a mixture. Applications of EOSs are of great importance in predicting the pressure-volume-temperature (PVT) relationship and other thermodynamic properties of hydrocarbon fluids and equilibrium calculations.

Researchers have used various mixing rules to employ EOS in predicting various thermodynamic properties of

chemical mixtures (Al-Manthari et al., 2019). The prediction accuracy of EOS varies with the properties being predicted and the system conditions. Two-parameter EOS has been widely applied in the petroleum industry; although accuracy has sometimes been improved by employing EOS with three or more parameters, this is not always the case (Nasrifar and Bolland, 2005, Babalola and Oduwole, 2014). Therefore, a good compromise between the complexity of the EOS model and its prediction accuracy is often required. (Nasrifar and Bolland, 2006). Still, in pursuit of higher accuracy, coupling of two or more EOS using coupling rules has come into focus in recent times (Al-Manthari et al., 2019). For all these applications of EOS, the performance of the mixing rule (MR) used is crucial.

Apparently, for equilibrium calculations and mixture properties prediction, mixing rules (MRs) are used in EOSs. However, the accuracy of EOSs has been found to be non-identical and not particularly adequate for predicting liquid densities of multicomponent hydrocarbon mixtures (Al-Manthari et al., 2019). Performance of some mixing rules for multicomponent systems properties prediction has been found to be poor but quite encouraging for some simple binary or ternary mixtures (Babalola, 2005). Modifications for improving mixing rules have been focused mainly on the attractive force parameter ( $a$ ), which seems to play a significant role in mixing dissimilar molecules. Over the years, the Van der Waals Mixing Rule (with Geometric Mean Average of the attractive parameter) has been exploited in extending the use of EOSs to multicomponent mixtures. However, they are valid only when molecular size differences of components in a mixture are not too significant (Jian et al., 2000) yet, other mixing rules have not been adequately utilized. Al-Manthari et al. (2019) alluded that Waldman-Hagler (WH) combining rules, used in Van der Waal mixing rules, lacked predictability in most EOSs; consequently, researchers are in continuous search for the best pair of EOS and mixing rule among available ones.

This work presents a study of four different Mixing Rules (MRs) employed in three different equations of State (EOSs) to account for the intermolecular forces of attraction between dissimilar molecules of different substances that form simple mixtures. First, the combined effects of the co-volumes of all constituent species of the mixtures were considered, and the densities of the mixtures were predicted. After which, the density results obtained by using these MRs in the selected EOSs were compared with simulated experimental data and the effectiveness of the MRs were determined and compared.

## 2 Research Methodology

### 2.1 Equation of states (EOSs)

The four mixing rules treated here have been proposed in the literature, and some have been in use for some decades. They are termed here as Geometric Mean Average (GMA), Whole Square Root Average (SRA), Expanded Geometric Average (EGA), and Simple

Average (SA) for the attractive force parameter were used in three Equations of State (EOS) for the intermolecular forces of attraction between dissimilar molecules of Ammonia–Water and Methyl acetate—water—toluene thermodynamic systems. Densities of these mixtures were predicted using three EOS and compared, with laboratory simulated data and the effectiveness of the MRs determined.

An equation of state (EOS) is an analytical expression that relates pressure ( $P$ ) to temperature ( $T$ ) and volume ( $V$ ). The Simplest and most widely known EOS is the ideal gas EOS (Ahmed, 2001). Three two-parameters EOS are selected for this study, namely: Van der Waals (1873), Redlich-Kwong (1949), and Peng-Robinson (1976) EOS abbreviated respectively as VW, RK, and PR. Van der Waals EOS is quite simple. PR and RK EOS require less pure component constants and binary interaction parameters than many recently developed EOS and have gained wider acceptance (Estela-Vribe et al., 2004). Nasrifar and Bolland, 2006 found that RK and PR EOSs, are simple, accurate, and more reliable in predicting thermodynamic properties of natural gas mixtures compared to other EOS models. The EOS used in this work is given in PVT and compressibility factor ( $Z$ ) terms in Table 1.

