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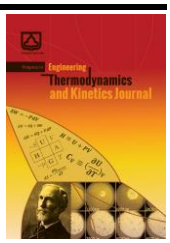

Research Article

Thermodynamic modeling of vapor-liquid equilibrium systems including biodiesel in high and low pressures using cubic equations of state

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ABSTRACT

In this study, the Vapor-Liquid Equilibrium (VLE) of pure and binary mixtures of the systems including fatty acid Ethyl or Methyl esters and alcohols is analyzed by two simple cubic equations of state; Cubic-Square-Well (CSW EoS) and the Peng-Robinson (PR EoS). To achieve this purpose, first, the parameters of the equations of state for pure systems were optimized using the experimental vapor pressure and liquid density. Both models showed acceptable accuracy; however, the PR EoS with AARD=1.01% demonstrated better results for pure systems. Then, the results of the pure systems were used to correlate the phase behavior of the binary mixtures at low and high pressures using one binary interaction parameter in equilibrium systems. The results for the binary fatty acid ester systems showed deviations as AARD=0.45% and AARD=0.23% for PR and CSW EoSs, respectively. For alcohol+fatty acid ester binary systems, the pressure deviations were AARD=5.04% and AARD=14.14% for PR and CSW EoSs, respectively. Therefore, the results showed that the CSW and PR equations of state can be applied to calculate the phase behavior of these types of systems with good accuracy and simplicity. Therefore, they can be used in designing, modeling, and optimization of biodiesel units.

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1. Introduction

Biodiesel fuel, as a mixture of fatty acid esters including methyl or ethyl ester, is known as a clean and renewable fuel. Fatty acids are widely used in various industries such as cosmetics [1], pharmaceuticals [2], and food industries [3], etc. This fuel is produced from materials such as animal fat, vegetable oil (edible – nonedible), and restaurant waste [4,5].

Among several ways to produce this kind of fuel, the most common one is the trans-esterification method. In this method, oil reacts with alcohol to produce several biodiesel and glycerin products [6,7]. Due to the depletion of oil reserves and increasing environmental pollution, acquiring more information on the physicochemical properties of the components of equilibrium systems is important for designing, modeling, and optimization of biodiesel fuel production and consumption [8]. Therefore, many papers have been published on evaluating the correlation of the phase behavior of VLE systems with the activity coefficient and the fugacity coefficient. Silva et al. [9] determined the VLE data for some systems including, ethyl palmitate+ethyl stearate, ethyl palmitate+ethyl oleate and ethyl palmitate+ethyl linoleate at pressure range 5.3329-9.3326 kPa. Tang et al. [8] measured the vapor-liquid equilibria of the system ethyl myristate+ethyl palmitate at 0.5, 1, and 1.5 kPa and applied the NRTL and two UNIFAC based models to describe the experimental data. Shimoyama et al. [10], determined the vapor-liquid equilibrium for methanol+methyl laurate and methanol+methyl myristate systems near the critical temperature of methanol with the Peng-Robinson equation of state. Oliveira et al. [11] determined the VLE data for the low-pressure systems with the Cubic–Plus–Association (CPA) equation of state and in the other work, Oliveira et al. [12] measured the vapor-liquid equilibrium of the systems fatty acid ester+alcohol at pressure 2-12 MPa with the Cubic–Plus–Association (CPA) equation of state.

In this work, the parameters of the two equations of state (PR, CSW) for the fatty acid ethyl or methyl ester and methanol and ethanol systems were obtained using the correlation of the vapor pressure and liquid density. Then equilibrium data for six binary systems including fatty acid ethyl or methyl ester at low pressure [8,16,17,18] and four binary systems including fatty acid ethyl/methyl ester+alcohol at high pressure [10,15] were correlated by two equations of state. In addition, we determined the preferable model to describe the phase behavior of equilibrium systems.

The novelty of this work is (i) to explore the ability of the simple cubic equations of state (PR and CSW) for optimizing pure and binary systems including biodiesel and (ii) to obtain the

parameters of these models and finally, (iii) to compare the performance of the simple cubic EoSs with each other and with the complex equation of state such as CPA [11].

2. Thermodynamic Modeling

The VLE analysis in this work was done based on two cubic equations of state, namely PR EoS and CSW EoS.

