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Research Article

Modeling of the Vapor-Liquid Equilibria Properties of Binary Mixtures for Refrigeration Machinery

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Abstract

The presence of both critical and azeotropic states in the vapor-liquid equilibria (VLE) is a very important issue in the chemical and refrigeration engineering. The knowledge of the phase behavior (subcritical phase/supercritical phase) of refrigerant allows designing and optimizing the refrigeration industrials processes. However, it is rare to find data for this information, which poses a great challenge for researchers to develop predictive and correlative thermodynamic models. The present study proposes the computation of the compositions and pressures of critical and azeotropic points of the isothermal VLE as well as the correlation of experimental VLE data. Firstly, experimental data (PTxy) was used to predict the vapor-liquid phase of both critical and azeotropic behaviors and to determine their properties using the relative volatility model. Secondly, the thermodynamic model (PR-MC-WS-NRTL) was applied to correlate the data of the binary refrigerant systems and describe their isothermal (VLE) behavior. The results proved that there is good agreement between predicted values obtained by the developed model and the experimental reference data. The relative error of both critical and azeotropic properties does not exceed 4.3 % for the molar fraction and 7.5 % for the pressure using relative volatility model. On other hand the relative deviation is respectively less than 2.60 % and 2.58 % for the liquid and vapor mole fractions using (PR-MC-WS-NRTL) model. This shows the ability of these models to give a reliable solution to predict and modulate the phase behavior of the binary refrigerant systems.

Keywords: *Binary mixtures; critical point; azeotropic point; relative volatility; mixing rules.*

1. Introduction

Search for eco-friendly and sustainable fluids to replace the conventional working fluids such as CFCs (chlorofluorocarbons), CFCs (hydrochlorofluorocarbons), and HFCs (hydrofluorocarbons) is the major challenge for the industrial field and especially the refrigeration engineering due to the release of both CFCs and HCFCs, which have high ozone depletion potentials (ODPs). The CFCs and HCFCs are therefore being phased out as a result of the international Montreal Protocol on substances that deplete the ozone layer enacted in 1987. This led to the urgent need in the refrigeration industry to find an alternative for these substances. One possible class of refrigerants is HFCs on account of their zero ODPs. However, these types of fluids are also regulated by the international Kyoto Protocol (1997) due to their global warming potentials (GWPs) [1].

The current search for environmentally friendly refrigerants is driven by the recent approval of increasingly restrictive regulations that limit the use of substances with high GWP, and the need to maintain high process efficiencies (Figure 1). In this context, refrigerant blends like the binary or ternary and or even quaternary systems containing fluids with low GWP are of special importance, since their excellent environmental characteristics, thermodynamic properties, and high cycle performance [2].

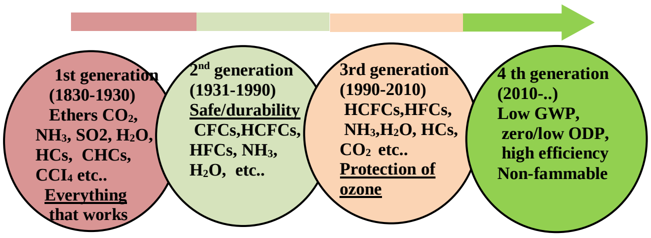

Figure 1. Different generations of refrigerants [3].

The detailed knowledge of the thermodynamic properties of these refrigerant mixtures, and particularly the fluid-phase behavior in both subcritical and supercritical regions in a wide range of temperatures and pressures is necessary to design and optimize the thermodynamic systems involving these mixtures, in the production and separation units such as organic cycles, heat pumps, refrigeration systems, etc.

For instance, to design evaporator or condenser devices with and without phase changing in the mechanical vapor compression cycle for refrigeration machines, it is important to know the state of the blend and to evaluate the level of the temperature glide when they change phase in both the condenser and evaporator. In this case, it is

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important to know if the blend system behaves like a single-fluid (azeotropic behavior) or not.

