

## Prediction of VLE data for alternative refrigerant mixtures

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**Abstract**—The inevitability of a disaster associated with the depletion of the ozone layer led to the decision to phase out conventional chlorine containing refrigerants and their mixtures. This necessitates the use of non-chlorine substances as refrigerants. In the present work, three different types of mixing rules, namely (i) the classical van der Waals one fluid mixing rule, (ii) the composition dependent mixing rules of the Margules type, and (iii) the conformal solution van der Waals mixing rules are used with the Peng-Robinson (PR) equation of state, to predict the VLE data of 27 alternative refrigerant mixtures, and the results are compared with the experimental data. It is found that the composition-dependent mixing rule coupled with the PR equation of state is quite suitable for predicting the VLE data.

**Key words:** VLE Data, Alternative Refrigerant Mixtures, PR Equation of State, Mixing Rules, Optimum Binary Interaction Parameters

### INTRODUCTION

The prediction of Vapor Liquid Equilibrium (VLE) data is an indispensable area of interest in the field of chemical engineering, since a large number of industrial processes deal with phase contacting. A design engineer may choose either to use the known experimental data or to predict the behavior of the systems under consideration. Usually, the experimental data is not available for many systems and at all the desired conditions. Therefore, the limited amount of available data can be used to develop a model, which in turn can be used to predict the data at the required operating conditions.

Because of the Montreal protocol in 1987, the refrigeration industry has to phase out the use of ChloroFluoroCarbons (CFCs) and HydroChloroFluoroCarbons (HCFCs). These conventional refrigerants cause potential damage to the ozone layer due to the chlorine oxide radicals (ClO<sup>•</sup>) formed by the chlorine atoms. Therefore, non-chlorine containing substances can be used as alternative refrigerants. Some of the thermodynamic properties of Hydrofluorocarbons (HFCs) match with those of CFCs, hence one can think of using HFC's as substitutes for CFC's. However, no pure fluid that can replace the CFCs has been found till date. Therefore, it is necessary to find mixtures as alternative refrigerants [Barley et al., 1997]. Azeotropic mixtures have been tried out as substitutes. However, these mixtures do not possess thermo-physical properties close to CFCs [Fermiglia and Pricl, 1999]. The VLE data of several possible non-azeotropic mixtures have to be studied to select the components as well as the composition. However, the number of such mixtures is quite large and it would be economically unviable to experimentally determine the thermodynamic properties of all possible alternative refrigerant mixtures. It is essential to identify the most suitable thermodynamic model for the prediction of VLE data by using the limited amount of available data.

Different researchers have used different models to predict the VLE data of alternative refrigerant mixtures. Kleiber [1994] used

the UNIFAC model, while Barley et al. [1997] used Wilson's model. Koo et al. [2000] used the Peng-Robinson (PR) equation of state and Kim et al. [2000] used the Soave-Redlich-Kwong (SRK) and Carnhan-Starling-De Santis (CSD) equations of state. Lim et al. [2005] used the CSD equation of state to predict the VLE data of binary system R134a and propane and found good agreement with the experimentally determined values in the temperature range 268.15 to 318.15 K. Nishiumi et al. [1997] measured the VLE data for the binary system R125+R152a in the temperature range 268.15 to 373.15 K and correlated the data using the extended BWR equation of state. Nishiumi and Ohno [2000] correlated the experimentally determined VLE data of R125+R134a in the temperature range 303.75 to 363.15 K using an extended BWR equation of state and evaluated the optimum binary interaction parameters. It is desirable to check the predictive capability of an equation of state with different mixing rules. In the present work the PR equation of state is used with three different mixing rules to predict the VLE data of alternative refrigerant mixtures. The present study reveals that the PR equation of state with composition dependent mixing rule of the Margules type, with two binary interaction parameters is able to predict the VLE data with high degree of accuracy.