Table 1 – PVT and Z relations for the selected EOSs

Equation of State (EOS)	Mathematical Expressions
Van der Waals (VW)	$P = \frac{RT}{v-b} - \frac{a}{v^2}$ $Z^3 - (1+B)Z^2 + AZ - AB = 0$
Redlich-Kwong (RK)	$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)}$ $Z^3 - Z^2 + (A-B-B^2)Z - AB = 0$
Peng-Robinson (PR)	$P = \frac{RT}{(v-b)} - \frac{a_c\alpha}{v(v+b)+b(v-b)}$ $Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0$

### 2.2 Mixing rules

Mixing rules are used to describe prevailing forces between dissimilar molecules of different substances forming mixtures. Generalized Mixing Rule expressions for the attractive force term ( $a_m$ ) and repulsive force term ( $b_m$ ) are given in following equations:

$$a_m = \sum_{i=1}^m \sum_{j=1}^m x_i x_j a_{ij}; \quad (1)$$

$$b_m = \sum_{i=1}^m x_i b_i, \quad (2)$$

where  $x$ ,  $a$ , and  $b$  – the mole fraction, the attractive force parameter, and the co-volume or repulsive force parameter, respectively.

Several relationships for attractive forces between two molecules ( $a_{ij}$ ) have been defined, and these definitions have resulted in various mixing rules (MRs). Attractive force terms for mixtures ( $a_m$ ) are obtained by different modifications of  $a_{ij}$  in equation (1) but the same repulsive force term ( $b_m$ ) as expressed in equation (2), which has

hardly undergone any significant modification over the years, is employed for all four MRs. This repulsive force term is the volume of a molecule of a constituent species at infinite pressure. It accounts for the force of repulsion between dissimilar molecules in a mixture and is called the co-volume. The four MRs employed in this work for the attractive force term ( $a_m$ ) are as follows:

1) geometric mean average (GMA) of the attractive force parameter (van der Waals et al., 1873) given as follows:

$$a_{ij} = \sqrt{a_i a_j}, \quad (3)$$

which, when substituted in equation (1), give rise to Van der Waal mixing rules as expressed in equations:

$$a_m = \sum_{i=1}^m \sum_{j=1}^m x_i x_j \sqrt{a_i a_j}; \quad (4)$$

2) the whole square root average (SRA) of the attractive force parameter was proposed by Babalola, 2005 as expressed in equation:

$$a_{ij} = \sqrt{\frac{a_i + a_j}{2} + (a_i a_j)^{1/2}}. \quad (5)$$

Using equation (5) in (1) gives rise to another mixing rule expressed as follows:

$$a_m = \sum_{i=1}^m \sum_{j=1}^m x_i x_j \sqrt{\frac{a_i + a_j}{2} + (a_i a_j)^{1/2}}; \quad (6)$$

3) expanded geometric average (EGA) of the attractive force parameter was also proposed by Babalola (2005) as follows:

$$a_{ij} = \frac{2\sqrt{a_i a_j} + a_i + a_j}{4}. \quad (7)$$

When equation (7) is substituted into equation (1), another Mixing Rule is obtained and expressed as follows:

$$a_m = \sum_{i=1}^m \sum_{j=1}^m x_i x_j \frac{2\sqrt{a_i a_j} + a_i + a_j}{4}; \quad (8)$$

4) the simple average (SA) of the attractive force parameter (Jian et al., 2001) expressed as follows:

$$a_{ij} = \frac{a_i + a_j}{2}. \quad (9)$$

Equation (9) in combination with (1) yields yet another Mixing Rule given as follows:

$$a_m = \sum_{i=1}^m \sum_{j=1}^m x_i x_j \frac{a_i + a_j}{2}. \quad (10)$$

Binary interaction parameters, PIBs, ( $K_{ij}$ ) are sometimes used to correct attractive parameters. However, BIPs are temperature and EOS-dependent; therefore, to have a fair comparison of results, they are deliberately set at zero (0) for all EOS employed in this work.

