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Modifying the κ-Parameter in the Peng Robinson Equation of State to Improve Prediction of Vapor Pressure at Low Temperature and Binary Mixture Phase Equilibria

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***Abstract*— Equation of state formulation, modification and application have remained active research areas since the success of Van der Waals equation of state in 1873.one way of improving the accuracy of a cubic EoS is through the modification of the κ parameter by using the alpha function. A new modification of the κ parameter is proposed and fitted to 2nd order polynomial as a function of the parameter R_C reported in 1983 by Kuwairi and Maddox in their published generalized method to calculate the heat of vaporization for polar and nonpolar compounds. The modified κ parameter is tested against experimental vapor pressure and liquid density data for polar and nonpolar compounds in the range of ($T_r = 0.33$ to $T_r = 0.97$) and found to be more accurate than other earlier modifications. The modified κ parameter is also used to predict interaction coefficients for several polar and nonpolar binary mixtures and gave reasonable accuracy when compared to published experimental data.**

Keywords*— *Equation of state, vapor pressures, modified κ parameter, Peng-Robinson EOS

I. INTRODUCTION

Cubic equation of state (EoS) is one of the most important methods for the prediction of the thermodynamic properties of pure compounds and mixture (Rezakazemia et al., 2018). [1]

The first cubic equation of state was proposed by van der Waals in 1873 for the prediction of the vapor pressure of real gases [2]. Redlich and Kwong in 1949 modified the form of the attractive term of van der Waals EoS and introduced the variable $T_r^{0.5}$ to the energy parameter of the attractive term [3]. Soave, 1972 adopts the form of Redlich-Kwong (RK) EoS and proposed an alpha function for the attractive term [4]. Peng and Robinson (1976) modified the RK EoS and adopted Soave alpha function. Peng-Robinson (PR) EoS can accurately predict the vapor pressure of nonpolar and weakly polar compounds with great deviation for polar compounds at reduced temperatures ($T_r \geq 0.6$). but as with other two parameter EoS, it failed to predict accurately vapor pressure of pure polar compounds for ($T_r < 0.6$) [5].

The alpha function is an important variable in the attractive term of cubic EoS. The alpha function affects the predictive accuracy of PR EoS for the vapor pressure of pure compounds. Many alpha functions were modified to improve the prediction of vapor pressures for polar compounds.

There are usually two ways to obtain vapor pressure data. The first is to conduct direct experimental measurements, which are tedious and sometimes time consuming. The second is to use predictive procedure based on either empirical correlations or direct application of equations of state.

Most equations of state can predict vapor pressure within a reasonable agreement to corresponding experimental data when they are applied at a relatively high reduced temperature $T_r \geq 0.6$ but when the equations of state are applied at a low reduced temperature between the triple point and $T_r \approx 0.6$ they predict poorly vapor pressure. and consequently, poorer prediction of phase equilibria Calculation.

Recent advances in computers have permitted widespread efforts in finding an equation of a state or modifying existing one which is simple to use and yet accurate enough for most engineering calculation.

II. EQUATION OF STATE

A. *The Peng – Robinson (PR) Equation of State*

Peng and Robinson (1976), published an equation that yields improved correlation for pure component vapor pressures and better estimates of liquid densities.

$$P = \frac{RT}{V-b}\frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

Which can be written as:

$$Z^3 - (l - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{2}$$

Where

$$A = \frac{ap}{R^2T^2} \tag{3}$$

$$B = \frac{bP}{RT} \tag{4}$$

$$Z = \frac{PV}{RT} \tag{5}$$

In the two-phase region, the largest root is for the compressibility factor of the vapor while the smallest positive root corresponds to that of the liquid.