### CRITERION FOR EQUILIBRIUM

For a closed system containing vapor and liquid phases, with each phase consisting of *c* components, in a state of equilibrium at specified temperature *T* and pressure *P*, the criterion of equilibrium gives

$$\hat{f}_i^l = \hat{f}_i^v \quad (1)$$

$$\text{or } \hat{\phi}_i^l x_i P = \hat{\phi}_i^v y_i P \quad (2)$$

where

$x_i, y_i$  = Mole fractions of component *i* in liquid and vapor phases, respectively.

$\hat{\phi}_i^l, \hat{\phi}_i^v$  = Fugacity coefficient of component *i* in liquid and vapor phases, respectively.

*P* = Pressure at which the system exists.

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Or

$$K_i = \frac{Y_i}{X_i} = \frac{\phi_i^v}{\phi_i^l} \quad (3)$$

where  $K_i$  is the K factor or equilibrium constant for component  $i$ .

In the Equation of State (EOS) approach, the reference state is the ideal gas state and the fugacity coefficient is a measure of deviation from this state for both the vapor and liquid phases.

### EQUATION OF STATE (EOS) APPROACH

The equations of state inspired on the two term van der Waals form are quite attractive due to their simplicity and low computational costs. In the present work, the Peng-Robinson EOS is used with three different mixing rules to correlate the data. The Peng-Robinson (PR) EOS is given by

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (4)$$

The values of the parameters are given by

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (5)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (6)$$

$$a(T) = a(T_c) \alpha \quad (7)$$

$$\alpha^{1/2} = 1 + \kappa(1 - T_R^{1/2}) \quad (8)$$

$$\kappa = f(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (9)$$

$$T_R = T/T_c \quad (10)$$

where  $T_c$ =Critical Temperature  
 $P_c$ =Critical Pressure  
 $T_R$ =Reduced Temperature  
 $\omega$ =Acentric Factor  
 $R$ =Universal Gas Constant

### MIXING RULES

The mixing rules used in the prediction of VLE data of mixtures are as important as the EOS itself. Quite often the classical van der Waals one fluid mixing rule with one binary interaction parameter is used. However, better mixing rules are to be employed as the systems become complex in nature. Tsionopoulos and Heidman [1985] pointed out that it is unlikely that the performance of a new EOS will be better unless improved mixing rules are used.

Three different approaches are used in modifying the mixing rules. In the first approach, Patel and Teja [1982] retained the one parameter mixing rule and introduced some additional correction terms. In the second approach, Mollerup [1981] and Mathias and Copeman [1983] used the volume dependent mixing rules. In the third approach, Huron and Vidal [1979] and Stryjek and Vera [1986] used the composition-dependent mixing rule, where the classical binary interaction parameter is changed into a composition-dependent term with two interaction parameters. The widely used mixing rules are

given below.

#### 1. Van der Waals One Fluid Mixing Rules

The energy parameter  $a$  and the volume parameter  $b$  are given by

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (11)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (12)$$

where the cross terms  $a_{ij}$  and  $b_{ij}$  are given by

$$a_{ij} = \sqrt{a_i a_j} (1 - K_{ij}) \quad (13)$$

$$b_{ij} = \left( \frac{b_{ii} + b_{jj}}{2} \right) (1 - l_{ij}) \quad (14)$$

where  $K_{ij}$  and  $l_{ij}$  are the binary interaction parameters.

When  $l_{ij}=0$ , one gets

$$b = \sum_i x_i b_{ii} \quad (15)$$

#### 2. Composition Dependent Mixing Rules

These mixing rules were proposed by Huron and Vidal [1979] and Stryjek and Vera [1986] as modifications to the van der Waals mixing rules to improve the prediction capability of VLE calculations. These mixing rules are given by Eqs. (11) and (15). Two binary interaction parameters  $K_{ij}$  and  $K_{ji}$  are used with composition dependence for the parameter 'a'. Stryjek and Vera proposed the composition dependence for the interaction parameter as

$$a_{ij} = \sqrt{a_i a_j} (1 - x_i K_{ij} - x_j K_{ji}) \quad (16)$$

which is a Margules type cross term.