### 2.3 Thermodynamic systems

Densities of an industrial refrigerant (Ammonia – Water system) and an esterification mixture (Methyl acetate – Water – Toluene system) were here predicted at their respective system operating conditions. Ammonia-water system has been known to be environmentally

friendly, cheaply available, energy-efficient, has no global warming potentials, and has therefore been used in industrial refrigeration plants for over 130 years. From chemistry, two products of esterification of methanol and acetic acid are Methyl acetate and water, although both have been known to form binary azeotropes, making their separation difficult. In the industry, toluene is mainly added as an entrainer to make their separation easy. In continuous esterification plants, a mixture of these three components (in the vapor phase) forms the overhead product of the first distillation column. This stream is later separated into organic and aqueous phases. The organic phase contains toluene and methyl acetate, which are separated in the second distillation column. The density of the ternary system, Methyl acetate – water – toluene, is an important physical property in the design of the first distillation column and that of Methyl acetate - Water is helpful in the design of the second column. Methyl Acetate is a crucial chemical substance in perfumery (Bertram, 1982). The physical properties of the mixture constituents are given in Table 2, while Table 3 shows the operating conditions of the binary and ternary thermodynamic systems used in this work.

Table 2 – Physical properties of each component of the mixtures

Component	Critical temperature $T_c$ , °C	Critical pressure $P_c$ , Pa	Acentric factor $\omega$
Ammonia	132.40	111.50	0.253
Water	374.15	218.40	0.343
Methyl acetate	233.70	46.30	0.326
Toluene	320.60	41.60	0.262

Table 3 – Operating conditions of two thermodynamic systems

System	Operating parameter	
	Temperature $T$ , °C	Pressure $P$ , atm
Ammonia – water	-54	0.316
Methyl acetate – water – toluene	60	1

### 2.4 Computer lab simulation

Four mixing rules, namely, Geometric Mean Average (GMA), Whole Square Root Average (SRA), Expanded Geometric Average (EGA), and Simple Average (SA) for the attractive force parameter, together with a repulsive force term, were used in Van der Waals, Redlich- Kwong and Peng Robinson Equations of State, to predict the densities of two simple mixtures; a binary mixture (Ammonia – Water system) and a ternary mixture (Methyl acetate – Water – Toluene system).

For the Van der Waals EOS and the three MRs, these are the essential steps in predicting the density of these mixtures. The EOS parameters,  $a_i$  and  $b_i$  For each of Ammonia and Water, were computed, at their critical conditions. Mixture parameters  $a_m$  and  $b_m$  were then evaluated using Van der Waals Mixing Rule denoted as GMA – equations (4). These parameters were then

computed using other MRs, at various percentage compositions of each mixture component. Thereafter, the EOS A and B coefficients were evaluated at operating conditions (temperature and pressure) of the system. A third-degree polynomial of the Van der Waals EOS was then solved for compressibility factor ( $Z$ ). Three roots were obtained, the highest being the Compressibility Factor of the vapor phase ( $Z^V$ ) and the lowest being the Compressibility Factor of the liquid phase ( $Z^L$ ). The apparent molecular weight of the binary mixture ( $M_a$ ) was then determined by finding the summation of the product of mole fraction and molecular mass for each component. Liquid and the vapor densities ( $\rho^L$  and  $\rho^V$ ) of the mixture were then obtained, at various compositions of the components, using the density model proposed by Ahmed (2000):

$$\rho = \frac{n(\sum_{i=1}^n x_i M_i)P}{ZRT}, \quad (11)$$

where  $\rho$  – the mixture density;  $n$  – the mole fraction;  $x_i$  – composition of each component of the mixture;  $M_i$  – the relative molecular mass of each component of the

mixture;  $P$  – system operating pressure;  $Z$  – the gas constant;  $T$  – the system's operating temperature.

Similar procedures were repeated for density prediction of the ternary system, Methyl acetate – Water – Toluene. Predicted densities with different mixing rules were compared with density data obtained from ASPEN HYSIS at varying compositions of each component and system operating conditions.

## 2.5 Validation of HYSIS data

HYSIS data were validated and were found reliable and could serve as experimental values (lab data). For validation of Aspen HYSYS data, a 50 ml Pyrex Borosilicate Glass density bottle was used on a Hanchen electronic analytical weighing balance (JJ224BC) with 0.1mg precision to accurately measure the densities of Ethanol – Water mixture at various compositions of ethanol and water (Table 4) at room temperature and atmospheric pressure. Results of the validation step are presented in Figure 1.