This information can be acquired primarily through some experimental measurements. However, experimental data on the thermodynamic properties (critical and azeotropic points) of refrigerant blends are scarce. To overcome the problem of lack of the data on various kinds of refrigerant systems (binary mixture, ternary mixture, quaternary mixture, etc.) on an industrial scale, the researchers propose the use of numerical methods with thermodynamic developed models which are very reliable in solving many problems of the engineering under temperature and pressure conditions [4-8],these models are mainly divided into predictive or correlative thermodynamic models including equations of state, mixing rules and activity coefficient models [9].

The use of these thermodynamic models has motivated many numbers of several researchers to develop computational models to determine VLE properties of the refrigerant blends and especially the azeotropic and critical points. Teja and Rowlinson [10] computed homogeneous azeotropes of binary mixtures using an equation of state (EoS) as a tool for the VLE prediction.

Artemenko and Mazur [11] developed a model computation for the prediction of azeotrope formation in a mixture that does not require VLE computation. The model computation employs neural networks and global phase diagram methodologies to correlate azeotropic behavior for the binary working fluids based only on critical pressure, critical temperature and acentric factors of the individual refrigerants in mixtures. Fidkowski et al [12] presented an interesting homotopy continuation model for finding homogeneous azeotropes. Tolsma and Barton [13] developed Fidkowski's work to calculate heterogeneous azeotropes and presented the necessary proofs regarding the computation of all homogeneous and heterogeneous azeotropes for multi-component blends. Kolar and Kojima [14] predicted critical points for fifteen binary systems using the PSRK group contribution equation of state.

In other work, Dong et al [15] presented a simple model based on the Newton method to determine the homogeneous azeotropes for the binary blends, they have used the Wilson activity coefficients model and Antoine equation in their approaches, then they verified their model, with six binary blends. Heidemann and Khalil [16] developed a new computational procedure for the calculation of critical points with cubic equations of state for multi-component blends. Dan Nichita [17] has developed a computational modification of the Heidemann-Khalil method for calculating critical points.

Maier et al [18-19] presented an arithmetic model based on interval analysis and Newton algorithm to verify the existence of homogeneous azeotropes and to locate all homogeneous azeotropes. He et al [19] presented a new correlation, based on the computational method and newly obtained experimental data, to predict the critical temperature and the critical pressure of multi-component mixtures. Hu et al [20] predicted the VLE properties of many (HFCs) binary refrigerant systems with a corresponding equation. The mathematical model only needed the vapor pressures, critical constants and dipole moments of pure refrigerants, without any adjustable parameters or interaction coefficients. In the study of Dong et al [21], the authors proposed four approaches based on the UNIFAC model to predict the azeotropes without any experimental data for binary refrigerant mixtures. The thermodynamic criterion of the four methods is the first derivative of the pressure with respect to the composition, which equals zero at the azeotropic point for binary systems; they concluded that by using those methods, the cost and time of experiments could be saved.

From the literature review survey about the study of both critical and azeotropic properties cited above, it was noticed that the most approaches made by authors are difficult to implement, due to the mathematical computation complexity, since convergence is often difficult to obtain the vapor-liquid equilibria properties.

Our main objective in this paper is to use two thermodynamic models simple, rapid and accurate described by our team [22], to predict and determine the fluid-phase behavior of six binary refrigerant systems and especially the azeotropic and critical properties for those blends

- Firstly from the experimental data PTxy (Relative volatility);
- Secondly with the prediction model (PR–MC–WS–NRTL).

The six binary mixtures studied are: [R744 (Cas: 124-38-9)+R134a (Cas: 811-97-2)], [R1234ze (Cas: 29118-24-9)+R744(Cas: 124-38-9)], [R1234yf (Cas: 754-12-1)+R290 (Cas: 74-98-6)], [R1234yf (Cas: 754-12-1)+R600a(Cas: 75-28-5)], [R32 (CAS: 75-10-5)+R1234yf (Cas: 754-12-1)], [R32 (Cas: 75-10-5)+R152a(Cas: 75-37-6)],

The properties of the pure substances composing those binary mixtures are presented in Table1; they were obtained from the following references [24-30].