#### 3. Conformal Solution Van der Waals Mixing Rules

These mixing rules were proposed by Kwak and Mansoori [1986] and were used by Benmekki and Mansoori [1987, 1988]. These mixing rules differ depending on the EOS used. For the PR EOS, the temperature dependent term can be rewritten as

$$a(T, \omega) = a(T_c) \{ 1 + k(1 - T_R^{1/2}) \}^2 = c + dRT - 2\sqrt{cdRT} \quad (17)$$

$$\text{where } c = a(T_c)(1 + \kappa^2) \quad (18)$$

$$d = a(T_c) \frac{\kappa^2}{RT_c} \quad (19)$$

The parameter 'b' is the same as in the PR-EOS. The mixing rules are given by

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (20)$$

$$c = \sum_i \sum_j x_i x_j c_{ij} \quad (21)$$

$$d = \sum_i \sum_j x_i x_j d_{ij} \quad (22)$$

The cross terms or the combining rules are given by

$$b_{ij} = (1 - l_{ij})^3 \left( \frac{b_{ii}^{1/3} + b_{jj}^{1/3}}{2} \right) \quad (23)$$

$$c_{ij} = (1 - k_{ij})^3 \left( \frac{c_{ii} c_{jj}}{b_{ii} b_{jj}} \right)^{1/2} b_{ij} \quad (24)$$

$$d_{ij} = (1 - m_{ij})^3 \left( \frac{d_{ii}^{1/3} + d_{jj}^{1/3}}{2} \right)^3 \quad (25)$$

where  $K_{ij}$ ,  $m_{ij}$  and  $l_{ij}$  are adjustable binary interaction parameters.

$$\bar{c}_i = \sum_j x_j c_{ij} \quad (35)$$

$$\bar{d}_i = \sum_j x_j d_{ij} \quad (36)$$

## THERMODYNAMIC MODELS

The Peng-Robinson (PR) Equation of State (EOS) is selected in this work to predict the VLE data. The following three different thermodynamic models are selected to predict the VLE data of alternative refrigerant mixtures.

Model 1: PR EOS with van der Waals one Fluid Mixing Rules

Model 2: PR EOS with composition Dependent Two Parameter Mixing Rules.

Model 3: PR EOS with Conformal solution Van der Waals Mixing Rules

### 1. Model 1

If the PR EOS is coupled with the van der Waals one Fluid Mixing Rules, gives

$$\ln \phi_i = (Z-1)B'_i - \ln(Z-B) - \frac{A}{B2\sqrt{2}}(A'_i - B'_i) \ln \left\{ \frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B} \right\} \quad (26)$$

where

$$A'_i = \frac{1}{a} \left\{ 2a_{ii}^{1/2} \sum_j x_j a_{ij}^{1/2} (1 - k_{ij}) \right\} \quad (27)$$

$$B'_i = \frac{b_i}{b} \quad (28)$$

$$A = \frac{aP}{R^2 T^2} \quad (29)$$

$$B = \frac{bP}{RT} \quad (30)$$

### 2. Model 2

By using the van der Waals one fluid Margules type mixing rules along with the PR EOS, we get the following expression for the fugacity coefficient:

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left( \frac{a_i}{a} + 1 - \frac{b_i}{b} \right) \ln \left\{ \frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B} \right\} \quad (31)$$

$$\text{where } \bar{a}_i = 2 \left[ \sum_j x_j \sqrt{a_{ij} a_{jj}} (1 - x_i k_{ij} - x_j k_{ji}) + x_i x_j^2 \sqrt{a_{ij} a_{jj}} (k_{ji} - k_{ij}) \right] \quad (32)$$

