



A Predictive Correlation for Vapor-Liquid Equilibrium of CO₂ + n-Alkane Ternary Systems Based on Cubic Mixing Rules

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Abstract

The accurate description of the phase equilibria of CO₂ and n-Alkane multicomponent mixtures over a wide range of temperature, pressure, and n-Alkane molecular weight, requires models that are both consistent and mathematically flexible for such highly non-ideal systems. In this study, a predictive correlation was proposed for the vapor-liquid equilibrium data (VLE) of CO₂ and n-Alkane ternary systems, based on the Peng-Robinson equation of state (PR EOS), coupled with cubic mixing rules (CMRs). The ternary interaction parameters (TIP) correlation is developed using binary VLE data and tested for CO₂ + n-Alkane + n-Alkane ternary systems. For this purpose, binary VLE data of CO₂ + n-Alkane and n-Alkane + n-Alkane systems for n-Alkane from C₃ to C₂₄, covering a total of about 70 references, used to correlate TIP in the ranges of 0.5-31 MPa and 230-663 K. Two temperature-dependent TIP correlations, based on acentric factor ratio, have been tuned with more than 2000 data points of the CO₂ + n-Alkane and the n-Alkane + n-Alkane binary systems with AARD of 3.13% and 6.71%, respectively. The generalized predictive correlation was proposed based on the proper three-body interaction contributions and successfully tested for VLE data of the CO₂ + n-Alkane + n-Alkane ternary systems.

Keywords:

CO₂,
n-Alkane,
Peng-Robinson EOS,
Predictive Model,
Ternary Interaction,
Vapor-Liquid Equilibrium

Introduction

The separation process design at elevated pressure is involved with accurate knowledge based on the equilibrium behavior of individual fluid phases. Carbon dioxide's unique behavior at elevated pressures makes a prominent ability as a solvent in most industrial separation processes. The increasing attention of CO₂ + n-Alkanes high-pressure systems in a wide range of industrial field, e.g., CO₂ injection as a method for enhanced oil recovery [1-4], supercritical extraction and separation processes [5-7], and natural gas storage [8], lead to a growing demand to investigate in the vapor-liquid equilibrium of CO₂ + n-Alkanes systems. The large quadrupole moment, the unique critical behavior of carbon dioxide and the widely molecular weight range of n-Alkane demonstrate the large molecular interaction [9]. Therefore, in many binary and ternary systems within the CO₂ + n-Alkane homologous series, due to their highly asymmetric interaction, the prediction of such complex behavior in a wide range of pressures and temperatures is too difficult.

Equations of state (EOSs) are the frequently used methods to describe the mathematical relationship between pressure, volume, and temperature (PVT) of fluids; however, among them, cubic EOS is the most commonly used [10,11]. The cubic equation of state, due to its intrinsic simplicity and efficiency, is widely used in separation processes describing the phase equilibria of CO₂ + n-Alkane systems in liquid, vapor, and supercritical states, over wide ranges of conditions [10,12]. Generally, Cubic EOS uses convenient mixing rules to predict

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multicomponent mixtures, so the fluid properties are represented in a way that first, the property of an individual component is accounted for, and then the intermolecular force correction provides a realistic and flexible thermodynamic model [11].

Conventionally used, quadratic mixing rules (QMRs), double summations in mole fraction, can model binary interaction effects for binary, ternary, and higher fluid phase equilibria [13]. One of the most effective features of quadratic mixing rules for precise prediction is composition dependency, but in contrast, it needed extensive experimental data and involved a lot of numerical jobs to determine the compositional functionality [14]. On the other hand, quadratic mixing rules showed that they are not able to predict the ternary CO₂ + n-Alkane systems as well as assuming all molecular interactions, so the more flexible mixing rules require presenting an enhanced model for the ternary interactions [15]. Among all flexible multicomponent models, Mathias et al. [16] considered a triple summation in the mole fraction called cubic mixing rules (CMRs). Although finding multicomponent experimental data to correlate TIP is too tricky, they proposed special binary interaction parameters based on cubic mixing rules that could be able to estimate TIP from available binary experiments and predicting multicomponent phase equilibrium by such ternary parameters for all ternary subsystems without available experimental information.

Prediction of binary CO₂ + n-Alkane behaviors by such parameter in a wide range of alkenes' molecular weight required a comprehensive correlation model for interaction parameters. Therefore, choosing an astounding independent variable representing molecular features has a significant role [17]. Moreover, some approaches were accomplished during the past studies to correlate the binary interaction parameters for CO₂ and hydrocarbon systems based on the components' property. Kato et al. [18] represented a binary interaction parameter correlation for VLE of CO₂ and C₁-C₁₀ n-paraffin in a wide range of temperature of subcritical to supercritical based on PR EOS and classic mixing rules. The proposed linear temperature-dependent interaction correlation based on the logarithm of paraffin's acentric factor shows an accurate prediction, especially for light paraffin. In 1988, Valderrama et al. [12] repeated Kato's work by proposing a linear inverse temperature-dependent interaction correlation whose constants are a linear function of paraffin's acentric factor. Results show a more accurate prediction in both bubble pressure and composition results than Kato's work, but there are no differences in the VLE predictions.

Kordas et al. [19] proposed a generalized correlation for the interaction coefficient of CO₂-alkane binary systems from C₁ to C₄₄, as a function of CO₂ reduced temperature and alkane acentric factor, based on the modified Peng-Robinson equation of state (t-mPR EOS). Since hydrocarbon contains more than one ring, the correlation is unable to apply in many asymmetric systems. Li et al. [20] augmented a new generalized binary interaction parameter correlation for CO₂-n-Alkane binary systems from C₁₀ to C₄₄ using the Peng-Robinson equation of state (PR EOS) with the modified alpha function. The proposed interaction parameter correlation is a function of both the reduced temperature of CO₂ and the acentric factor of n-Alkane. As a result, their model predicts CO₂-n-Alkane binary systems with appropriate accuracy even for heavy n-Alkane.

While a few studies have recently been implemented on the TIP of CO₂ + n-Alkane systems, Cismondi et al. [21] used the RK-PR EOS coupled with the cubic mixing rules for both the attractive and the repulsive mixture parameters to model VLE of CO₂ + n-Alkane (C₁₄ to C₂₂). The temperature-dependent interaction parameters were applied as an exponential function, and results showed a generally successful description of asymmetric CO₂ + n-Alkane binary systems, although it seems the prediction of heavy n-Alkane systems accompany by more deviations. Despite rare research on the correlation of TIP of CO₂ + n-Alkane systems based on the binary experimental data, Cismondi et al. [13] applied CRMs for a unique correlation of n-Alkane carbon number-dependent interaction parameters for TIP of CO₂ + n-Alkane systems.

The CRM was employed for both the attractive and the repulsive mixture parameters and consider a temperature dependency parameter to develop a prediction model in a wide range of conditions. In general terms, their correlation showed an excellent ability to predict different types of fluid phase equilibrium, although it has incredible low accuracy in predicting the liquid phase composition.