At the critical point, we have

$$a(T_c) = 0.45724\frac{R^2T_c^2}{P_c} \tag{6}$$

$$b(T_c) = 0.0778\frac{RT_C}{P_C} \tag{7}$$

$$Z_c = 0.307 \tag{8}$$

Similar to SRK equation

$$a_i(T) = a_i(T_c)\alpha_i(T_{ri}, \omega_i) \tag{9}$$

$$b_i(T) = b_i(T_C) \tag{10}$$

$$\alpha_i^{0.5} = 1 + k\,(1 - T_{ri}^{0.5} \tag{11}$$

However, correlation for k is different:

$$\kappa = 0.37464 + l.54226\omega_i - 0.26992\omega_i^2 \tag{12}$$

The mixing rules used were

$$a_m = \textstyle\sum_i \sum_j x_i x_j a_{ij} \tag{13}$$

Where

$$a_{ij} = (1 - \delta_{ij})a_i^{0.5}a_j^{0.5} \tag{14}$$

δ_{ij} Being an empirically determined binary interaction coefficient characterizing the binary formed by component i and component j.

The binary interaction parameter (BIP) for the mixture in the attractive term of the equation of state (EoS) is required for predicting accurately their vapor–liquid equilibrium (VLE) properties. Generally, a BIP is necessary to adequately describe the properties of a mixture. When predicting the VLE of mixtures, the results obtained by the empirical correlation of BIP are more consistent with the experimental data than with the prediction results obtained by considering BIP as a constant. The obtaining an accurate BIP for the system is key to ensure the accuracy of the physical property prediction. However, it is complicated to obtain the experimental data for BIPs. Therefore, several attempts have been made to establish equations to estimate the BIP based on the combination of cubic EoS with appropriate mixing rules.

$$b = \textstyle\sum x_i b_i \tag{15}$$

Peng and Robinson derived the following expression for the fugacity coefficient of a pure component:

$$ln\,\phi = Z - 1 - ln(Z - B) - \frac{A}{2\sqrt{2}B}\,ln\,(\frac{Z+2.414B}{Z-0.414B}) \tag{16}$$

In addition, that of a component k in the mixture:

$$ln\,\phi_K = \frac{b_k}{b}(Z-1) - ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum x_i a_{ik}}{a} - \frac{b_k}{b}\right) * \frac{ln(Z+2.414B)}{Z-0.414B} \tag{17}$$

B. *Kuwairi – Maddox Generalized Correlation for Heat of Vaporization.*

In 1982, Kuwairi and Maddox published generalized correlation for estimation of the latent heat of vaporization based on the Peng-Robinson equation of state and has the advantages of being applicable for use with most common vapor pressure correlations, and general applicability to most polar and nonpolar compounds.

$$\Delta Z_v = 1 - EXP\,(1 - (\alpha))^{\frac{R_C}{R_a}} \tag{18}$$

With this expression for Z_V the latent heat of vaporization can be expressed as:

$$\Delta H_v = \psi\,R\,T_c\,\left(1 - EXP\,\left[1 - (\alpha)^{\frac{R_C}{R_a}}\right]\right) \tag{19}$$

Where ψ is slope of the line relating vs $\frac{1}{T_r}$, which can be derived from any valued and accurate vapor pressure correlation.

TABLE I. Ψ VALUES FROM VAPOR PRESSURE EQUATIONS

Vapor Pressure Equation	$\Psi = \frac{\Delta H_v}{R\,T_c\,\Delta Z_v} = -\frac{dP_{vr}}{d(\frac{1}{T_r})}$

Antoine , Equation	$\frac{\mathrm{B}}{\mathrm{T_r}}\left(\frac{\mathrm{T_r}}{\mathrm{T_r}-\frac{\mathrm{C}}{\mathrm{T_C}}}\right)^2$
Lee Kesler Equation	$6.09648 - 1.28862\ \mathrm{T_r} + 1.016\ \mathrm{T_r^7} + \omega(15.6875 - 13.4721\mathrm{T_r} + 2.615\mathrm{T_r^7})$
Gomez Nieto and Thodos Equation	$7 \quad \Upsilon\ \mathrm{T_r^8} - \mathrm{m}\ \beta\ \mathrm{T_r^{1-m}}$

C. Modification Peng Robinson Equation of State

These modifications to the PR EoS have been grouped in four main categories according to the nature of the modification: (a) by changing the dependence structure of α with temperature or the expressions for parameter a and b, (b) by introducing deviation functions (like volume translation),(c) by incorporating new parameters or terms in the equation of state, and finally (d)by modifying the mixing rules for mixture applications.