### 3. Model 3

The PR EOS when coupled with conformal solution van der Waals mixing rules yields the following expression for the fugacity coefficient:

$$\ln \phi_i = (Z-1) \left( 2 \frac{\bar{b}_i}{b} - 1 \right) - \ln \left( Z - \frac{bP}{RT} \right) - \frac{1}{2\sqrt{2}bRT} \left[ \frac{a}{2} - \frac{a\bar{b}_i}{b} + \bar{c}_i \left( 1 - \sqrt{\frac{dRT}{c}} \right) + \bar{d}_i \left( RT - \sqrt{\frac{cRT}{d}} \right) \right] \ln \left[ \frac{Z+(1+\sqrt{2})bP/RT}{Z+(1-\sqrt{2})bP/RT} \right] \quad (33)$$

$$\text{where } \bar{b}_i = \sum_j x_j b_{ij} \quad (34)$$

## RESULTS

In the present work, the  $P-x_i-y_i$  data (given  $T$  and  $x_i$ ) is used to estimate the binary interaction parameters in the chosen models by optimizing an Objective Function (OF). In the present work, the objective function used is a sum of two functions - OFP and OFY [Benmekki and Mansoori, 1987]:

$$\text{OF} = \text{OFP} + \text{OFY} \quad (37)$$

$$\text{where OFP} = \sum_{i=1}^N \left( \frac{P_{exp} - P_{cal}}{P_{exp}} \right)_i^2 \quad (38)$$

$$\text{OFY} = \sum_{i=1}^N \left( \frac{y_{1exp} - y_{1cal}}{y_{1exp}} \right)_i^2 \quad (39)$$

$P_{exp}$ ,  $P_{cal}$  = Experimental and calculated pressures, respectively.

$y_{1exp}$ ,  $y_{1cal}$  = Experimental and calculated  $y_1$ , respectively.

$N$  = Number of data points.

For the optimization of the Objective Function (OF), a function *fmins* of the MATLAB, which uses the Nelder Mead Simplex Algo-

**Table 1. Systems studied and the sources of experimental data**

No.	System	Data source
1	R23-R600a	Lim et al. [2000]
2	R32-R125	Lee et al. [1999]
3	R32-R134a	Chung and Kim [1997]
4	R32-R143a	Kim et al. [2000]
5	R32-R152a	Lee et al. [1999]
6	R32-R236ea	Koo et al. [2000]
7	R32-R236ea	Bobbo et al. [2000]
8	R32-R236fa	Bobbo and Camporese [1999]
9	R32-R600a	Lim et al. [1999]
10	R125-R236ea	Bobbo et al. [2000]
11	R125-R236fa	Bobbo et al. [1999]
12	R125-R600a	Lee et al. [2000]
13	R134a-R116	Kleiber [1994]
14	R134a-R152a	Kleiber [1994]
15	R134a-R227ea	Koo et al. [2000]
16	R134a-R236fa	Bobbo et al. [1998]
17	R134a-R290	Kleiber [1994]
18	R134a-R600a	Bobbo et al. [2000]
19	R143a-R236fa	Bobbo et al. [2000]
20	R143a-R600a	Lim et al. [2000]
21	R152a-R600a	Lim et al. [2000]
22	R227ea-R600a	Lee et al. [2000]
23	Propylene-R152a	Kleiber [1994]
24	Propylene-R23	Kleiber [1994]
25	Propylene-R116	Kleiber [1994]
26	Propylene-R134a	Kleiber [1994]
27	R600a-R236fa	Bobbo et al. [1998]

rithm, is employed. At the optimum values of the binary interaction parameters, the average absolute deviations in pressure and composition are calculated as

$$\frac{\Delta P}{P} = \left( \frac{OFP}{N} \right)^{1/2} \quad (40)$$

$$\frac{\Delta y_1}{y_1} = \left( \frac{OFY}{N} \right)^{1/2} \quad (41)$$

The potential non-chloro alternative refrigerants, HydroFluoro-Carbons (HFC), mixtures are considered in the present study. Twenty seven binary systems of HFC mixtures have been studied in the present work. The systems studied and the sources of experimental data are presented in Table 1, while the critical constants and acentric factors of the compounds are presented in Table 2.