In this research, we propose a new generalized temperature-dependent ternary interaction parameter (TIP) correlation in term of acentric factor (ω) ratio for ternary CO₂ + n-Alkane (1) + n-Alkane (2) system, getting more accurate predictions of CO₂ + n-Alkane multicomponent vapor-liquid equilibria using the PR EOS. For this purpose, the binary information data of CO₂ + n-Alkane and n-Alkane (1) + n-Alkane (2) separately used to fit the two individual ternary interaction parameter models based on acentric factor ratios. Finally, the proposed model utilized by these two correlations to predict different types of interactions for ternary CO₂ + n-Alkane (1) + n-Alkane (2) system was tested by available ternary vapor-liquid data.

Mathematical Model

Applying the proper equation of state is an essential problem to represent the exact relationship between temperature, pressure, and molar volume. However, the benefit of an equation of state in predicting the phase behavior of real mixtures strongly depends on the used mixing rules than in the form of an equation of state. Moreover, the modern type equation of state like PC-SAFT, Having more than three real molar volume roots at a given temperature, has a complicated structure to show vapor-liquid equilibria. Therefore, the simple van Der Waal's type cubic equations of state, whose solution is not more than three real molar volume roots, is more practically applicable [21]. In this research, one of the most widely used and successfully applied cubic EOSs in the petroleum and chemical industry [22], the Peng and Robinson equation of state (PR EOS) [23] used:

$$P = \frac{RT}{v-b} - \frac{a_c \alpha(T)}{v^2 + 2bv - b^2} \quad (1)$$

$$a_c = 0.457235529 \frac{(RT_c)^2}{P_c} \quad (2)$$

$$\alpha(T) = \left[1 + m \left(1 - \left(\frac{T}{T_c} \right)^{0.5} \right) \right]^2 \quad (3)$$

$$m = 0.37646 + 1.5422\omega - 0.26992\omega^2 \quad \omega < 0.49 \quad (4)$$

$$m = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 \quad \omega \geq 0.49 \quad (5)$$

Using an EOS for modelling the mixture's behavior involved in applying suitable mixing rules, calculates EOS parameters (here are a and b) of the mixtures. In recent studies, quadratic mixing rules (QMR) are frequently applied using binary interaction parameters to predict phase behavior of CO₂ + n-Alkane systems in the wide range of temperatures and pressures [12,17,19,20,24]. However, many attempts were made to formulate a ternary intermolecular collision based on binary interaction parameters, but finding a proper method was still unsolved. Among the recently used mixing rules, the cubic mixing rule (CMR) can predict ternary repulsive and attractive interaction [14]. Also, CMRs provide a more flexible model that makes it possible to model ternary systems without any lack of considering the corresponding binary subsystems [25]. In this research, the CMR is used:

$$a = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k a_{ijk} \quad (6)$$

$$a_{ijk} = (a_i a_j a_k)^{(1/3)} (1 - k_{ijk}) \quad (7)$$

$$b = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N x_i x_j x_k b_{ijk} \quad (8)$$

$$b_{ijk} = \left(\frac{b_i + b_j + b_k}{3} \right) (1 - l_{ijk}) \quad (9)$$

where k_{ijk} and l_{ijk} are respectively, the energy interaction parameter and the covolume interaction parameter, and N is the number of components in a multicomponent mixture [14]. The temperature dependency of the ternary covolume interaction parameter (l_{ijk}) was likely to be ignored while the energy interaction parameter was considered as a temperature variable function. Moreover, it has been found that the attractive interaction parameter has two finite limits both at zero and at infinite temperature, but the proper functionality of the temperature dependency behavior is still not clear [13]. Besides, one of the most applicable forms of temperature dependency, proposed by Cismondi et al. [17], the exponential form, is able to model temperature variation of attractive interaction parameters in a wide range of temperatures:

$$k_{ijk} = k_{ijk}^{\infty} + k'_{ijk} e^{-T/T_{ijk}^*} \quad (10)$$

From Eq. 10 depending on the sign of k'_{ijk} , k_{ijk} behaviors are rising or declining in the variation of temperature. At both finite limits, zero and infinite temperature, parameter k_{ijk} respectively tends to become $k_{ijk}^0 = (k_{ijk}^{\infty} + k'_{ijk})$ and k_{ijk}^{∞} . The exponential rate (T_{ijk}^*) is the determining factor to manipulate k_{ijk} variation through a wide range of temperatures [17].

Methodology

Our purpose is to represent an optimized PR EOS model based on a temperature-dependent cubic mixing rule predicting both binary and ternary molecular interaction of CO₂ + n-Alkane systems over a wide range of conditions. Approach to this object is required in many steps of research consequently given here: 1- propose a correlation model for ternary interaction parameter based on an independent variable, 2- collect experimental data from binary vapor-liquid equilibrium information, 3- define an objective function and an optimization method to fit experimental data, 4- examine ternary interaction parameter for the ternary CO₂ + n-Alkane vapor-liquid equilibrium. Next, we explain and discuss some details and considerations of these steps to define our methodology, achieving the goals.

Ternary Interaction Parameter

Generally, for a three-component system, both ternary energy interaction parameters (k_{ijk}) and covolume interaction parameters (l_{ijk}) included different seven configurations mentioned as $\{k_{112}, k_{122}, k_{113}, k_{133}, k_{223}, k_{233}, k_{123}\}$ and $\{l_{112}, l_{122}, l_{113}, l_{133}, l_{223}, l_{233}, l_{123}\}$ [25]. We can find the ternary parameters by two different applicable methods: a) using experimental information on ternary or higher systems to regress ternary parameters, and b) predicting the ternary parameters from correlation obtained from experimental data binary systems. The first method is so complicated and needs more data on ternary systems, but the last is possible. For a binary system of components 1 and 2, the three-particle collision can occur between two molecules of component 1 and one of component 2 and, at the opposite end, where two molecules of

component 2 and one component of 1 collide each other. Hence, for a binary system, the cubic mixing rules represent two independent TIP for both energy and covolume parameters, i.e., $\{k_{112}, k_{122}, l_{112}, l_{122}\}$. This reduction provides an ability to use binary VLE data fitting the TIP and leads to decreasing computerized effort to fit experimental data [13].