2.1. Peng-Robinson equation of state

After the publication of the Van der Waals (VdW) and SRK equations of state, Peng and Robinson conducted a comprehensive study for the evaluation of hydrocarbon systems.
They showed that the SRK equation of state requires correction in predicting fluid properties, particularly along the critical area. Finally, they proposed the following equation [10]:

$$P = \frac{RT}{V-b} - \frac{a}{V^2+2bV-b^2} \quad (1)$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha^2 \quad (2)$$

$$\alpha = \left(1 + k\left(1 - \sqrt{T_r}\right)\right) \quad (3)$$

$$k = 0.37464 + 1.54226\omega - 0.266992\omega^2 \quad (4)$$

$$\mathrm{b} = 0.0778 \frac{RT_c}{P_c} \quad (5)$$

In the above equations: R is gas constant, T is temperature, T_C is critical temperature and P_C is critical pressure, V is molar volume. Parameters a and b are the energy and size, respectively. ω is the acentric factor and the subscript c denotes the critical properties. In the original form of the PR equation of state, the parameters of the model are calculated from the critical properties. Therefore, there are no adjustment parameters for pure systems. However, some researchers attempted to directly obtain the model parameters using experimental VLE data similar to the CPA EoS [11]. Also, for a fair comparison between the ability of the EoSs for the description of the VLE data, the second approach was used and the parameters of the PR and SRK EoSs were directly obtained using Pure VLE data. Therefore, the equation was described as follows:

$$P = \frac{RT}{V-b_0} - \frac{a}{V^2+2b_0V-{b_0}^2} \quad (6)$$

$$a = a_0 * \alpha^2 \quad (7)$$

$$\alpha = \left(1 + k\left(1 - \sqrt{T_r}\right)\right) \quad (8)$$

In the above equations, the parameters a_0 and b_0 and k are considered as adjustable parameters of the models.

Cubic-Square-Well equation of state:

The pressure equation of the CSW equation of state was obtained as [13]:

$$P_{CSW} = \frac{RT}{v-4\tau v_0} + \frac{zRT}{2}\frac{(1-m-w)mv_0}{(mv+v_0w)(mv+v_0(1-m))} \quad (9)$$

$$m = 4\sqrt{2}\pi\lambda^3 - 3/4\sqrt{2}\pi(\lambda^3 - 1) \quad (10)$$

$$v_0 = N_A\sigma_i^3/\sqrt{2} \quad (11)$$

$$Z = (4\sqrt{2}\pi/3)\lambda^3 - 1 \quad (12)$$

$$w = exp\left(\left(\frac{\varepsilon}{kT}\right) - m\right) \quad (13)$$

where, ε is the square –well potential depth, N_A is Avogadro's number, z is maximum attainable coordination number, v_0 is closed packed volume, m is an orientational parameter, λ is the square-well potential parameter, $\tau = \sqrt{2}\frac{\pi}{6}$, v is molar volume and σ is diameter of the particle. The parameters of pure components are ε, σ, λ that can be obtained by optimization of the thermodynamic properties of the pure systems.

The following mixing rules were used to calculate the parameters of mixtures based on pure parameters and extend the application field of the equations of state to mixtures. In the study of the phase equilibrium for binary systems, it has been tried to determine the binary interaction parameter (k_{ij}) according to equations of state by applying appropriate mixing rules.

Mixing rules for the PR and SRK EoSs:

$$b = \sum_{i=1}^{N} xi\ bi \quad (14)$$

$$a = \sum_{i=1}^{N}\sum_{i=1}^{N} x_i x_j a_{ij} \quad (15)$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \qquad k_{ij} = k_{ji}$$