The selected systems range from almost ideal (R134a/R236fa) to highly non-ideal (R134a/R600a) systems. Only isothermal VLE data at a single temperature is considered. The experimental and predicted VLE data, for all the three thermodynamic models, for the system R134a/R600a (a typical alternative refrigerant mixture) are presented in Table 3. The average absolute percent deviations

in pressure and vapor phase composition for all the 27 systems are presented in Table 4.

The minimum and maximum deviations in pressure observed for Model 3 are 0.3 for the system R134a-R52a and 8.49 for the system R134a-R236fa, respectively, while the minimum and maximum percent deviations in vapor phase composition for Model 3 are 0.37 for the system R134a-R52a and 6.51 for the system R600a-R236fa, respectively.

The optimum binary interaction parameters  $k_{ij}$  for Model 1 [see Eq. (27)]  $k_{ij}$  and  $k_{ji}$  for Model 2 [see Eq. (32)] and  $l_{ij}$ ,  $k_{ij}$  and  $m_{ij}$  for Model 3 [see Eqs. (23) to (25)] obtained from minimization of the objective function for the three models are presented in Table 5.

The results obtained indicate that for thirteen out of the twenty seven systems studied, the Model 2 (PR EOS with composition dependent mixing rules) predicted the VLE data with least average pressure deviations. For five systems (R32/R134a; R143a/R236fa; R134a/R227ea; R125/R236fa and R600a/R236fa) the predicted VLE data by Model 2 is not better than the data predicted by both Models 1 and 3. Of the remaining nine systems, the three systems R125/R600a, R227ea/R600a and Propylene/R116 are highly non-ideal and Model 3 yields better VLE data for these systems. This behav-

**Table 2. Critical constants and acentric factors of alternative refrigerants**

No.	Refrigerant	Formula	Chemical name	$T_c$ (K)	$P_c$ (bar)	$\omega$
1	R23	CHF <sub>3</sub>	Trifluoromethane	299.070	47.730	0.2634
2	R32	CH <sub>2</sub> F <sub>2</sub>	Difluoromethane	351.600	57.540	0.2710
3	R116	C <sub>2</sub> F <sub>6</sub>	Hexafluoroethane	292.850	29.412	0.2554
4	R125	C <sub>2</sub> HF <sub>5</sub>	Pentafluoroethane	339.33	35.817	0.3035
5	R134a	C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	1,1,1,2-Tetrafluoroethane	374.255	40.150	0.3261
6	R143a	C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	1,1,1-Trifluoroethane	364.040	37.268	0.2611
7	R152a	C <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	1,1-Difluoroethane	386.600	44.414	0.2611
8	R227ea	C <sub>3</sub> HF <sub>7</sub>	1,1,1,2,3,3,3-Heptafluoropropane	375.95	29.412	0.3632
9	R236ea	C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	1,1,1,2,3,3-Hexafluoropropane	412.44	34.564	0.3770
10	R236fa	C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	1,1,1,3,3,3-Hexafluoropropane	398.07	31.583	0.2913
11	R290	C <sub>3</sub> H <sub>8</sub>	Propane	370.02	42.055	0.1514
12	R600a	C <sub>4</sub> H <sub>10</sub>	Isobutane	408.200	36.024	0.1830
13	Propylene	C <sub>3</sub> H <sub>6</sub>	Propene	364.850	45.452	0.1480