As mentioned earlier, the TIP for pairs of CO₂ and n-Alkane molecules affected by many independent variables included the operational condition and molecular structure. It is well-known that the temperature has the main role, and the acentric factor is the most reported parameter that could be used in developing the BIP correlation [12,17,20]. Subsequently, many formulations have been tested to correlate interaction parameters, e.g., linear, fractional, polynomial, logarithmic types, or their combinations. Our study examines new forms of formulation for ternary interaction parameters, based on the binary experimental data, applying for three components or higher, systems:

$$k_{ijk} = a + b \frac{w_i}{w_j} + c \frac{w_j}{w_k} + d \frac{w_k}{w_i} \quad (11)$$

$$l_{ijk} = e + f \frac{w_i}{w_j} + g \frac{w_j}{w_k} + h \frac{w_k}{w_i} \quad (12)$$

The basic form of this formula was obtained from binary interaction correlation represented by Valderrama et al. [26]. So the rational term assured the effect of asymmetric behaviors of each pair of components. Theoretically, if all components were the same, the correlation yields a constant that has a physical meaning equal to interaction parameters. For this reason, the constants $\{a, b, c, d\}$ and $\{e, f, g, h\}$ could be considered as a type of interaction parameter in a while that they are only a function of temperature. Although the covolume interaction parameters (l_{ijk}) have not significant temperature dependency, the temperature dependency of energy interaction parameters (k_{ijk}) is defined based on Eq. 10 represented by:

$$a = a_1 + a_2 \exp(-T/a_3) \quad (13)$$

$$b = b_1 + b_2 \exp(-T/b_3) \quad (14)$$

$$c = c_1 + c_2 \exp(-T/c_3) \quad (15)$$

$$d = d_1 + d_2 \exp(-T/d_3) \quad (16)$$

Another object was the accounting n-Alkane + n-Alkane interaction in ternary CO₂ + n-Alkane + n-Alkane systems since needed different interaction parameters. Using binary CO₂ (1) + n-Alkane (2 or 3) data, makes an ability to correlate some TIP aspect of ternary systems $\{k_{112}, k_{122}, k_{113}, k_{133}\}$ and $\{l_{112}, l_{122}, l_{113}, l_{133}\}$. We then set an auxiliary strategy to surplus this issue by using the binary VLE data of the n-Alkane + n-Alkane system. We optimized a different set of interaction parameters correlation to achieve the ternary intermolecular collision behavior of n-Alkane + n-Alkane + n-Alkane systems $\{k_{223}, k_{233}\}$, and $\{l_{223}, l_{233}\}$.

The last problem was using an appropriate contribution of the ternary interaction parameter $\{k_{123}\}$ and $\{l_{123}\}$ to predict three different body collisions. Therefore, in this study the geometric and arithmetic averages, which are the most attractable mixing rules, of TIP related to those binary systems ($\{k_{112}, k_{122}, k_{113}, k_{133}\} + \{k_{223}, k_{233}\}$ and $\{l_{112}, l_{122}, l_{113}, l_{133}\} + \{l_{223}, l_{233}\}$) are used to achieve this object. A new contribution proposed that the CO₂ + n-Alkane systems' parameter affects twice more than the n-Alkane + n-Alkane systems' parameter. The proposed model presented in the equation below:

$$k_{123} = (k_{112}k_{122}k_{113}k_{133}k_{223}k_{233})^{1/6} \quad (17)$$

$$l_{123} = (l_{112}l_{122}l_{113}l_{133}l_{223}l_{233})^{1/6} \quad (18)$$

$$k_{123} = (k_{112} + k_{122} + k_{113} + k_{133} + k_{223} + k_{233})/6 \quad (19)$$

$$l_{123} = (l_{112} + l_{122} + l_{113} + l_{133} + l_{223} + l_{233})/6 \quad (20)$$

Table 1. The pressure and temperature range of binary CO₂ + n-Alkane VLE data

CO ₂ +n-Alkane	No.	Temperature (K)	Pressure (bar)	references
CO ₂ -C ₃	96	230-361.15	19.4-44.8	[27, 28]
CO ₂ -C ₄	268	250-418.8	23.3-82.1	[15, 29-32]
CO ₂ -C ₅	113	277.67-463.15	22.4-96.7	[33-35]
CO ₂ -C ₆	114	293.15-393.15	6.3-115.9	[36-39]
CO ₂ -C ₇	80	310.65-477.2	18.3-131.3	[40, 41]
CO ₂ -C ₈	70	313.14-372.5	5.2-137.7	[42-44]
CO ₂ -C ₉	42	315.12-415.82	20.3-167.7	[45, 46]
CO ₂ -C ₁₀	123	319.11-583.65	14.4-164.6	[47-50]
CO ₂ -C ₁₁	38	315.12-418.82	20.3-167.7	[46]
CO ₂ -C ₁₂	50	318.14-417.91	9.5-203.7	[51, 52]
CO ₂ -C ₁₄	26	344.3	110.3-163.8	[53]
CO ₂ -C ₁₅	49	293.15-353.15	5.6-160.3	[54, 55]
CO ₂ -C ₁₆	36	308.15-663.75	6.9-165.4	[47, 56, 57]
CO ₂ -C ₁₈	6	323.1	9.9-59.6	[58]
CO ₂ -C ₁₉	35	313.15-333.15	9.3-79.5	[59]
CO ₂ -C ₂₀	55	323.2-573.35	6.2-307.8	[52, 60, 61]
CO ₂ -C ₂₂	52	323.15-473.2	9.6-314.9	[60, 62]
CO ₂ -C ₂₄	17	373.15-573.15	10-98.5	[60, 63]

Database

Many experimental studies have been done on the vapor-liquid equilibrium of CO₂ + n-Alkane and n-Alkane + n-Alkane systems, during the last century. Most of them represented vapor and liquid phase composition at the temperatures and the pressures from the subcritical state to the supercritical phase. Totally 39 binary CO₂ + n-Alkane (C₃ to C₂₄) VLE literature data (1270 data point) and 27 binary n-Alkane + n-Alkane VLE literature data of normal alkane from C₃ to C₂₄ (958 data point) collected and shown in Tables 1 and 2, respectively. Table 1 shows that the test temperature varied from 230 K to 663.75 K, and the test pressure is in the range from 5.2 bar to 314.9 bar where covers all subcritical and supercritical regions. The same condition is attended for n-Alkane + n-Alkane data, as in Table 2, the test temperature varied from 260 K to 623 K, and the test pressure is in the range of 1 kPa to 76.8 bar.

Also, the range of reduced temperature and reduced pressure on these data, based on the carbon dioxide critical temperature and critical pressure, is reported in Table 3. It seems that all the data points distributed well around the critical point of CO₂ will make our optimization able to consider all ranges of the behavior of vapor-liquid equilibrium.

Objective Function

The VLE calculations have been performed at a given T and P based on ϕ - ϕ method, applicable at pressures from subcritical state to supercritical, to find the composition of both liquid and vapor phase [81]. The adjustable parameters, whose are the all constant of interaction's correlation, must optimize, and so there needed to take a suitable objective function representing both phase composition deviation. Among the entire objective function were introduced by the past work [82,83], because of the high sensitivity of the relative deviation in molar composition near the zero, the absolute deviation of the molar composition of both Vapor (y) and liquid (x) phases has a better agreement than relative deviation. Therefore, the objective function is defined as Eq. 21.

$$Error = \sqrt{\frac{1}{ns} \sum_1^{ns} \frac{1}{2 \cdot nd} \sum_1^{nd} [(x_{1,calc} - x_{1,exp})^2 + (y_{1,calc} - y_{1,exp})^2]} \quad (21)$$

A typical RMSE deviation that n_s is the number of systems and n_d is the number of data points including each system.