Table 4 – Mixture densities by experiment and by ASPEN HYSIS for ethanol – water system

Composition $x$ , % (mole)		Density by experimental measurement, kg/m <sup>3</sup>				Density by Aspen HYSIS (kg/m <sup>3</sup> )	% AAD
Ethanol	Water	Run1	Run2	Run3	Average		
90	10	796.6	798.2	797.80	797.53	799.0	0.2
75	25	838.6	838.4	838.30	838.43	817.8	2.5
50	50	848.6	850.7	852.10	850.47	847.3	0.4
25	75	893.9	892.0	894.30	893.40	897.8	0.5
10	90	950.6	952.1	951.80	951.50	950.0	0.2

## 3 Results and Discussion

### 3.1 Results of HYSIS

As evident from the plots in Figure 1, simulated density results from ASPEN HYSIS are highly accurate and closely match those obtained by experimental laboratory measurements. The simulated results showed an overall accuracy level of 0.1843 and a percentage absolute average deviation of 3.5 % as calculated using the expression given in the following equation:

$$\%AAD = \sum_{i=1}^N \left\| \frac{\|Experimental - Predicted\|}{Experimental} \right\| x \frac{100\%}{N}. \quad (12)$$

### 3.2 Densities of ammonia – water system

For Ammonia -Water System, when the four MRs; GMA, SRA, EGA, SA, are separately used in Van der Waals, Redlich Kwong, and Peng Robinson EOS, density data are predicted. The predicted densities are then compared to the laboratory data. The percentage absolute average deviation between the experimental and predicted data for each MRs was evaluated using equation (12). The lower the % AAD value, the closer the predicted density value by the MR to the value obtained from laboratory experiments. Table 5 displays the percentage absolute average deviation (% AAD) of predicted density results with GMA, EGA, and SA from the experimental value.

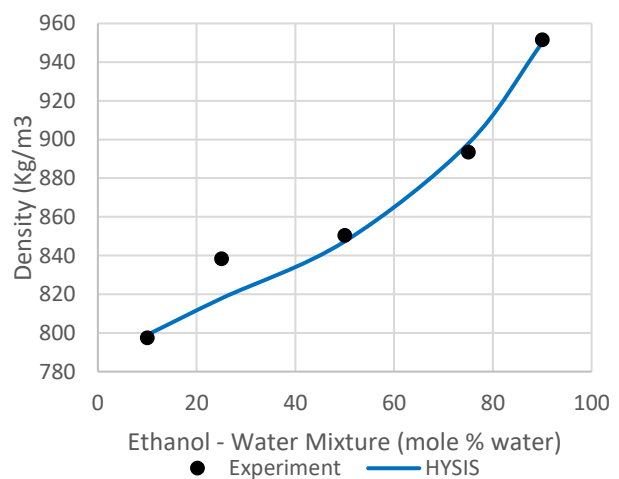


Figure 1 – Variation of density with composition for ethanol-water mixture

The results show that GMA and EGA used in Peng Robinson EOS gave density results reasonably close to the experimental results and relatively good results with Redlich-Kwong EOS, but not with Van der Waals EOS.

Table 5 – Absolute average deviation for GMA, EGA, and SA for ammonia – water binary system

Equation of state (EOS)	Mixing rule (MR)	% AAD
Van der Waals	GMA	46.8
	EGA	46.7
	SA	59.7
Redlich-Kwong	GMA	20.6
	EGA	20.5
	SA	29.9
Peng-Robinson	GMA	9.9
	EGA	9.9
	SA	18.9

On the other hand, SA gave somewhat close results with Peng-Robinson EOS, but not that good with Redlich-Kwong EOS and very poor results with Van der Waals EOS. For this system, GMA and EGA with Peng Robinson EOS gave the least % AAD of 9.9, followed by SA with Peng Robinson EOS with % ADD of 18.9. Thus, GMA, EGA, and SA in the other two EOS gave results that are too far from the experimental values.

Density obtained using the four MRs in the Van der Waals EOS are shown in Figure 2 and plotted on the same axes against compositions. As evident in Figure 2, SRA overestimates densities of the mixture with an Absolute Average Deviation of over 168 %, so it was dropped. Similar trends are observed with SRA in Redlich-Kwong and Peng-Robinson EOSs.