**Table 3. Experimental and predicted VLE data for the system R134a(1)-R600a(2) at 303.68 K**

$X_{1,exp}$	$y_1$				P (kPa)			
	Expt.	Model 1	Model 2	Model 3	Expt.	Model 1	Model 2	Model 3
0.0000	0.0000	0.0000	0.0000	0.0000	410.7000	403.6074	404.5912	403.6074
0.0825	0.3111	0.3077	0.3141	0.3181	580.8000	563.5638	571.8180	573.1887
0.1308	0.3994	0.3999	0.4029	0.4063	649.9000	634.5351	642.0659	642.9190
0.2239	0.4977	0.5075	0.5038	0.5055	739.5000	734.9225	736.8799	735.3936
0.2865	0.5427	0.5532	0.5461	0.5468	781.3000	781.8396	779.4768	776.2502
0.4822	0.6298	0.6412	0.6305	0.6290	854.2000	864.2236	853.6971	846.4251
0.6230	0.6817	0.6883	0.6809	0.6794	879.6000	889.9174	878.0639	869.5135
0.7837	0.7572	0.7558	0.7572	0.7581	884.3000	894.1051	881.4702	872.6379
0.8276	0.7861	0.7824	0.7867	0.7887	877.9000	887.9130	875.1874	866.5199
0.9133	0.8652	0.8578	0.8658	0.8695	849.2000	857.6906	846.9362	839.7167
1.000	1.000	1.000	1.000	1.000	780.9000	782.2503	783.3664	782.2503
Deviations ( $\Delta y_1/y_1$ ) %		1.127	0.571	1.026	( $\Delta P/P$ ) %	1.429	0.777	1.104

**Table 4. The average percent deviations in pressure and vapor phase composition for the Models 1, 2 & 3**

No.	System	No. of data points	$(\Delta P/P)\%$			$(\Delta y_i/y_i)\%$		
			Model 1	Model 2	Model 3	Model 1	Model 2	Model 3
1	R23-R600a	18	2.756	1.524	3.300	1.428	1.579	2.290
2	R32-R125	9	1.768	1.577	1.767	0.895	0.708	0.877
3	R32-R134a	5	1.390	1.540	1.420	0.640	0.450	0.450
4	R32-R143a	10	1.019	0.851	1.119	0.821	0.848	0.835
5	R32-R152a	9	2.310	1.283	2.280	2.300	2.022	2.320
6	R32-R227ea	10	1.266	0.675	1.833	1.149	1.169	1.435
7	R32-R236ea	12	0.930	0.702	0.910	1.130	0.703	0.730
8	R32-R236fa	9	4.568	4.513	4.442	3.000	3.158	2.880
9	R32-R600a	20	3.159	1.964	2.876	1.867	2.060	3.224
10	R125-R236ea	10	0.653	0.563	0.615	0.568	0.535	0.583
11	R125-R236fa	10	4.760	4.809	4.32	3.550	3.693	3.380
12	R125-R600a	12	1.550	1.403	1.110	1.120	1.112	1.150
13	R134-R116	10	5.040	3.022	3.034	3.320	3.022	3.870
14	R134a-R52a	9	0.306	0.412	0.301	0.359	0.399	0.369
15	R134a-R227ea	9	0.869	0.949	0.882	2.321	1.002	2.411
16	R134a-R236fa	9	5.686	5.767	8.49	4.014	4.171	3.938
17	R134a-R290	11	1.462	1.378	2.242	1.437	1.403	2.848
18	R134a-R600a	11	1.479	0.777	1.104	1.127	0.571	1.026
19	R143a-R236fa	9	7.739	8.010	7.790	4.763	4.589	4.626
20	R143a-R600a	9	0.952	0.949	1.101	1.961	1.961	1.237
21	R152a-R600a	10	1.430	1.447	10582	2.180	2.185	2.065
22	R227ea-R600a	13	1.297	1.140	0.885	1.126	1.060	0.594
23	Propylene-R23	8	1.970	1.515	1.490	2.673	2.507	2.127
24	Propylene-R116	8	4.634	4.694	4.780	2.130	2.163	2.093
25	Propylene-R134a	10	2.103	1.969	1.871	0.548	0.514	2.044
26	Propylene-R152a	9	1.426	1.241	2.597	1.610	1.659	1.630
27	R600a-R236fa	15	5.676	5.798	5.523	6.142	6.230	6.511