Table 2. The pressure and temperature range of binary n-Alkane+n-Alkane VLE data

n-Alkane + n-Alkane	No.	Temperature (K)	Pressure (bar)	references
C ₃ -C ₄	94	260-323.15	0.7-16.4	[32, 64]
C ₃ -C ₅	23	363.15-453.15	20.6-44.8	[65]
C ₃ -C ₆	24	363.15-453.15	20.6-48.2	[66]
C ₃ -C ₇	33	363.15-523.15	20.6-48.2	[67]
C ₃ -C ₈	28	363.15-473.15	24.1-5.1	[67]
C ₃ -C ₁₀	46	278.15-511.48	1.7-68.9	[68]
C ₃ -C ₁₂	25	419.15-547.67	4-76.8	[51]
C ₄ -C ₅	20	413.15-463.15	24.1-34.4	[69]
C ₄ -C ₆	68	403.15-503.15	22.4-37.9	[69]
C ₄ -C ₈	36	423.15-548.15	20.6-41.3	[67]
C ₄ -C ₁₀	61	310.9-510.9	1.7-48.2	[70]
C ₅ -C ₆	32	298.7-308.7	0.2-0.9	[71]
C ₅ -C ₈	34	303.7-313.7	0.05-0.97	[71]
C ₅ -C ₁₀	19	317.7-333.7	0.48-1.46	[71]
C ₅ -C ₁₂	19	299.59-480.93	0.7-1	[72]
C ₆ -C ₇	17	343.7-369.4	1	[73]
C ₆ -C ₁₆	33	472.3-623	6.1-39.4	[74]
C ₆ -C ₂₄	32	473-622.9	6.1-46.7	[75]
C ₇ -C ₈	19	370.6-394.4	0.94	[76]
C ₇ -C ₁₂	18	345.2-482.1	0.4-1	[72]
C ₈ -C ₁₀	27	349.15-392.2	0.2	[77]
C ₈ -C ₁₂	26	349.3-429.8	0.2	[77]
C ₁₀ -C ₁₂	27	393-403.5	0.2	[77]
C ₁₂ -C ₁₆	45	368.9-544.2	0.01-1	[78]
C ₁₂ -C ₁₈	75	374.9-576.9	0.01-1	[79]
C ₁₄ -C ₁₆	77	396.7-544.9	0.01-1	[80]

Table 3. The number of data within a specific range of reduced temperature and reduced pressure of data bank, based on the carbon dioxide critical temperature and critical pressure

Range	No. of CO ₂ + n-Alkane data point		No. of n-Alkane+n-Alkane data point	
	Tr	Pr	Tr	Pr
<1	182	914	108	958
1-1.5	1029	200	554	0
>1.5	60	114	296	0

Optimization Method

By fitting binary VLE data, choosing a fast and robust optimization method that can adjust multivariable objective function for the high asymmetric systems is vital. However, the frequently used techniques like evolutionary computation (e.g., genetic algorithms [84,85]) can optimize objective function precisely, they could not provide a unique solution, especially for objective functions including multi locally optimum. This way, Eberhart and Kennedy [86,87] developed a different algorithm through simulating social behavior called particle swarm optimization (PSO). In contrast, with evolutionary computation, that used genetic operators, a particle swarm optimizer evolved the individuals by cooperation and competition among the individuals. Although fitting the objective function is not the PSO's main concern, it tends to analyze the approaching degree of particles based on the iterative measures according to a predefined closure function. This feature provides an interest reduction on convergence time and could boost the robustness of the PSO method [88].

Table 4. Parameters used in the PSO algorithm

PSO parameter	Value
Number of particles in swarm (N_{part})	60
Number of iterations (MaxIter)	10000
Number of decision variables (N_{var})	16
Cognitive component (c_1)	2.0
Social component (c_2)	2.0
Velocity factor (v1)	1.2
Inertia weight	1.0
Initial Upper and Lower bond of variables	[-1 1]
Tolerance of OF (TolF)	1e-6
Stopping Criteria of Eq. 22 (TolX)	0.1%

In this study, the PSO was implemented to the minimized objective function of Eq. 21 (TolF), and stopping criteria are defined based on the approaching degree of particles (TolX):

$$TolX = \frac{100}{v} \sum_{i=1}^v \left(\frac{Max(s_i) - Min(s_i)}{Mean(s_i)} \right) \quad (22)$$

The s_i is the value of swarmed particles in the i th dimension of variable space (v). Table 4 shows the selected parameters for the PSO algorithm. In this table, the cognitive and social component determines the ratio of movement around the individuals and the entire swarms' best position and velocity factor imply the acceleration of particles in movement.

Using Ternary Data to Test the Model

Two correlative three-suffix binary interaction models were obtained on the way that the optimization performed separately on both binary VLE data series. The last correlation, the three-suffix ternary interaction model, generated within Eqs. 17 to 20 based on two correlations. Finally, the model consisting of three optimized correlations is required to verify how it works on the ternary or a higher system. In this research, the ternary VLE data of CO₂ + n-Butane + n-Decane [89] and CO₂ + n-Hexane + n-Decane are used [24]. The number of data and the temperature and pressure ranges of test data, covered by training ranges, are available in Table 5.

Results and Discussions

In this section, the performance of the optimized correlation of the proposed model's parameters to predict the binary and ternary interaction of CO₂ + n-Alkane vapor-liquid equilibrium in the wide ranges of temperatures and pressures and alkanes from propane to tetracosane are analyzed. The proposed correlation of interaction parameters was verified with ternary vapor-liquid data of CO₂ + n-Alkane + n-Alkane systems.

Optimized TIP

Particle swarm optimization is used to optimize the constants of Eqs. 11 to 19. The regulated parameter of the PSO algorithm is shown in Table 4. 16 constants must be adjusted for each model, and the number of swarm size is selected as 60. Moreover, the tolerance of function value was calculated based on the deviation of individual swarm function value that did not exceed 10^{-6} . The constant of the TIP model optimized at a given temperature, for CO₂ + n-Alkane and n-Alkane + n-Alkane system, by using Eq. 21 based on the root mean square error

of the liquid phase and the gas phase. Hence, the optimized values of Eqs. 11 to 19 constants are tabulated in Table 6.