Table 1. Properties summary of various fluid candidates.

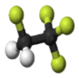
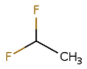
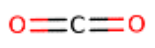
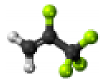
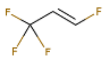
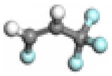
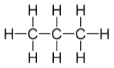
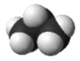
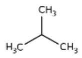
Substance	Type	Cas N°	Tc [K]	Pc [MPa]	GWP	ODP	Chemical structure	Molecular structure
R134a	HFC	811-97-2	374.21	4.0593	1430	0		
R152a	HFC	75-37-6	386.41	4.5168	124	0		
R744	Natural	124-38-9	304.13	7.3770	1	0		

Table 1. Properties summary of various fluid candidates "(continue)".

R1234yf	HFO	754-12-1	367.85	3.3823	4	0		
R1234ze	HFO	29118-24-9	382.51	3.6349	6	0		
R290	Natural	74-98-6	369.89	4.2512	3	0		
R600a	Natural	75-28-5	407.85	3.6400	3	0		
R32	HFC	75-10-5	351.26	5.7820	650	0		

2. Computational Models

The detailed knowledge of the VLE properties for the binary working fluids (Figure 2) is very important in engineering applications. Nowadays, several theoretical and empirical models have been proposed for a better representation of the VLE, taking into account the behavior of the various systems commonly encountered in energetic applications.

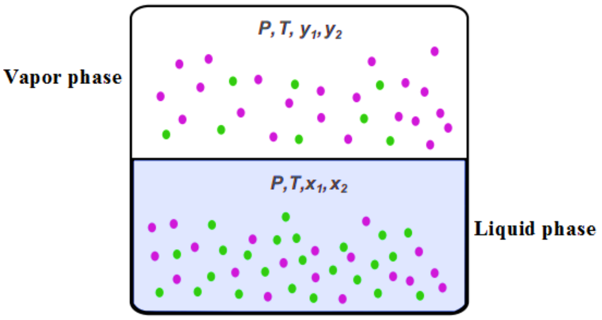


Figure 2.VLE of binary refrigerant system.

The temperature change during heating or cooling process in the condenser and the evaporator requires knowledge of the VLE data for the different phenomena of vapor-liquid equilibria of working fluids (Figure 3).

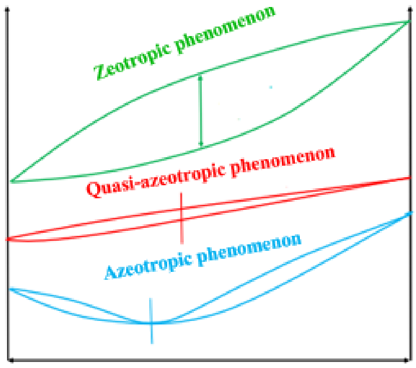


Figure 3. Different phenomena of vapor-liquid equilibria of binary refrigerant system.

In this study two modeling approaches (Figure 4) was proposed to predict and determine the isothermal (VLE) properties. Especially the azeotropic and the critical properties (x_{az}, P_{az}, x_c, and P_c) in the isothermal (VLE) of the binary refrigerant systems for refrigeration machinery.

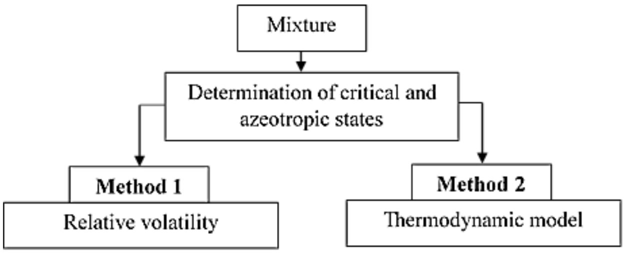


Figure 4. Methods proposed.

In the first section, the relative volatility model was used to predict and estimate the both critical and azeotropic properties in the binary refrigerants based on (PTxy) experimental data.

In the second section, the thermodynamic model: «PR-MC-WS-NRTL» was chosen in order to predict and describe the behavior of both azeotropic and critical states in the binary refrigerant systems.