**Table 5. Optimum binary interaction parameters of the systems**

No.	System	Temp. (K)	(Model 1)	(Model 2)		(Model 3)		
			$k_{ij}$	$k_{ij}$	$k_{ji}$	$l_{ij}$	$k_{ij}$	$m_{ij}$
1	R23-R600a	293.15	0.1910	0.1719	0.2011	0.0003	-0.0003	-0.1097
2	R32-R125	303.15	0.0149	0.0256	0.00006	0.0047	0.0026	-0.0061
3	R32-R134a	273.15	-0.00026	-0.0039	0.0028	-0.0097	0.1411	0.1136
4	R32-R143a	263.15	0.0133	0.0161	0.0104	0.0062	0.0032	-0.0081
5	R32-R152a	303.15	0.0155	0.0347	-0.0039	0.0048	0.0027	-0.0062
6	R32-R227ea	298.15	0.0230	0.0127	0.0328	0.0103	0.0054	-0.1032
7	R32-R236ea	288.15	-0.0174	-0.0112	-0.0224	0.0041	0.0002	-0.0029
8	R32-R236fa	303.22	-0.0140	-0.0065	-0.0253	0.0060	0.0032	-0.0077
9	R32-R600a	301.80	0.2042	0.1847	0.2152	0.0003	-0.0005	-0.1246
10	R125-R236ea	303.19	0.0056	0.0074	0.0036	0.0010	0.0005	-0.0011
11	R125-R236fa	303.19	-0.0013	0.0008	-0.0043	0.0432	-0.2057	-0.0909
12	R125-R600a	303.15	0.1516	0.1485	0.1531	-0.0384	0.2572	0.1210
13	R134a-R116	251.00	0.0969	0.0858	0.1186	0.0289	-0.0023	-0.0170
14	R134a-R152a	298.00	-0.0070	-0.0082	-0.0073	-0.0022	-0.0002	0.0016
15	R134a-R227ea	298.15	0.0159	-0.0017	0.0306	0.0039	0.0022	-0.0051
16	R134a-R236fa	303.62	-0.0078	-0.0099	-0.0075	0.0607	-0.1012	0.0023
17	R134a-R290	298.00	0.1646	0.1647	0.1640	0.0002	0.0002	-0.0820
18	R134a-R600a	303.68	0.1613	0.1474	0.1699	0.0285	0.0143	-0.0368

Table 5. Continued

No.	System	Temp. (K)	(Model 1)	(Model 2)		(Model 3)		
			$k_{ij}$	$k_{ij}$	$k_{ij}$	$l_{ij}$	$k_{ij}$	$m_{ij}$
19	R143a-R236fa	283.11	-0.0169	-0.0263	-0.0107	-0.0143	0.0151	0.0010
20	R143a-R600a	333.15	0.1325	0.1330	0.1316	0.0489	-0.0514	-0.0392
21	R152a-R600a	303.20	0.1210	0.1175	0.1228	0.0004	0.0004	-0.0178
22	R227ea-R600a	323.15	0.1369	0.1413	0.1330	-0.0584	0.2243	0.0737
23	Propylene-R23	265.00	0.1072	0.1084	0.1052	0.0438	-0.0402	-0.0344
24	Propylene-R116	275.00	0.1538	0.1520	0.1558	-0.0447	0.2906	0.1676
25	Propylene-R134a	298.00	0.1074	0.1000	0.1104	0.0005	0.0007	-0.0515
26	Propylene-R152a	285.00	0.0871	0.0943	0.0500	0.0006	0.0008	-0.0471
27	R600a-R236fa	303.68	0.1464	0.1449	0.1466	0.0266	0.0136	-0.0346

ior may be attributed to the extra parameter used in Model 3.

### CONCLUSIONS

The present study shows that the VLE data of alternative refrigerant mixtures can be predicted with better accuracy by using the PR EOS with composition-dependent mixing rules with two binary interaction parameters. An increase in the binary interaction parameters from one to two leads to an enhancement in the accuracy of the predicted VLE data. However, further increase in the number of interaction parameters does not necessarily improve the accuracy of the predicted VLE data. Therefore, a two parameter mixing rule of Margules type coupled with PR EOS provides sufficiently accurate VLE data for engineering needs.

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