Mixing rules for CSW EoS:

$$m = \sum_i \sum_j x_i x_j\, m_{ij} = 4\sqrt{2}\pi{\lambda_{ij}}^3 - 3/4\sqrt{2}\pi({\lambda_{ij}}^3 - 1) \quad (16)$$

$$v_{0i} = N_A\sigma_i^3/\sqrt{2} \quad (14)$$

$$Z_i = (4\sqrt{2}\pi/3)\lambda_{ii}{}^3 - 1 \quad (17)$$

$$w = \sum_i \sum_j x_i x_j w_{ij} = \sum_j \sum_i x_i x_j (exp\left(\left(\frac{\varepsilon_{ij}}{kT}\right) - m_{ij}\right)) \quad (18)$$

$$z = \sum_i x_i z_i \quad (19)$$

$$v_0 = \sum_i x_i v_{oi} \quad (20)$$

$$\varepsilon_{ij} = (1 - k_{ij})\sqrt{\varepsilon_i \varepsilon_j} \quad (21)$$

$$\lambda_{ij} = \frac{\lambda_i \sigma_i + \lambda_j \sigma_j}{\sigma_i + \sigma_j} \quad (22)$$

The expression of the chemical potential and fugacity coefficient of PR and CSW EoS is given in Appendix A. The systems studied in this work are listed in Table 1, with pressure details. The low-pressure systems are at a pressure range of 0.5–13.3 KPa and the high-pressure systems are in the pressure range of 2–9 MPa.

Table1. Details of the vapor-liquid equilibrium systems used in this study.

	System	Pressure (MPa)	No. of data point	Ref.
High Pressure	Ethanol-Ethyl laurate	2.23-7.09	22	[15]
	Ethanol-Ethyl myristate	2.11-6.93	19	[15]
	Methanol-Methyl laurate	2.16-8.49	20	[10]
	Methanol-Methyl myristate	2.41-8.42	19	[10]
Low Pressure		Pressure (kPa)		
	Ethyl palmitate-Ethyl oleate	5.3,9.3	22	[17]
	Ethyl palmitate-Ethyl linoleate	9.3	11	[17]
	Ethyl palmitate - Ethyl stearate	5.3	9	[17]
	Methyl laurate-Methyl myristate	3.9, 5.3, 6.6, 13.3	20	[18]
	Ethyl myristate-Ethyl palmitate	0.5, 1, 1.5	42	[8]
	Methyl myristate -Methyl palmitate	0.5, 1, 1.4, 3.9, 5.3, 6.6, 13.3	54	[17, 18]

3. Results and Discussion

3.1. Pure systems

Each of the two EoSs considered in this study has three parameters. The parameters of the PR EoS for pure systems are a_0, b and k, and the same for CSW EoS are $\varepsilon, \sigma, \lambda$.

These parameters were obtained by simultaneous optimization of the saturated vapor pressure and the liquid density of the pure components. The objective function to be minimized is as follows:

$$oF_1 = \frac{1}{N} * \sum_i \left| \frac{P^{exp} - P^{cal}}{P^{exp}} \right| * 100 \quad (23)$$

$$oF_2 = \frac{1}{N} * \sum_i \left| \frac{\rho^{exp} - \rho^{cal}}{\rho^{exp}} \right| * 100 \quad (24)$$

$$OF = 0.3 * oF_1 + 0.7 * oF_2 \quad (25)$$

In the above relation, N is the number of calculated experimental points, and symbols exp and cal represent experimental data and calculated value, respectively. Cubic EoSs show better results in predicting vapor-phase properties than liquid-phase properties. Therefore, in the objective function to improve the correlating results for liquid phase density, weights of 0.3 and 0.7 were used for the vapor pressure and liquid phase density, respectively. The parameters of the equation of state for pure compounds have been studied along with a wide range of temperatures, which are given as reduced temperatures in Tables 2-3.

To check the accuracy of the equations of state and determine the deviation of the model results from the experiments, the average absolute relative deviation (AARD $_{Total}$) was used.

Table 2. Values of PR pure compound parameters and reduced temperatures of the studied systems.

Compound	T_r	$a_0(m^6.Pa/mol^2)$	$b_0\ (m^3/mol)$	k
Methyl myristate	0.55-0.90	10.97	0.00028	1.32
Ethyl caprate	0.55-0.90	7.87	0.00020	1.24
Methanol	0.54-0.89	0.94	0.00003	1.00
Ethanol	0.54-0.90	1.29	0.00005	1.23
Ethyl palmitate	0.55-0.90	13.42	0.00034	1.56
Methyl palmitate	0.55-0.90	12.60	0.00032	1.43
Methyl stearate	0.55-0.90	14.87	0.00036	1.50
Ethyl linoleate	0.55-0.90	13.98	0.00036	1.68
Methyl linoleate	0.55-0.90	13.92	0.00034	1.52
Ethyl laurate	0.55-0.90	9.61	0.00026	1.37
Methyl laurate	0.55-0.90	8.81	0.00024	1.25
Ethyl myristate	0.55-0.90	11.50	0.00030	1.41
N-Tetradecane	0.55-0.90	8.829	0.00020	1.22
Methyl linolenate	0.55-0.90	13.61	0.00030	1.51
Ethyl stearate	0.55-0.90	15.17	0.00038	1.62
Methyl oleate	0.55-0.90	14.19	0.00035	1.53
Ethyl oleate	0.55-0.90	15.18	0.00037	1.49