2.1 Relative Volatility Model

The relative volatility (αij) represents the ratio of the equilibria constants of the (i) and (j) components. The model of the (αij) for binary working fluids is expressed as follows [2]:

$$\alpha_{12} = \frac{K_1}{K_2} = \frac{(y_1/x_1)}{(y_2/x_2)} \tag{1}$$

With:

$$x_1 + x_2 = y_1 + y_2 = 1 \tag{2}$$

In the remainder of this work, this model will be used for all the computations of the relative volatility.

The algorithm for calculating critical and azeotropic properties from the relative volatility is given as:

- For each isotherm, trace either the relative volatility (α_{12}) according to the molar fraction of the most volatile pure substance x_1, or according to the pressure;
- Using Excel software, the plotted points are either fitted using a second order polynomial curve or a linear trend line;

- The equation of the curve of tendency is equalized to unity;
- By solving the obtained equation, the values of both critical and azeotropic properties are obtained.

2.2 Thermodynamic Correlation for the VLE Properties

The need of predicting the (isothermal/isobaric) VLE behavior of working fluids (binary mixture, ternary mixture, etc.) is primordial to design and optimize the different processes in the cooling systems. The VLE properties of the working fluids for a wider range of temperatures, pressures, and compositions can be obtained by theoretical models. It is well known that the phase diagrams (isothermal/isobaric) can provide important and effective information for the thermodynamic analysis of the energetic systems such as heat pumps, refrigeration systems and air-conditioning.

Therefore, to correlate the isothermal VLE behavior of the binary refrigerant systems and predict the both azeotropic and critical properties, the thermodynamic model: “PR–MC–WS–NRTL” was proposed and employed in the present work (Figure 5).

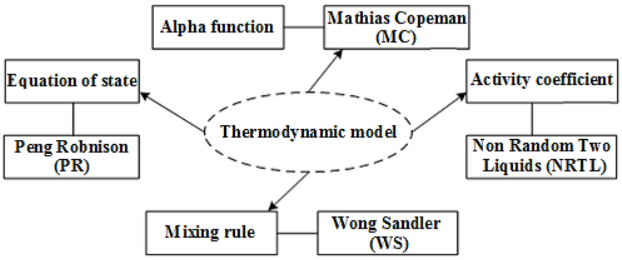


Figure 5. Thermodynamic model proposed.

The Peng−Robinson (Peng and Robinson, 1976) equation of state (PR–EoS) is one of the most popular equation of state (EoS) used to describe the thermo-physical properties and especially the (VLE) of fluids in the academic and industrial fields. It has an advantage of both simple form and its calculation accuracy can meet the general engineering requirements.

The second model proposed in this study to correlate the experimental data combines the popular cubic equation of state of (PR–EoS) with the Mathias–Copeman (MC) alpha function, and the NRTL excess free energy model, using the Wong–Sandler (WS) mixing rules.

The cubic equation of state of (PR-EoS) [24] can be written as:

$$P=\frac{RT}{v-b}-\frac{a\alpha(T)}{\left(v^2+2vb-b^2\right)} \tag{3}$$

Where P is the pressure in MPa, R is the universal gas constant in J mol^{-1} K^{-1}, v is the molar volume in m^3 mol^{-1}, T is the temperature in K and a, b are the energy and co-volume parameters of (PR–EoS).

For a pure component i, the parameters of (PR–EoS) can be given as:

$$a=0.457240\frac{R^2T_c^2}{P_c} \tag{4}$$

$$b=0.07780\frac{RT_c}{P_c} \tag{5}$$

The values of critical temperature (Tc) and critical pressure (Pc) for each pure refrigerants are provided in Table 1.

The (MC) alpha function [25] is:

$$\alpha(T)=\left(1+c_1\left(1-\sqrt{\frac{T}{T_c}}\right)+c_2\left(1-\sqrt{\frac{T}{T_c}}\right)^2+c_3\left(1-\sqrt{\frac{T}{T_c}}\right)^3\right)^2 \tag{6}$$

If T >T$_c$:

$$\alpha(T)=\left(1+c_1\left(1-\sqrt{\frac{T}{T_c}}\right)\right)^2 \tag{7}$$

Where c_1, c_2 and c_3 are three adjustable parameters of Mathias Copeman (MC), which has been listed in Table 2.