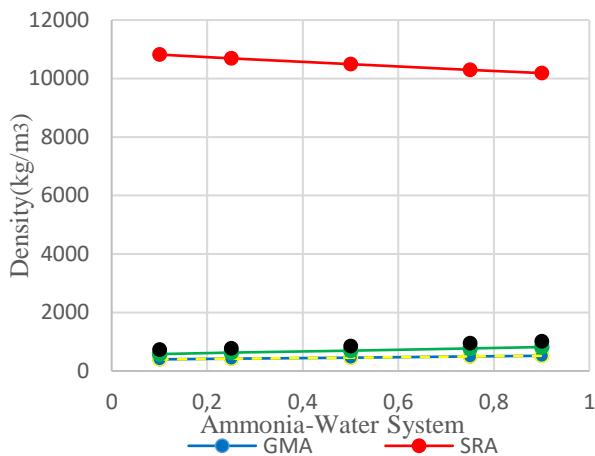


Figure 2 – Comparing predicted densities with four MRs in Van der Waal EOS with Laboratory Data

The whole Square root Average of EOS parameter (SRA) in the three EOS considered for the binary system consistently gave unrealistic density values, with an Absolute Average Deviation of over 168 %, so it was dropped. Consequently, Figures 3–5 are expanded plots of densities against compositions with GMA, EGA, and SA in Van der Waals, Redlich Kwong, and Peng-Robinson EoS for ammonia-water binary system.

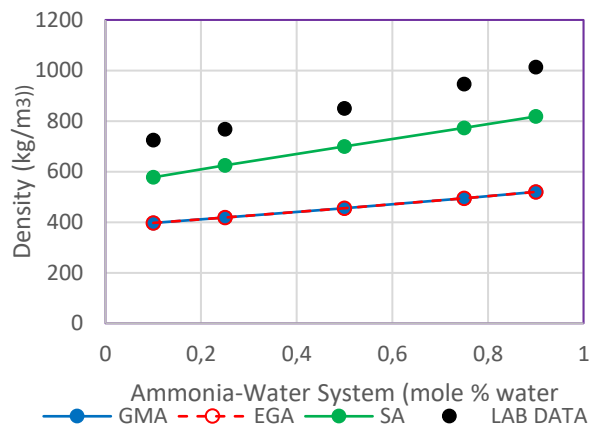


Figure 3 – Predicted densities with GMA, EGA and SA in Van der Waal EOS alongside lab data

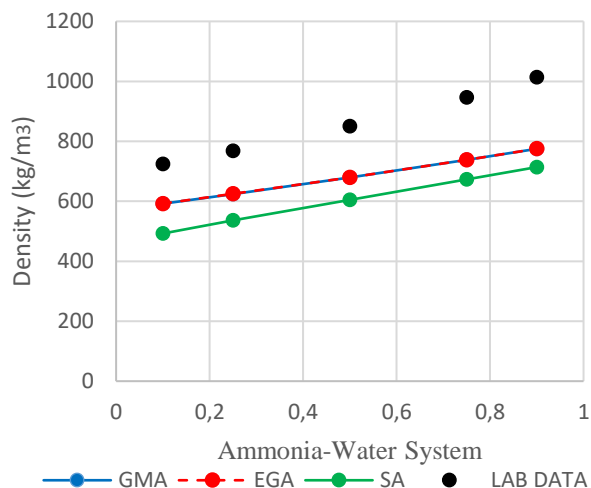


Figure 4 – Predicted densities with GMA, EGA, and SA in Redlich-Kwong EOS against composition

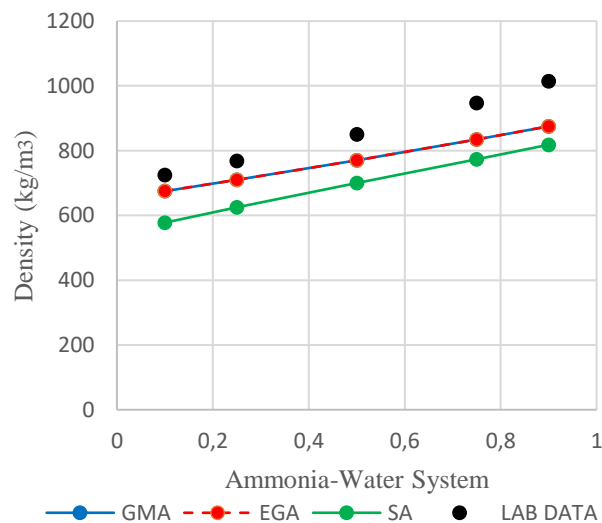


Figure 5 – Predicted density with GMA, EGA, and SA in Peng Robinson EOS against composition