Table 3. Values of CSW pure compound parameters and reduced temperatures of the studied systems.

Compound	Tr	(m)σ	(K)ε/k	λ
Methyl myristate	0.55-0.90	5.81E-10	2562.09	1.05
Ethyl caprate	0.55-0.90	5.43E-10	2083.78	1.08
Methanol	0.54-0.89	2.96E-10	1190.00	1.17
Ethanol	0.54-0.90	3.30E-10	1534.67	1.08
Ethyl palmitate	0.55-0.90	6.14E-10	3208.95	1.02
Methyl palmitate	0.55-0.90	6.02E-10	2901.35	1.04
Methyl stearate	0.55-0.90	6.26E-10	3207.94	1.03
Ethyl linoleate	0.55-0.90	6.24E-10	3447.86	1.02
Methyl linoleate	0.55-0.90	6.16E-10	3188.70	1.03
Ethyl laurate	0.55-0.90	5.66E-10	2529.81	1.05
Methyl laurate	0.55-0.90	5.57E-10	2202.73	1.08
Ethyl myristate	0.55-0.90	5.92E-10	2759.05	1.04
N-Tetradecane	0.55-0.90	5.63E-10	2074.59	1.08
Methyl linolenate	0.55-0.90	6.09E-10	3206.51	1.03
Ethyl stearate	0.55-0.90	6.35E-10	3426.56	1.02
Methyl oleate	0.55-0.90	6.20E-10	3217.26	1.02
Ethyl oleate	0.55-0.90	6.31E-10	3177.06	1.03

Tables 4-5 represent the percentage of AARD $_{\text{Total}}$ calculated based on the vapor pressure and fluid density using two state equations. The results of the comparison of the AARD $_{\text{Total}}$ equations are shown in Fig. 1. As shown in details, both equations have a good ability to predict the vapor pressure and liquid density at the same time. The absolute average relative deviations calculated for each model are listed in Tables 4-5. In comparison, The PR EoS can provide a better correlation with the CSW EoS for the pure systems.

The better results of the PR EoS comparing the CSW EoS for pure section may be due to the fact that biodiesels are long-chain molecules, while the CSW equation developed based on small and spherical molecules.

Table 4. Vapor pressure deviation, liquid density deviation, and total deviation of the results of PR EoS with respect to the experiment.

Compound	$\%AARD_P$	$\%AARD_{density}$	$\%AARD_{Total}$
Methyl myristate	0.38	1.36	0.87
Ethyl caprate	0.20	0.91	0.56
Methanol	1.62	0.75	1.19
Ethanol	0.92	1.35	1.14
Ethyl palmitate	0.85	1.07	0.96
Methyl palmitate	0.70	1.04	0.87
Methyl stearate	2.58	1.30	1.94
Ethyl linoleate	2.42	0.95	1.69
Methyl linoleate	0.21	1.16	0.69
Ethyl laurate	0.54	0.88	0.71
Methyl laurate	1.46	0.63	1.05
Ethyl myristate	0.32	0.85	0.59
N-Tetradecane	0.85	0.55	0.70
Methyl linolenate	0.25	1.31	0.78
Ethyl stearate	0.72	1.18	0.95
Methyl oleate	0.82	1.19	1.01
Ethyl oleate	1.42	1.44	1.43
$AARD_{Total}$			**1.01**

Table 5. Vapor pressure deviation, liquid density deviation, and total deviation of the results of CSW EoS with respect to the experiment.