One of the most important of these modifications in (2017) Peyman Mahmoodi and Maryam Sedigh published a modification of Peng Robinson equation of state (Peng and Robinson) by proposing a new correlation for the α function with three adjustable parameters,$\mathrm{C_1}$, $\mathrm{C_2}$ and $\mathrm{C_3}$. [6]

The modification is:

$$\alpha(T) = exp[\,2\, C_1\left(1-\sqrt{T_r}\right) - \left(C_2\left(1-\sqrt{T_r}\right)\right)^2 + \frac{2}{3}\left(C_3\left(1-\sqrt{T_r}\right)\right)^3\,] \qquad (20)$$

The adjusted empirical parameters $\mathrm{C_1}$, $\mathrm{C_2}$, $\mathrm{C_3}$ of the alpha function were fitted individually for each pure compound and the absolute value of $\mathrm{C_3}$ has to be smaller than$1.25 * |\,\mathrm{C_1}|$.

III. METHADOLOGY AND PROCEDURES

In this work, an attempt is made to improve the Peng Robinson (PR) equation of state by modifying the κ parameter appearing in the equation of the alpha cohesion term.

$$\alpha_{PR} = \left(1+\kappa\left(1-\sqrt{T_r}\right)\right)^2. \qquad (21)$$

Since Kuwairi and Maddox equation [7]cited earlier has shown excellent ability to predict the heat of vaporization of polar and nonpolar compounds, covering a wide range of temperature , by proposing a new fitted correlating parameter $\mathrm{R_C}$ as a function of the acentric factor for polar and nonpolar compounds as follows:

For nonpolar: -

$$R_C = 5.7763 - 18.887\,(\omega)^{0.688} + 15.614\,(\omega)^{0.838} \quad (22)$$

For polar: -

$$R_C = 6.3959 - 13.999\,(\omega)^{0.529} + 9.7185\,(\omega)^{0.693} \quad (23)$$

Therefore, in this work an attempt is made to modify the κ parameter in the equation defining the α term in the Peng Robinson EOS and fitting it to a second degree polynomial using $\mathrm{R_C}$ as a correlating parameter. Experimental vapor pressure data for some selected polar and nonpolar compounds and the adjusted empirical parameters a, b, and c of the alpha function in the subcritical regions were fitted with the experimental vapor pressures of ten nonpolar and ten polar compounds by using the nonlinear least squares fitting.

Extensive experimental vapor pressure data were used to find the coefficients of the proposed polynomial in the form:

$$\kappa = a + b\,R_C + c\,R_C^2 \qquad (24)$$

The following algorithms have been proposed to carry at the objectives of this work:

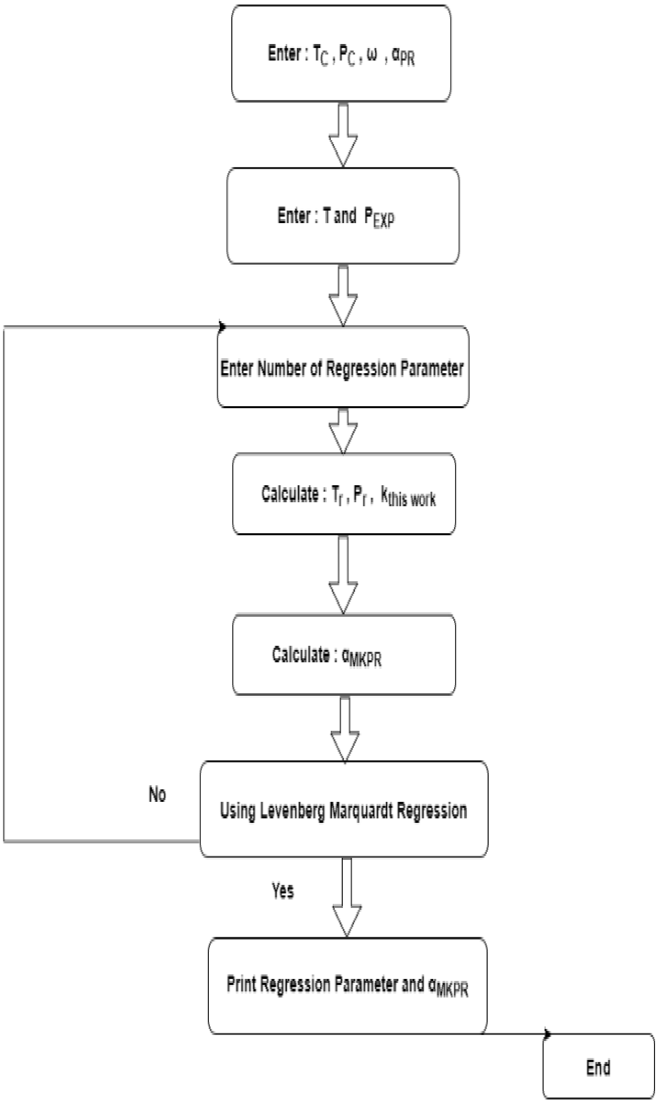

Fig. 1. Algorithm for fitting Peng Robinson Equation of State Parameter

Only four two parameter EOS will be investigated and their results compared to the Peng and Robinson equation with the modified κ proposed in this work. They will be from now and on as SRK (Soave and Redlich Kwong); PR (Peng and Robinson); MS (Mahmoodi and Sedigh); and MKPR (Modified κ Peng Robinson).

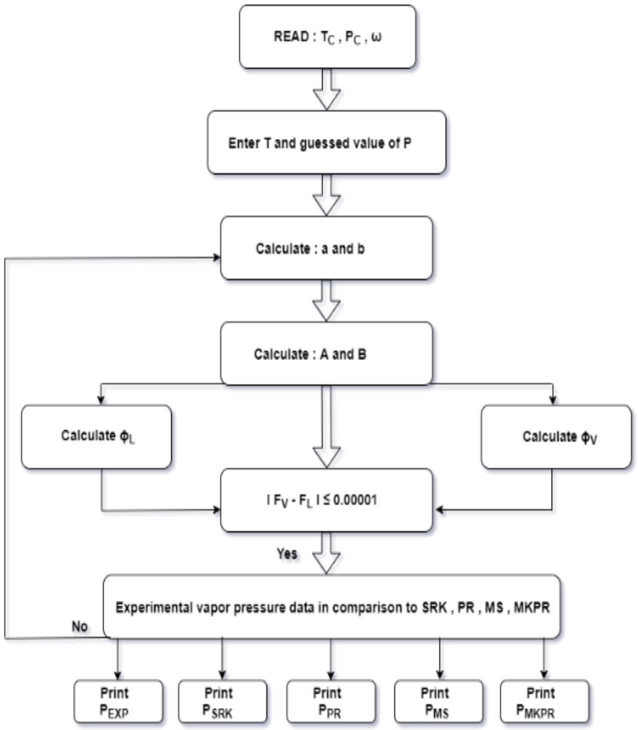

Fig. 2. Vapor Pressure Algorithm of experimental data in comparison with Soave Redlich Kwong , Peng Robinson , Mahmoodi Sedigh and Modified κ Peng Robinson

MATLAB code was written and executed to perform calculations of all outlined in the algorithms in figure 1 and 2. Ten nonpolar compounds, ten polar compounds, and their experimental vapor pressure data were targeted in this work covering T_r range (0.33 → 0.97).

TABLE II. Nonpolar compounds

Compound	formula	Ref.No
Methane	(CH_4)	11
Ethane	(C_2H_6)	8
Propane	(C_3H_8)	8
Propylene	$C_3H_8)$	11
Butane	(C_4H_{10})	8
Nitrogen	(N_2)	8
Ethylene	(C_2H_4)	11
Cyclopropane	(C_3H_6)	8
2 Methylpropene	(C_4H_8)	8
Pentane	(C_5H_{12})	8

TABLE III. Polar compounds

Compound	formula	Ref.No
Phenol	(C_6H_5OH)	11
Diethyl ether	$(C_2H_5)_{20}$	8
Acetone	(C_3H_6O)	8
1-butanol	$(C_4H_{10}O)$	8
1-Pentanol	$(C_5H_{12}O)$	8
Propionaldehyde	(C_3H_6O)	8
Ethylene glycol	$(C_2H_6O_2)$	8
1-hexanol	$(C_6H_{14}O)$	11
Benzoic acid	$(C_7H_{14}O)$	11
1-Propanol	(C_3H_8O)	8