Table 5. The pressure and temperature range of ternary VLE test data including CO₂ + n-Alkane + n-Alkane systems

CO ₂ + n-Alkane + n-Alkane	No.	Temperature (K)	Pressure (bar)	references
CO ₂ -C ₄ -C ₁₀	15	344.3	90.3-115.7	[89]
CO ₂ -C ₆ -C ₁₀	12	342.5	20.1-111.1	[24]

Table 6. The optimized values of ternary interaction parameters related to Eqs. 11 to 19

	a ₁	b ₁	c ₁	d ₁	a ₂	b ₂	c ₂	d ₂
CO ₂ + n-Alkane	0.022752	0.114621	-0.09252	-0.10908	0.245921	-0.02323	0.038052	0.003359
n-Alkane + n-Alkane	0.057907	0.014665	0.015426	-0.04283	0.003884	0.78032	0.010412	-0.0089
	a ₃	b ₃	c ₃	d ₃	e	f	g	h
CO ₂ + n-Alkane	3.358613	314.0785	12.99091	17.26434	-0.01021	0.076685	-0.06842	54.59586
n-Alkane + n-Alkane	8.896787	3.261665	67.17521	30.62856	0.023683	0.017142	-0.01154	13.97777

Effect of Temperature

The intermolecular interaction varied with temperature, so we supposed an exponential function to show how much it depends on the temperature. So, this is an ordinary concern that there are two distinct limits: when the temperature increases to infinity that all gasses behave like an ideal gas, and when the temperatures closer to zero that all intermolecular interactions go to be maximized. Therefore, at the higher temperature, the interaction coefficient decreases to an asymptote, the infinite value. Also, approaching zero Kelvin, it appeared in maximum value, showing higher collision frequency.

TIP variation with temperature for three binary systems of CO₂ + n-Dodecane, n-Propane + n-Dodecane, and n-Decane + n-Dodecane in the range of 100 to 600 K represented in Fig. 1. The TIP data in different temperatures were calculated by using an optimized constant represented in Table 6. As can be seen in Fig. 1, TIP decreases with the temperature for all three systems. The interaction coefficient related to all systems at the temperature above 350 K does not significantly change by temperature. Moreover, the interaction coefficients have the highest value near the 0 K. From Fig. 1a, $k_{\text{CO}_2+\text{CO}_2+\text{n-Dodecane}}$ and $k_{\text{Propane}+\text{Propane}+\text{n-Dodecane}}$ get negative values by increasing the temperature, but in far temperatures, $k_{\text{n-Decane}+\text{n-Decane}+\text{n-Dodecane}}$ remain positive. In that case, the attraction of different size molecules increases by increasing the temperature. The same behavior is observable in Fig. 1b, where the k_{122} decreases by temperature and tends to negative values except for the same size molecules.

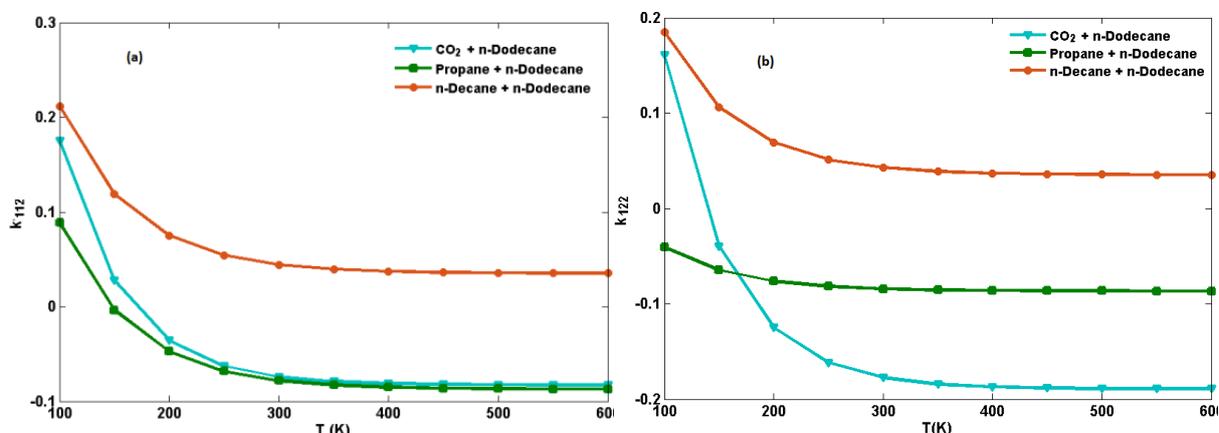


Fig. 1. The temperature dependency of TIP for CO₂-n Dodecane, Propane- n Dodecane, and n-Decane- Dodecane, a) k_{112} , b) k_{122}

Molecular Property Effect

The concept of interaction coefficient arises by the difference between attractive and repulsive forces along with the molecular size that has strong effects on it. Certainly, the molecule, such as carbon dioxide with a polar structure, can affect every particle to attract and yield an interaction parameter, which is shown in Fig. 2a. However, an exception can be seen for lighter alkane up to C₅ which is in the case of weakly London force in the lighter alkane. From this figure, a different behavior between k_{112} and k_{122} is observable that k_{122} has a lower value than k_{112} from C₅ to C₂₄. This difference appears on the energy of ternary interaction when a molecule by higher attraction adds to a pair of the weak molecule. In this case, by increasing the carbon number and decreasing the attraction capability of alkane, the value of k_{122} has dramatically reduced rather than k_{112} . Fig. 2b represents the variation of covolume interaction parameters with alkane carbon number. It can be seen that increasing the carbon number makes an increase in covolume interactions. Moreover, the value of l_{112} of increasing the carbon number tends to be stand-in far from l_{122} , and it is related to the effect of adding a larger size molecule to a pair of small size molecule that has a big effect.

The TIP variation of normal alkanes' binary systems is visualized based on the acentric factor ratio in Fig. 3. The acentric factor is an efficient characteristic to determine the size and shape differences, governing the three-dimensional collision. It can be seen that by increasing the acentric factor, cohesive energy interactions (k_{112} and k_{122}) increase, and covolume interaction parameters decrease.

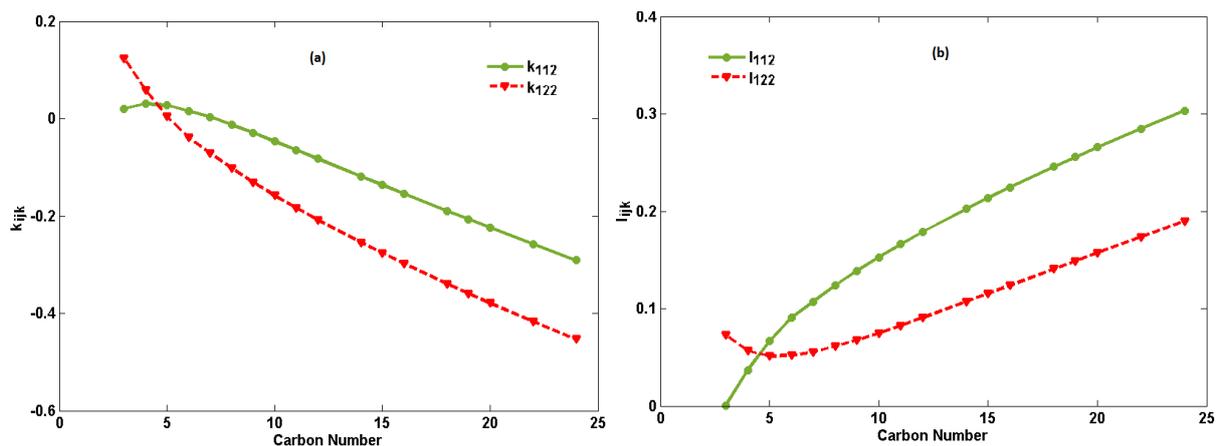


Fig. 2. Carbon number dependency of ternary interaction parameter for binary mixture of CO₂ + n-Alkane systems: a) repulsive energy interaction parameter (k_{ijk}), b) covolume interaction parameter (l_{ijk})