Compound	$\%AARD_P$	$\%AARD_{density}$	$AARD_{Total}$
Methyl myristate	2.81	4.71	3.76
Ethyl caprate	1.83	4.35	3.09
Methanol	2.05	2.68	2.37
Ethanol	0.59	2.37	1.48
Ethyl palmitate	5.87	4.47	5.17
Methyl palmitate	4.46	4.54	4.50
Methyl stearate	7.25	4.75	6.00
Ethyl linoleate	7.87	4.42	6.15
Methyl linoleate	4.39	4.72	4.56
Ethyl laurate	2.31	4.39	3.35
Methyl laurate	2.9	3.90	3.40
Ethyl myristate	3.66	4.34	4.00
N-Tetradecane	2.14	3.43	2.79
Methyl linolenate	4.37	4.86	4.62
Ethyl stearate	5.37	4.37	4.87
Methyl oleate	5.42	4.67	5.05
Ethyl oleate	5.79	4.85	5.32
$AARD_{Total}$			4.14

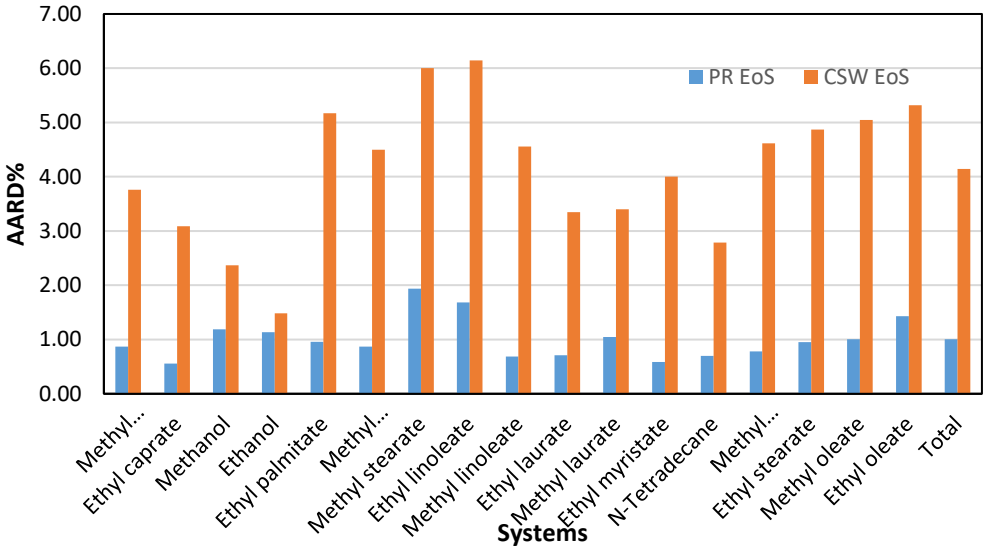

Fig. 1. Comparison of the results (AARD $_{\text{Total}}$) of the two models for pure systems.

3.2.Binary systems

In this section, using only one interaction parameter, the phase behavior of the binary systems is correlated based on PR and CSW EoSs. Applying a logical program based on the parameters obtained for pure systems for the PR and CSW EoS, the interaction parameter is estimated by calculating the bubble temperature for low-pressure systems and the bubble pressure for high-pressure systems. The results of calculating the binary interaction parameter (k_{ij}) are reported for the models in Table 6.

The results show that the obtained binary interaction parameter (k_{ij}) value of the CSW EoS is close to zero. This means that the pure parameters of the CSW EoS are suitable, and the mixing rules used in the model can adequately describe the behavior of the binary systems. The AARD% calculations for the systems are as follows:

For low-pressure systems:

$$\%AARD_T = oF_1 = \frac{1}{N} * \sum_i \left| \frac{T^{exp} - T^{cal}}{T^{exp}} \right| * 100 \quad (24)$$

For high-pressure systems:

$$\%AARD_P = oF_1 = \frac{1}{N} * \sum_i \left| \frac{P^{exp} - P^{cal}}{P^{exp}} \right| * 100 \quad (25)$$

$$\%AARD_P = oF_1 = \frac{1}{N} * \sum_i \left| \frac{P^{exp} - P^{cal}}{P^{exp}} \right| * 100 \quad (26)$$

Table 6. The binary interaction parameter (k_{ij}) for PR and CSW EoSs.