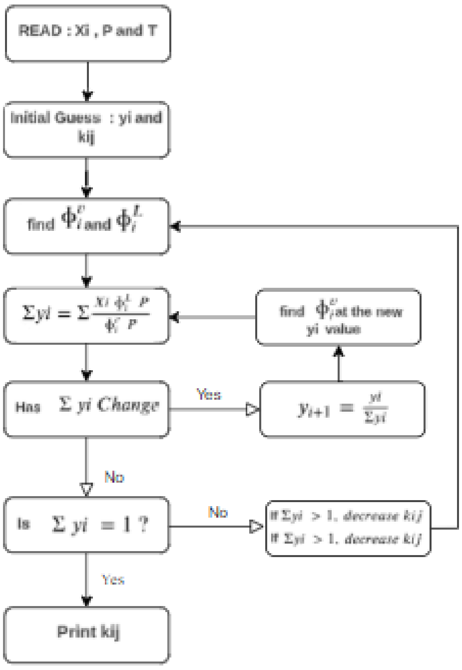

Fig. 3. Algorithmic flow-Chart diagram for the computation of BIPs (k_{ij}).

An iterative procedure, as depicted in the flow chart in Figure 3, was used to calculate the BIPs. At a given input set of experimental temperature (T), saturation pressure (P), and the liquid phase (x1), the procedure started with assuming values of the BIPs and the vapor phase composition.
Note: BIPs, binary interaction parameters.

Based on the calculated values of $\widehat{\phi}_l^L$ and $\widehat{\phi}_l^V$ iterations were performed using MATLAB until the summation of the compositions in the vapor phase stabilized at unity.

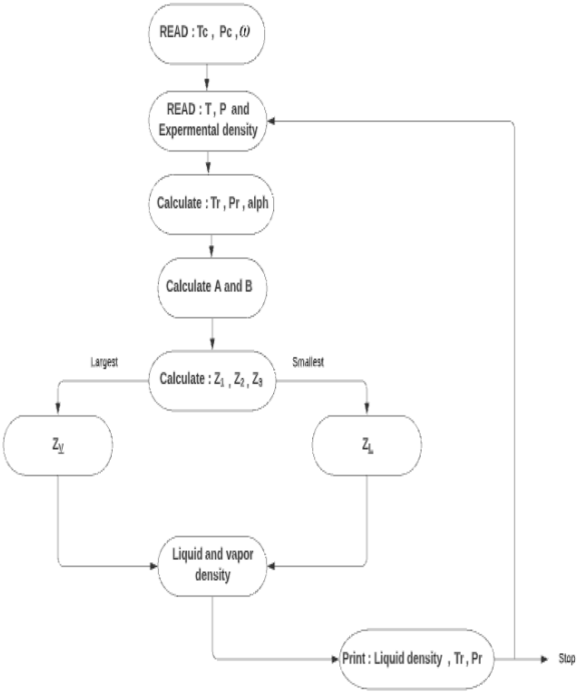

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Fig. 4. Algorithm for the calculation of liquid Densities

The density of a phase is calculated using the compressibility of the phase, which is predicted from a chosen equation of state. The density of the fluid is calculated using its compressibility factor as predicted by an appropriate equation of state.

IV. RESULTS

A. *Prediction of Vapor Pressure*

The proposed modification of the κ parameter as a function of R_C for polar and nonpolar compounds is fitted to 2nd order polynomial:

$$\kappa = a + b\, R_C + c\, R_C^2 \qquad (25)$$

Where

For nonpolar: -

$$\kappa = 2.7192 \; - (Rc * 0.831) + ((Rc\text{^}2) * 0.074) \qquad (26)$$

$$R_C = 5.7763 \; - \; 18.887(\omega)^{0.688} \; + \; 15.614\, (\omega)^{0.838} \; (27)$$

For polar: -

$$\kappa = 8.4696 - (4.5022 * \; Rc) + (0.6596 * \; (Rc \text{ ^ } 2))(28)$$

$$R_C = 6.3959 \; - \; 13.999\, (\omega)^{0.529} \; + \; 9.7185\, (\omega)^{0.693} \; (29)$$

The MKPR was tested against experimental vapor pressure for two polar and two nonpolar compounds.