CO₂ + n-Alkane Systems

Figs 4a to 4f show different P-xy diagrams for the binary mixtures of CO₂ with propane, n-hexane, n-decane, n-pentadecane, n-icosane, and n-docosane at different temperatures of 270, 308.15, 372.9, 313.14, 373.2, and 348.15 K that predicted by Peng-Robinson EOS coupled with cubic mixing rules using two different correlations for interaction parameters, the proposed model and the Cismondi model [13]. The proposed model could predict vapor-liquid equilibrium very accurately compared to the Cismondi model, especially for heavier n-Alkanes. Experimental data for the systems of CO₂ with propane (Fig. 4a) were predicted by the Cismondi model better than this work, but in another graph, it is clear that the proposed model can give a precise prediction for both liquid and vapor phases.

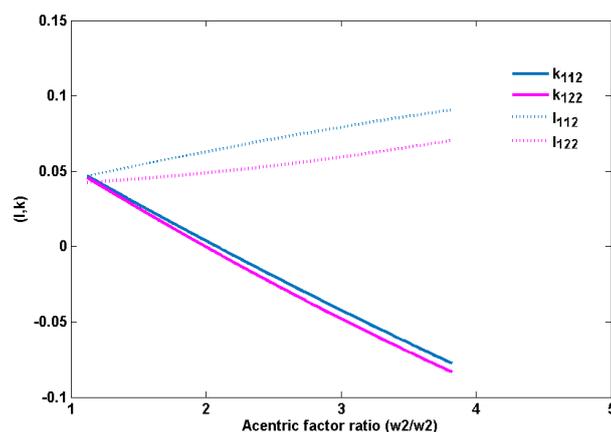


Fig. 3. The variation of ternary interaction parameter of normal alkanes' binary's systems related to the acentric factor ratio

In comparison with the Cismondi model, the deviation of the proposed model is represented in Fig. 5. It is observable that in the vapor phase, both models show the same deviation, and the vapor phase deviation decreases with increasing carbon number that it can be because of decreasing the volatility of heavy compounds in the CO₂ rich phase, eventually. This situation is slightly different for the liquid phase prediction, and the proposed model performed a more accurate evaluation of it. However, this difference was magnified for n-hexane and higher n-Alkane while the Cismondi model shows a higher deviation for the heavier compound.

n-Alkane + n-Alkane Systems

Figs. 6a and 6b represent the Pxy diagrams for the binary mixtures of propane + n-butane and propane + n-dodecane at two different temperatures. As an illustration, the proposed model can simulate the n-Alkane + n-Alkane ternary molecular interaction of both the close-size molecules and asymmetric pair molecules. Also, the prediction of the gas phase composition for asymmetric systems, represented in Fig 6b, is a slight deviation that shows an inability to vapor pressure prediction for the higher molecular weight of alkane in the CO₂ rich phase. The AARD percent of n-Alkane + n-Alkane vapor-liquid equilibrium prediction for all data is shown in Fig. 7. Through this graph, the systems are shown by lighter carbon in legend and heavier carbon in the horizontal axis. The %AARD is varied between nearly 1% for C₅-C₆ to %30 for C₅-C₁₂ that demonstrated on if the size difference increases, the model ability decreases.

CO₂ + n-Alkane + n-Alkane Systems

In this section, due to verifying the model, adjusted parameters reported in Table 6 obtained by particle swarm optimization were applied, and the final model was tested on some ternary systems, including CO₂ and n-Alkanes. The important concern is using proper mixing rules for the ternary interaction parameter, so four models were applied, and their deviation was compared. Table 7 specified the four models, used for validating the optimized parameters.

As shown in Table 7, the ternary interaction parameter of { k_{112} , k_{122} , k_{113} , k_{133} } and { l_{112} , l_{122} , l_{113} , l_{133} } calculated only by CO₂ + n-Alkane model (model 1). Also, the ternary interaction parameter of { k_{223} , k_{233} } and { l_{223} , l_{233} } evaluated based on two methods: the CO₂ + n-Alkane model (model 1) and the n-Alkane + n-Alkane model (models 2, 3, and 4). Finally, the ternary interaction parameter of { k_{123} } and { l_{123} } calculated based on three methods: the CO₂ + n-Alkane model (models 1 and 2), the geometric mixing rule, and the arithmetic mixing rule (models 3 and 4), which are the average value of the CO₂ + n-Alkane and the n-Alkane+n-Alkane models.