Systems	PR	CSW
Ethyl palmitate - ethyl oleate	-0.027	0.009
Ethyl palmitate - ethyl linoleate	-0.024	0.008
Ethyl palmitate - ethyl stearate	-0.044	0.007
Ethyl myristate-ethyl palmitate	-0.044	0.018
Methyl Laurate-methyl Myristate	0.025	0.015
Methyl myristate -methyl palmitate	0.024	0.002
Ethanol -ethyl laurate	0.009	0.067
Ethanol -ethyl myristate	0.015	0.086
Methanol -methyl laurate	0.071	0.188
Methanol -methyl myristate	0.082	0.201

The first system studied was ethyl palmitate-ethyl oleate at 5.33 kPa and 9.33 kPa. As presented in Fig. 2, all equations correlate well with these vapor-liquid equilibrium systems. Global absolute average relative deviations are 0.53%, and 0.23% for bubble temperature obtained for these systems, respectively for PR and CSW. Fig. 3 shows the vapor-liquid equilibrium system correlation results for ethyl palmitate-ethyl linoleate at the pressure of 9.3 kPa with all equations of state. The calculated values of $\%AARD_T$ for each model are presented in Table 7. The global mean absolute average relative deviations of the bubble temperature calculated using the two models (PR and CSW) were 0.45% and 0.23% for PR and CSW, respectively. According to the results, the CSW model was introduced as the superior model in the correlation of bubble temperature for low-pressure equilibrium systems, and then the PR model was the superior model. In 2014, Oliveira et al. [11] used the CPA EoS to predict the phase behavior of low-pressure systems. The results of their study are presented in Table 7. The CPA EoS, compared with the CSW EoS, has a lower ability to correlate the phase behaviors of the systems.

In general, the order of superiority of these three models can be compared to each other in the following form: CSW > PR > CPA. Based on the comparison of the three equations, it could be concluded that obtaining the best results by adding extra complexity to the model is not always beneficial. In fact, the conditions of the studied systems should be considered when improving the equations.

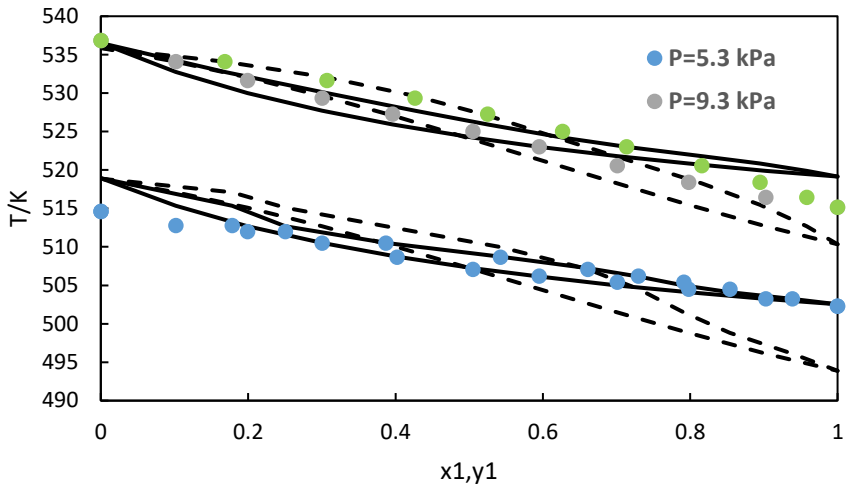

Fig. 2. $T - x_1 - y_1$ diagram for ethyl palmitate-Ethyl oleate at 5.3 and 9.3 kPa:(●) experimental data [17]; (▬) correlated results by the CSW EoS; (- -) predicted results by the PR EoS.