The following statistical method is used in order to carry out error analysis and therefore measure the performance of different equations:

Absolute Average Deviation Percent

$$(AAD) = \frac{1}{n}\sum_i^n = \frac{|P_{cal}^{sat} - P_{exp}^{sat}|}{P_{exp}^{sat}} * 100 \qquad (30)$$

Where P_{cal}^{sat} is the calculated value of saturated vapor pressure, and P_{exp}^{sat} is the experimental saturated vapor pressure. n is the number of experimental data. One of the most important objectives of this work is to improve in general the accuracy of the two parameter equations of state to predict vapor pressure for reduced temperature T_r below 0.6, and therefore expecting improved accuracy for other thermodynamic properties especially for mixtures.

Since PR EoS has been known for its general improved accuracy among other EoS i.e RK, SRK and MS. But PR has its own flaws when it comes to prediction of vapor pressure below $T_r < 0.6$. For this reason, PR EoS is targeted in this work by attempting to improve its capability to predict vapor pressure for polar and nonpolar compounds by improving the alpha function and correlating its k parameter with the R_C parameter reported by Kuwairi and Maddox in their generalized method to predict heat of vaporization for polar and nonpolar compounds.
The AAD is used to compare calculated values of vapor pressure with published experimental data among the improved PR in this work MKPR and other EoS ,i.e the original PR , SRK , and MS.

To compare the predictive ability of the alpha function in different forms, the ability of PR EoS to predict vapor pressure covering a wide range of reduced temperature from ($T_r = 0.33$ to $T_r = 0.97$) for polar and nonpolar compounds was markedly improved when compared the proposed correlation for the k parameter as function of the R_C parameter used by Kuwairi and Maddox equation [7] and slightly improved when compared to AlMahmoodi and Sedigh which is more complicated to use.

Comparing the Absolute Average Deviation Percent (AAD) of PR, AlMahmoodi - Sedigh and the proposed alpha function for the prediction of vapor pressure, it is shown that the proposed alpha function is more accurate than PR alpha function and AlMahmoodi – Sedigh in the reduced temperature range below 0.6.

Accurate correlation of vapor pressure would enable the MKPR equation of state to accurately predict phase equilibrium behavior.

Tables (IV) and (V) give summary of Absolute Average Deviation Percent (AAD) for polar and nonpolar compounds.

The accuracy in predicting vapor pressure at reduced temperature T_r below 0.6 in comparison to other methods.

TABLE IV. AAD (%) of vapor pressure between calculated values via PR, MS and MKPR for nonpolar compounds

Substance	No. of data points	T_r Range	MKPR	PR	MS
			Overall AAD (%)	Overall AAD (%)	Overall AAD (%)
Methane	10	0.37-0.68	0.88	5.58	-
Ethane	12	0.33-0.92	2.94	6.35	-
Propane	8	0.35-0.96	1.41	7.27	43.22
Butane	10	0.35-0.86	2.64	9.36	4.42
Propylene	10	0.33-0.94	8.73	21	-
Nitrogen	8	0.37-0.95	1.43	2.44	2.49
Cyclopropane	11	0.35-0.93	3.17	6.08	-
Ethylene	10	0.36-0.95	2.73	6.13	-
Methylpropene	9	0.35-0.98	3.64	9.51	-
Pentane	9	0.36-0.98	3.11	5.91	-
Toluene*	9	0.37-0.98	3.44	6.08	-
1 − Hexyene*	8	0.44-0.96	1.23	3.08	-

Substance	No. of data points	P_r Range	MKPR	PR
			Overall AAD (%)	Overall AAD (%)
Ethane-Propane	5	[illegible]	[illegible]	[illegible]
Hexane – Cyclohexane	6	[illegible]	1.23	1.67
1,3 Butadiene-Cyclohexane	5	0.006-0.071	8.23	10.06

Substance	No. of data points	P_r Range	MKPR	PR
			Overall AAD (%)	Overall AAD (%)
Methanol - Ethyl acetate	7	[illegible]	2.84	5.52
2-propanol – 1,2 ethanediol	5	[illegible]	1.097	1.65
Diethyl ether-Acetone	6	0.004-0.007	7.17	8.92