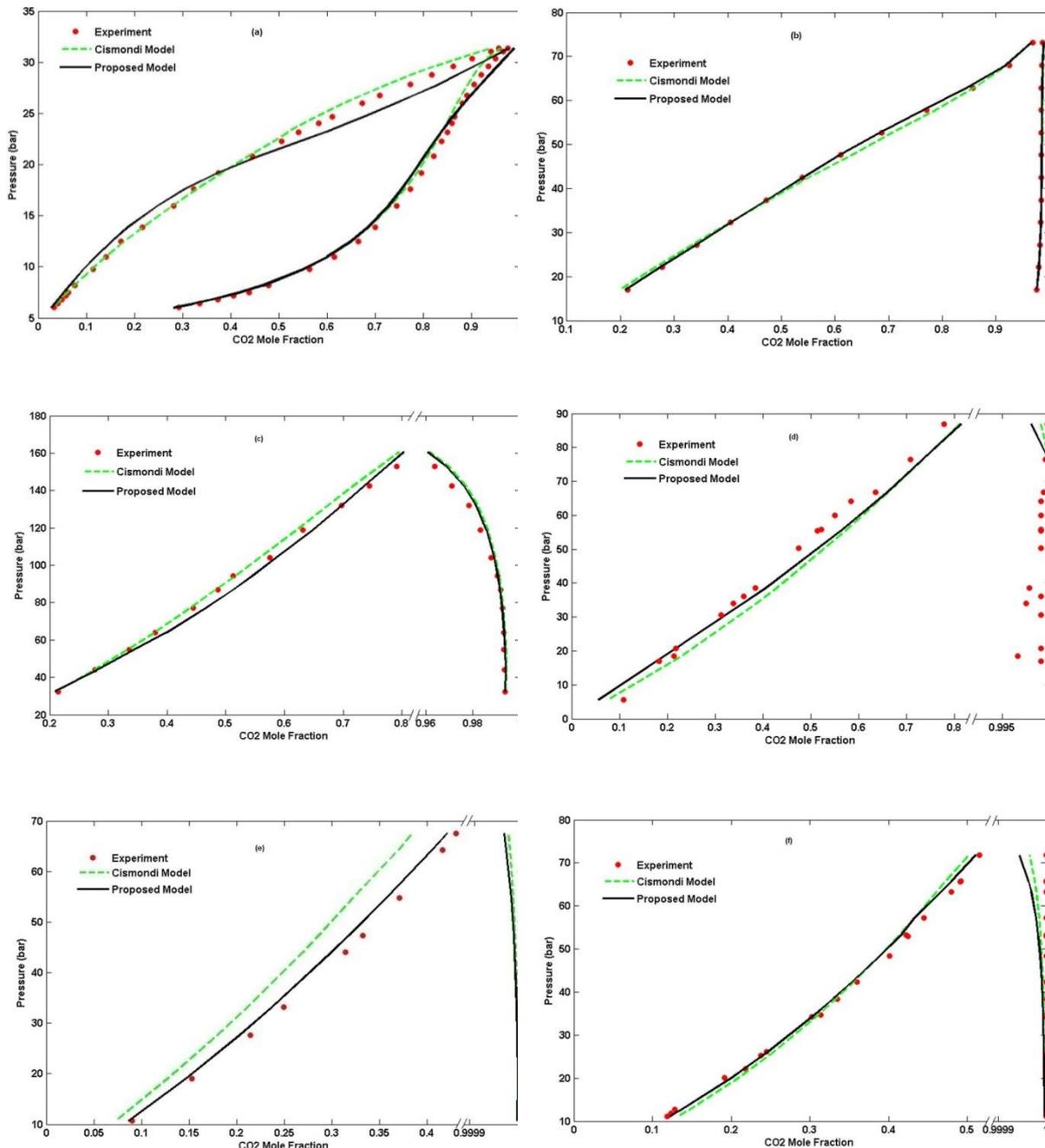


Fig. 4. P-xy diagrams for the binary mixtures of CO₂ with a) propane at 270 K, b) n-hexane at 308.15K, c) n-decane at 372.9 K, d) n-pentadecane at 313.14 K, e) n-eicosane at 373.2 K, and f) n-docosane at 348.15 K. Compared with Cismondi et al. model [13]

Two different ternary vapor-liquid equilibrium systems, CO₂ + n-Butane + n-Decane and CO₂ + n-Hexane + n-Decane, selected to validate the mentioned models. As shown in Table 8, all models give a better prediction for the vapor phase than the liquid phase. Moreover, the deviations on the CO₂ + n-Butane + n-Decane system is greater than the CO₂ + n-Hexane + n-Decane system, especially for model 1 that uses CO₂ + n-Alkane optimized parameters. It shows that using this model for the asymmetric hydrocarbon systems leads to a remarkable difference between simulation values and experimental measurements. The proposed models (models 1, 2, and 3) represented a significant decrease in total errors. Also, it can be seen that the geometric

and arithmetic mixing rules predict the liquid phase in the CO₂ + n-Butane + n-Decane system. Generally, it seems that model 3 and 4 have a better prediction than the two others.

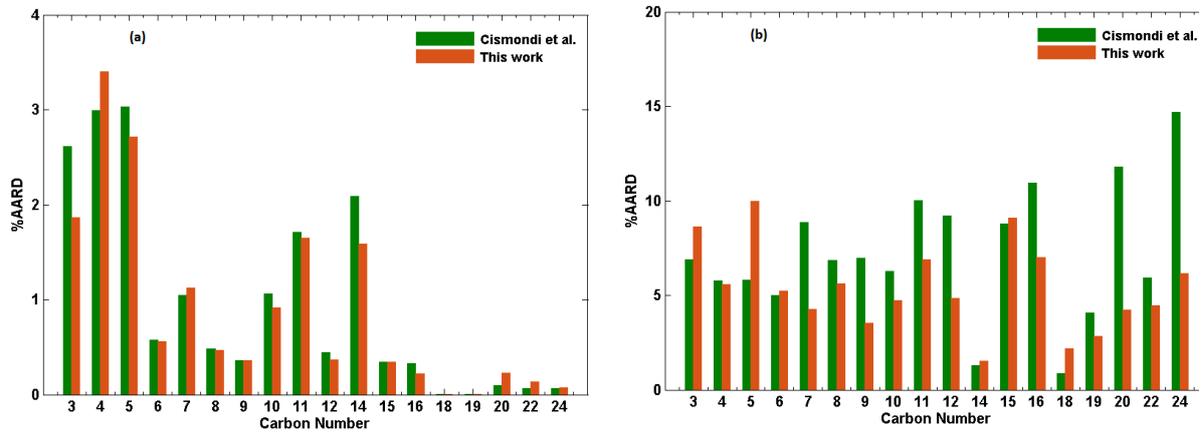


Fig. 5. The deviation of vapor phase (a) and liquid phase (b) calculated by the proposed model in comparison with Cismondi et al. [13] models

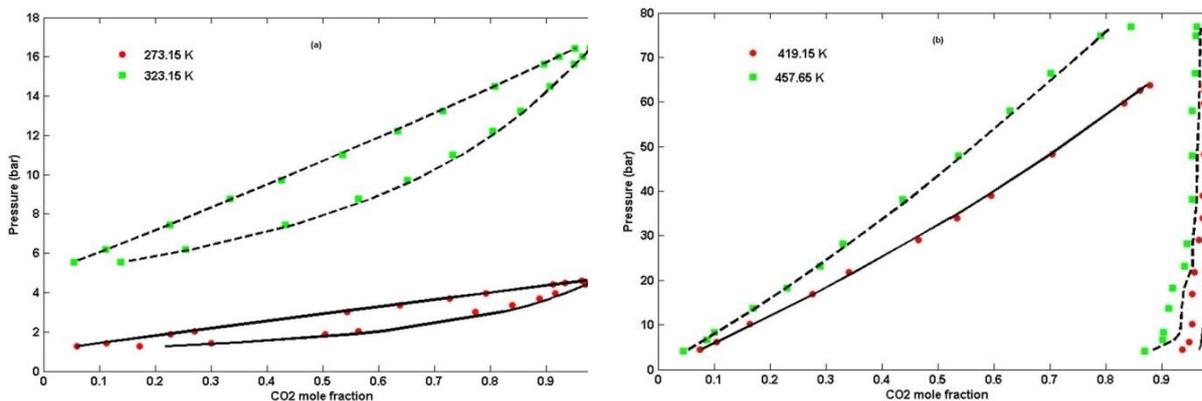


Fig. 6. Pxy diagrams for the binary mixtures of a) propane + n-butane and b) propane + n-dodecane binary VLE systems at two different temperatures