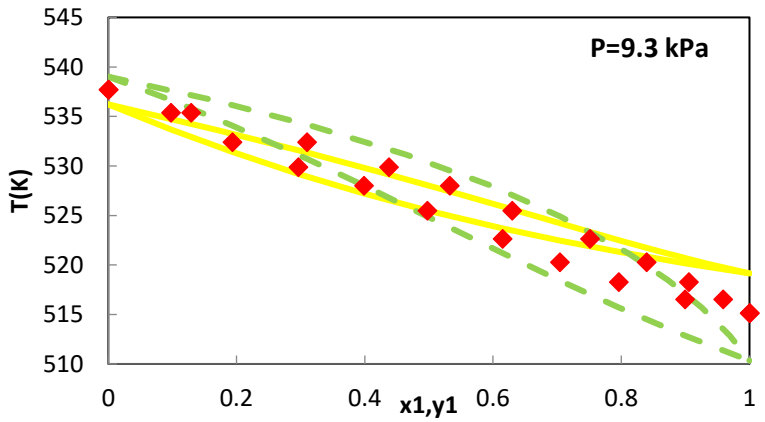

Fig. 3. $T - x_1 - y_1$ diagram for Ethyl palmitate (1) - Ethyl linoleate (2) at 9.3 kPa:(◆) experimental data [17]; (▬) correlated results by the CSW EoS; (- -) correlated results by the PR EoS.

Table 7. Absolute average relative deviations (AARD%) of PR and CSW EoSs for binary fatty acid systems and comparison results with CPA EoS.

	%AARD$_T$		
Systems	PR	CSW	CPA [11]
Ethyl palmitate - ethyl oleate	0.53	0.23	0.21
Ethyl palmitate - ethyl linoleate	0.35	0.34	0.19
Ethyl palmitate - ethyl stearate	0.56	0.09	0.10
Ethyl myristate-ethyl palmitate	0.49	0.24	0.47
Methyl Laurate-methyl Myristate	0.11	0.11	0.75
Methyl myristate -methyl palmitate	0.66	0.38	0.57
Global mean %AARD$_T$	**0.45**	**0.23**	**0.50**

After determining the bubble-temperature and choosing the best model, the bubble-pressure for vapor-liquid equilibrium systems including Ethanol-Ethyl laurate at 2-7 MPa, Ethanol-Ethyl myristate at 2-7 MPa, Methanol-Methyl laurate, and Methanol-Methyl myristate at 2-9 MPa, were estimated by equations of state and compared with experimental data. Fig 4. shows the experimental data of the Ethanol-Ethyl laurate system at 2-7 MPa along with the results calculated by PR and CSW equations of state. The global absolute average relative deviations of PR EoS are obtained as 3.2%, 2.3% for bubble-pressure and vapor mole fraction, respectively. The %AARD of bubble-pressure and vapor mole fraction obtained for these systems, by CSW are 6.28%, 0.74%. The results of the bubble-pressure and vapor mole fraction calculations for Ethanol-Ethyl laurate, Ethanol-Ethyl myristate, Methanol-Methyl laurate, and Methanol-Methyl myristate systems are shown in Table 8 for both given models.

The accuracy of the CSW equation has been greater in correlating the phase behavior of these systems; therefore, the value of the global mean average deviation for the vapor phase mole fraction obtained by the CSW model for alcohol-fatty acid binary systems is 0.53%. The global mean absolute average relative deviation for the PR EoS model was 2.01%. The basis for choosing the best model for calculation of the high-pressure systems is a model that has the lowest deviation in the calculation of the vapor phase mole fraction and bubble pressure simultaneously. Among the PR and CSW EoSs, the CSW EoS has a higher deviation in determining the bubble pressure of these systems. However, this model has a lower deviation in the calculation of the vapor mole fraction. In general, based on the results obtained from the global absolute average relative deviations, the PR EoS showed a lower deviation in two items of vapor phase mole fraction and bubble pressure simultaneously. However, it can be explicitly stated that both EoSs are suitable for correlating the phase behavior of the systems.

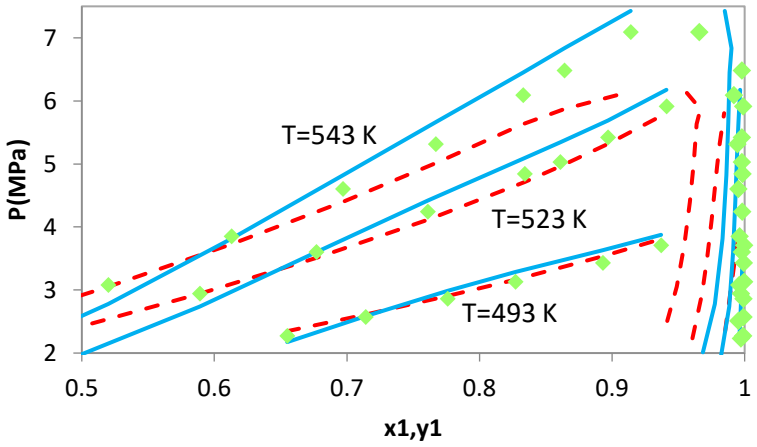

Fig. 4. $P - x_1 - y_1$ diagram for Ethanol (1) - Ethyl laurate (2) at 493 K-523 K-543 K:(◊) experimental data [15]; (-) correlated results by the CSW EoS; (- -) correlated results by the PR EoS.