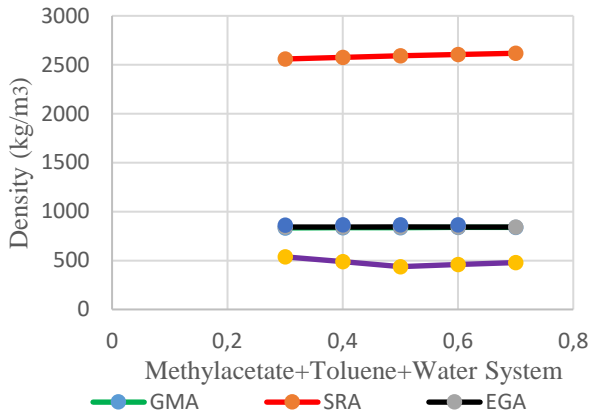


Figure 6 – Density data with four MRs in Peng-Robinson EOS against the composition of mixture components

### 3.3 Densities of the methyl acetate – toluene – water system

Experimental density data of Methyl Acetate – Toluene – Water ternary System, at varying compositions, and predicted density results with four mixing rules and each EOS are compared. Table 6 displays the deviation of predicted densities with GMA, EGA, and SA from the experimental value, in terms of percentage absolute average deviation (% AAD).

Table 6 – Absolute average deviation for GMA, EGA, and SA for methyl acetate – toluene – water

Equation of state (EOS)	Mixing rule (MR)	% AAD
Van der Waals	GMA	45.3
	EGA	44.2
	SA	46.7
Redlich-Kwong	GMA	18.2
	EGA	17.1
	SA	49.6
Peng-Robinson	GMA	3.4
	EGA	2.5
	SA	44.4

MA and EGA with Peng Robinson EOS gave excellent results with % AAD values of 3.4 and 2.5. Similarly, GMA and EGA are relatively good in Redlich Kwong EOS with % AAD values of 18.2 and 17.1, respectively. Van der Waals EOS does not give a good density prediction with GMA, EGA, and SA because their % AAD are 45.3, 44.2, and 46.7, respectively. SA does not give reasonable estimates of the mixture densities with the three EOSs considered, and SRA deviates too largely from experiment values, so it was discarded.

Experimental and predicted density data of Methyl acetate – Toluene – Water with the four MRs in Peng-Robinson EOSs are plotted against the composition of mixture components in Figures 6. As evident from the plot, the Whole Square Root Average of attractive force parameter (SRA) used in the PR EOS for the ternary Methyl acetate – Toluene – Water system is found to overestimates density data, with an unrealistic Absolute Average Deviation. Similar trends were observed with SRA in Van der Waals and Redlich-Kwong EOSs; hence SRA was knocked off.

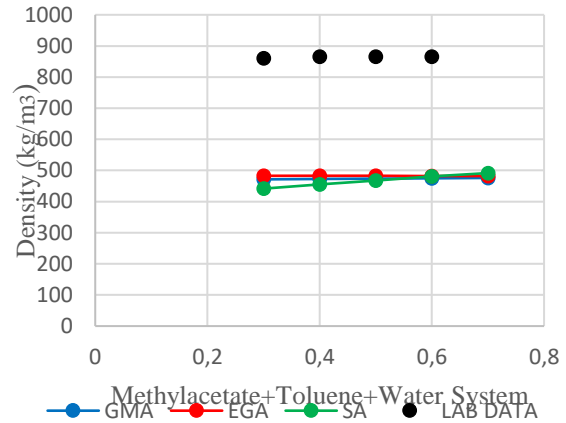


Figure 7 – Predicted density data with four mixing rules in Van der Waal EOS against compositions of mixture components