Substance	No. of data points	T_r Range	MKPR	PR
			Overall AAD (%)	Overall AAD (%)
Nitrogen	14	0.29-0.96	9.92	3.58
Propane	8	[illegible]	3.84	3.46

* Not included in the fitting procedure

TABLE V. AAD (%) of vapor pressure between calculated values via PR and MKPR for polar compounds

* Not included in the fitting procedure

B. *Prediction of the Binary Interaction Parameter BIPs.*

The MKPR has been applied to calculate binary interaction parameter for Ethane-Propane, Hexane – Cyclohexane,1,3 Butadiene – Cyclohexane, Methanol - Ethyl acetate, 2-propanol – 1,2 ethanediol, Diethyl ether-Acetone in comparison with Peng-Robinson equation of state. The experimental data used here were taken from Dortmund Data Bank (DDB).

The mean (AAD) of Modified κ Peng Robinson equation of state for the prediction BIP of three polar mixtures, are 7.17% for Diethyl ether - Acetone, 1.097% 2 – propanol – 1,2 ethandiol and 2.84% Methanol – Ethyl acetate are tabulated in Table VII. The MKPR EoS is better than PR EoS for Diethyl ether - Acetone, 2 – propanol – 1,2 ethandiol and Methanol – Ethyl acetate are 8.92%, 1.65% and 5.52%.

TABLE VI. AAD (%) of BIPs Between calculated values via PR and MKPR for non-polar mixture

TABLE VII. AAD (%) of BIPs Between calculated values via PR and MKPR for polar mixture

C. *Prediction of the Liquid Density*

1) *Nonpolar compounds: A comparison was made between the experiment data, the corresponding values of PR and proposed equation of state which were tabulated in Table VIII.*

TABLE VIII. AAD (%) of liquid density Between calculated values via PR and MKPR for Nonpolar mixture

Substance	No. of data points	T_r Range	MKPR	PR
			Overall AAD (%)	Overall AAD (%)
Phenol	8	0.39-0.95	6.41	13.27
Diethyl ether	13	0.36-0.96	14.9	25.36
1 − butanol	10	0.4-0.97	6.7	91.53
1 − Pentanol	10	0.4-0.97	7.47	62.28
Propionaldehyde	8	0.33-0.99	7.94	15.36
Acetone	6	0.39-0.96	5.6	8.7
Ethylene glycol	7	0.38-0.97	8.51	37.37
1 − hexanol	8	0.4-0.96	30.41	111.48
Benzoic acid	13	0.4-0.96	12.31	52
1 − Propanol	7	0.4-0.96	24.6	30.74
Water*	9	0.37-0.98	5.79	9.12
Nonanol*	9	0.41-0.96	0.47	1.48

2) *Polar compounds:* A comparison was made between the experiment data and the corresponding values of PR and proposed equation of state were tabulated in Table IX. The density of this component was calculated at temperatures ranging from 173.15 to 465.14°K and pressures ranging from 4.1e-6 to 11014.05mmH_g.

TABLE IX. AAD (%) of liquid density Between calculated values via PR and MKPR for polar mixture

Substance	No. of data points	T_r Range	MKPR	PR
			Overall AAD (%)	Overall AAD (%)
1 - Pentanol	15	0.33-0.97	3.35	9.89
1 - Propanol	15	0.32-0.86	3.16	4.14

V. CONCLUSIONS

The modified κ Peng Robinson was proposed for the prediction of the vapor pressure, binary interaction parameter, and liquid density of nonpolar and polar compounds. The ability of PR EoS to predict vapor pressure covering range of reduced temperature from ($T_r = 0.33$ to $T_r = 0.97$) for polar and nonpolar compounds was markedly improved when compared the proposed correlation for the κ parameter as function of the R_C parameter used by Kuwairi and Maddox equation [7] and slightly improved when compared to AlMahmoodi and Sedigh which is more complicated to use. The MKPR are most accurate than the other PR and AlMahmoodi – Sedigh for the prediction of vapor pressure and binary interaction parameter, but has similar precision with for the prediction of liquid density.

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