Table 8. Absolute average relative deviations (AARD%) of PR and CSW EoSs for the alcohol-fatty acid binary systems.

system	$\%AARD_P$		$\%AARD_y$	
	PR	CSW	PR	CSW
Ethanol-ethyl laurate	3.23	6.28	2.37	0.74
Ethanol-ethyl myristate	2.77	12.76	1.43	0.31
Methanol-methyl laurate	7.05	7.73	2.60	0.81
Methanol-methyl myristate	7.14	29.80	1.65	0.27
Global mean %AARD	**5.04**	**14.14**	**2.01**	**0.53**

4. Conclusion

Vapor-liquid equilibrium data for pure and binary systems containing methyl or ethyl ester and alcohol were explored using two simple cubic equations of state, PR EoS and CSW EoS. The results obtained from these two models (PR and CSW EoSs) were compared with each other and with the CPA equation of state as an association EoS. At first, the models were examined by determining the parameters to be adjusted for pure systems, and the PR EoS was introduced with a total absolute average relative deviation of 1.02% as the accurate model. Then, by determining the binary interaction parameters for all binary systems at low and high pressures, the CSW EoS with a global absolute average relative deviation of 0.23% for calculating the bubble-temperature of the binary mixtures of the fatty acid showed better results. However, the PR EoS in binary mixtures of alcohol-fatty acid with bubble-pressure AARD% of 5.04% and vapor mole fraction AARD% of 2.01 demonstrated better results than CSW EoS.

Appendix A. The fugacity coefficient for each species, i, in the mixtures.

The fugacity coefficient for each species, i, in the mixtures of the PR and CSW EoSs are as follows:

$$ln\phi_{i,PR=}\frac{B_i}{B}(Z-1)-ln(Z-B)+\frac{A}{2.828B}\left[\frac{B_i}{B}-\frac{2\sum_j y_j a_{ij}}{a}\right]+ln\left[\frac{Z+2.414B}{Z-0.414B}\right] \quad \text{A.1}$$

$$A=\frac{aP}{(RT)^2}\ ,\quad B=\frac{bP}{RT} \quad \text{A.2}$$

$$ln\phi_{i,CSW}=ln\left(\frac{RT}{Pv}\right)+ln(\frac{v}{v-4\tau v_0})+\frac{4\tau v_{0i}}{v-4\tau v_0}-\frac{z_i}{2}ln\left(\frac{mv+v_0w}{mv+v_0(1-m)}\right)$$
$$-\frac{z}{2}\left(\frac{2v\sum_j x_j m_{ij}+wv_{0i}+2v_0\sum_j x_j w_{ij}}{mv+v_0w}-\frac{2(v-v_0)\sum_j x_j m_{ij}+(1-m)v_{0i}+2v_0}{mv+v_0(1-m)}\right) \quad \text{A.3}$$

List of symbols

k	Boltzmann's constant ($1.38066*10^{-23}JK^{-1}$)
m	Orientational parameter
N_A	Avogadro's number ($6.02205*10^{+23}\ \ mol^{-1}$)
P	Pressure (Pa-MPa)
R	Gas constant (8.314 J/mol.K)
T	Temperature(K)
v	Volume (m^3)
z	maximum attainable coordination number
w	A function of temperature defined in Eq. (18)
v_0	closed packed volume(m^3/mol)
x_i	Mole fraction of component i

Greek letters

σ	Size parameter(m)
ε	square –well potential depth
λ	the square –well potential parameter
φ	Fugacity coefficient
τ	Constant (0.7405)

Subscripts

CSW	Cubic square-well

Superscripts

cal	Calculated properties
exp	Experimental properties

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