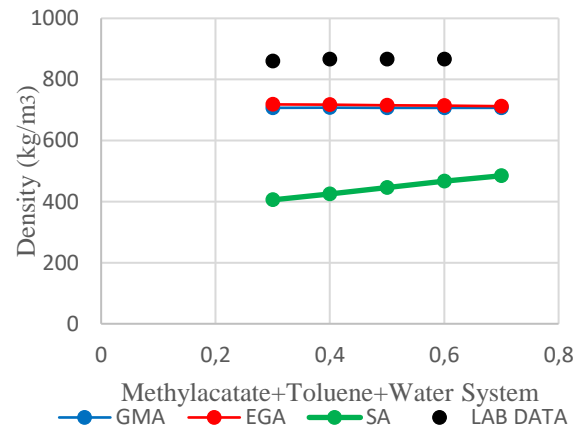


Figure 8 – Density data with GMA, EGA, and SA in Redlich Kwong EOS against compositions of mixture components

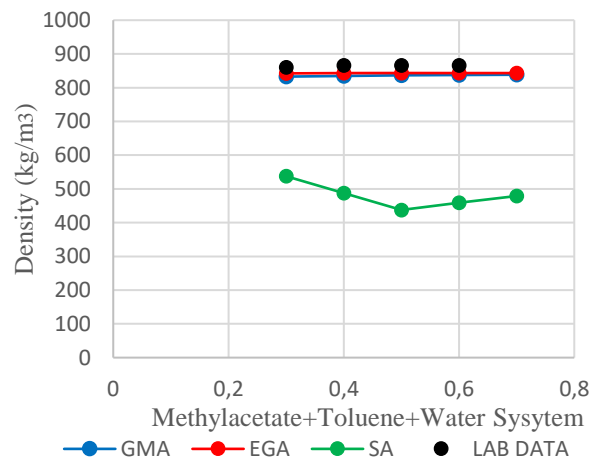


Figure 9 – Density data with GMA, EGA, and SA in Peng Robinson EOS against compositions of mixture components

Consequently, expanded density plots against the compositions with GMA, EGA, and SA in Van der Waals, Redlich Kwong, and Peng-Robinson EOS were made for the ternary system, and the plots are displayed in Figures 7–9.

## 4 Conclusions

Four Mixing Rules expressions have been accurately used to account for the intermolecular forces of attraction between dissimilar molecules of different substances that formed simple mixtures. The combined effects of co-volumes of all constituent species of the mixtures were also considered. The four MRs compared are; Geometric mean average (GMA), Whole Square Root Average (SRA), Expanded Geometric Average (EGA), and Simple Average (SA) of attractive force parameter. For the four MRs, it is assumed that all components of mixtures are similar; hence they are known as random mixing rules. We established that it is possible to adapt EOS to accurately predict densities values of simple mixtures by using Mixing Rules. GMA and EGA gave a reasonable estimation of the mixture attractive force parameter ( $a_m$ ) and hence good density prediction results for Ammonia – Water and Methyl acetate – Toluene – Water systems. Their predicted density results are approximately equal. SRA underestimate the mixture attractive force parameter ( $a_m$ ); consequently, it overestimated the mixture densities for the two thermodynamic systems. The accuracy of the predicted mixture density with different EOS, separately combined with different MRs, depends on the versatility of the EOS. When GMA and EGA are used in Peng Robinson EOS, the best density prediction is obtained. Redlich Kwong EOS also gives relatively good results.

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## 5 Abbreviations

% AAD	absolute average deviation in percentage;
$a, b, c$	parameters in the EOS;
$A, B, C$	parameters in the EOS;
$A$	reduced temp. function in the EOS;
EOS	equations of state;
MR	mixing rule;
$a_i$	attractive parameter of component $i$ ;
$a_j$	attractive parameter of component $j$ ;
$b_i$	co-volume parameter of component $i$ ;
$a_{ij}$	attractive parameter of components $i$ and $j$ combined;
$a_m$	mixture attractive force term;
$b_m$	mixture repulsive force term;
$K_{ij}$	the binary interaction parameter;
$N$	number of molecules;
$P$	pressure;
$R$	ideal gas constant;
$T$	temperature;
$V$	volume;
$\omega$	acentric factor;
$Z$	compressibility factor;
$Z_l$	compressibility factor of mixture in the liquid phase;
$Z_v$	compressibility factor of mixture in the vapor phase;
$\rho^L$	liquid density of the mixture;
$\rho^V$	vapour density of the mixture;
$x_i$	mole fraction of component $i$ in the liquid phase;
$x_j$	mole fraction of component $j$ in the liquid phase;
$c$	critical condition;
$r$	reduced condition;
$m$	molar value.