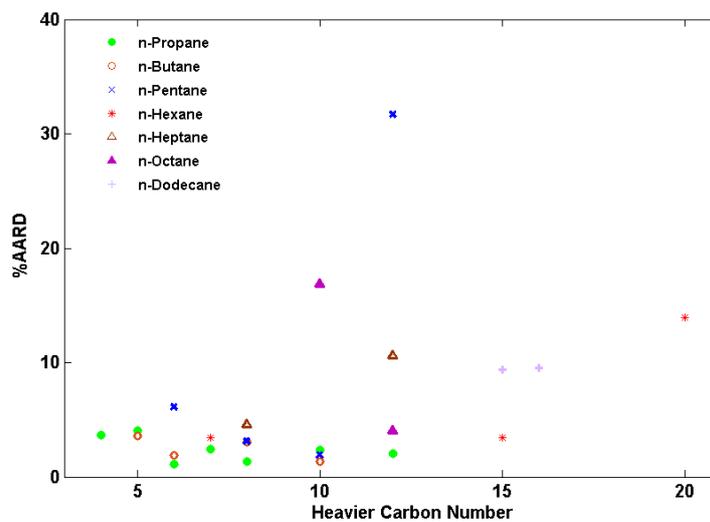


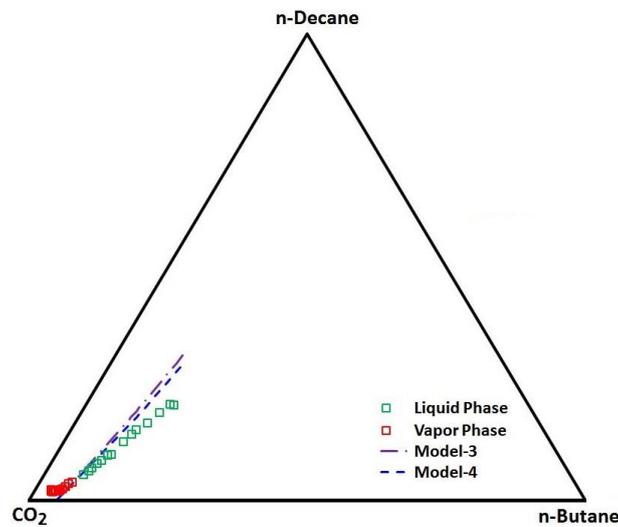
Fig. 7. Deviation of VLE data of n-Alkane+n-Alkane systems in %AARD. The heavier n-Alkane is shown in x-axis and the lighter n-Alkane is shown in legend

Table 7. Four models applied for three-body ternary interaction parameter

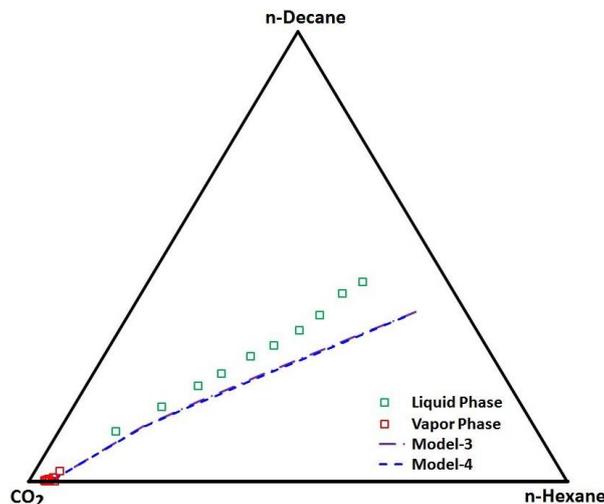
	{A112;A122;A113;A133}	{A223;A233}	{A123}
Model 1	CO ₂ + n-Alkane	CO ₂ + n-Alkane	CO ₂ + n-Alkane
Model 2	CO ₂ + n-Alkane	n-Alkane + n-Alkane	CO ₂ + n-Alkane
Model 3	CO ₂ + n-Alkane	n-Alkane + n-Alkane	geometric Mixing Rule
Model 4	CO ₂ + n-Alkane	n-Alkane + n-Alkane	arithmetic Mixing Rule

Table 8. Root mean square error of vapor and liquid phase for the ternary VLE equilibrium systems, CO₂ + n-Butane + n-Decane and CO₂ + n-Hexane + n-Decane, predicted by proposed model

RMSE	CO ₂ + C ₄ + C ₁₀		CO ₂ + C ₆ + C ₁₀	
	Liquid	vapor	Liquid	Vapor
Model 1	0.1580	0.0178	0.0693	0.0128
Model 2	0.0917	0.0162	0.0607	0.0113
Model 3	0.0855	0.0147	0.0684	0.0079
Model 4	0.0806	0.0154	0.0658	0.0092

**Fig. 8.** Simulation value vs. experimental value of CO₂ + n-Butane + n-Decane ternary VLE system

In Figs. 8 and 9, an analogy between the ability of proposed models 3 and 4 are drawn with the experimental value for two mentioned ternary systems in the ternary diagram. All data predicted well by these two models and the arithmetic mixing rule, model 4 gives results slightly better than the other. In Fig. 9, it can be seen that the prediction of the CO₂ + n-Hexane + n-Decane system along with lower deviation than the CO₂ + n-Butane + n-Decane system. The more asymmetric system (n-Butane and n-Decane) is harder to be predicted than the others.

**Fig. 9.** Simulation value vs. experimental value of CO₂ + n-Hexane + n-Decane ternary VLE system

Conclusion

A generalized temperature-dependent TIP correlation, based on acentric factor ratio, has been developed for CO₂ and n-Alkanes multicomponent systems. Therefore, the TIP correlation proposed for this system consists of two correlations related to CO₂ + n-Alkane and alkane +n-Alkane binary data. Moreover, particle swarm optimization (PSO) is a fast and robust method to adjust the constant of models through an experimental data point. The proposed TIP correlation provides an accurate prediction for 1270 data points of CO₂ + n-Alkane from C₃ to C₂₄ at both liquid and vapor phases. So, the model represented an overall AARD of 3.13% for this system and predicted heavy hydrocarbon behavior accurately as same as those of light hydrocarbons. Also, the TIP correlation regenerates accurately 958 data points of n-Alkane+n-Alkane systems with an overall AARD of 6.71%. Results show that by decreasing the carbon number difference, the prediction goes to being better, remarking asymmetric pair behavior modelling in the VLE system.

The three-body interaction $\{k_{123}\}$ and $\{l_{123}\}$, since the ternary interaction parameter for the binary system, is available, calculated by applying proper mixing rules of these correlations. So the effect of calculation base on the CO₂ + n-Alkane model was investigated. Also, two different contributions based on geometric and arithmetic averages are proposed. These models have applied to the ternary vapor-liquid equilibrium systems of CO₂ + n-Butane + n-Decane and CO₂ + n-Hexane + n-Decane. Generally, the obtained results for ternary systems remarked that vapor phase composition has better agreement with related experimental data. Furthermore, using geometric and arithmetic contributions leads to a desirable prediction for the liquid phase, especially for the lighter mixture. Results showed that applying the proposed method for ternary interaction parameters yields less than 5% benefit for the CO₂ + n-Hexane + n-Decane system while the CO₂ + n-Butane + n-Decane system gets more than 90% improvement at same conditions.

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