Table 2. Mathias–Copeman (MC) coefficients [26].

Compound	***c₁***	***c₂***	***c₃***
R134a	0.8497	0.0065	-0.0535
R744	0.7046	-0.3148	1.8908
R1234yf	0.8293	-0.8477	3.4559
R1234ze	0.8767	-0.7751	3.0689
R290	0.6000	-0.0006	0.1738
R600a	0.6524	-0.1493	0.5992
R32	0.8218	-0.3977	0.7622
R152a	0.7743	0.0576	-0.2902

To describe the isothermal vapor-liquid equilibria (VLE) behavior of the binary refrigerant systems, the Wong–Sandler (WS) mixing rules are used in this work to obtain (EoS) parameters for a binary refrigerant blends from those of the pure components. The Wong–Sandler mixing rules are chosen here from the excellent representation of the isothermal VLE properties of the binary working fluids.

These mixing rules for a (EoS) can be written as [27]:

$$b_m=\frac{\sum_i\sum_j x_ix_j\left(b-\frac{a}{RT}\right)}{1-\left(\frac{\sum_i x_i\frac{a_i}{b_i}}{RT}+\frac{g_\gamma^E(T,P=\infty,x)}{CRT}\right)} \tag{8}$$

$$b-\frac{a}{RT}=\sum_i\sum_j x_ix_j\left(b-\frac{a}{RT}\right)_{ij} \tag{9}$$

With:

$$\left(b-\frac{a}{RT}\right)_{ij}=\frac{1}{2}\left[\left(b-\frac{a}{RT}\right)_i+\left(b-\frac{a}{RT}\right)_j\right]\left(1-k_{ij}\right) \tag{10}$$

Where $k_{ij,}$ is an adjustable binary interaction parameter and C a numerical constant depends on the (PR-EoS).

The component activity parameters of binary blend systems are calculated with NRTL model [28].

$$\ln\gamma_i = \frac{\sum_{j=1}^{n}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{n}G_{ki}x_k} + \sum_{j=1}^{n}\frac{x_j G_{ij}}{\sum_{k=1}^{n}G_{ki}x_k}\left(\tau_{ij} - \frac{\sum_{k=1}^{n}x_k\tau_{kj}G_{kj}}{\sum_{k=1}^{n}G_{ki}x_k}\right) \quad (11)$$

The excess Gibbs energy model [28] chosen is the NRTL local composition model is:

$$g^E = \sum_i x_i \sum_j \frac{x_j \exp\left(-\alpha_{ji}\frac{\tau_{ji}}{RT}\right)}{\sum_k x_k \exp\left(-\alpha_{ki}\frac{\tau_{ki}}{RT}\right)}\tau_{ji} \quad (12)$$

Where τ_{ii} =0, α_{ii} =0, α_{ji} , τ_{ji} and τ_{ij} are adjustable parameters. It is recommended to use α_{ji} = 0.3 for systems like this one.

3. Results and Discussion

From the above procedures, the location of the critical and azeotropes points has been calculated in the following subsection. The studied binary blends are environment-friendly which containing natural and synthetic refrigerants.

3.1 Prediction of Azeotropic and Critical Properties

The experimental data (PTxy) are necessary for predicting the phase behavior of the binary refrigerant systems. Therefore, for each isotherm in a binary mixture, the values of relative volatility (α_{12}) have been calculated and plotted according to the molar fraction of the most volatile pure substance x_1.In fact, it is well known that the relative volatility is supposed vary as a decreasing function (exponential or polynomial) of the liquid molar fraction, this can be verified from the following results.

Figures 6-11 illustrate the variation of relative volatility versus different molar fractions of the binary refrigerant systems:(R1234yf+R600a),(R1234yf+R290),(R744+R134a),(R744+R1234ze),(R32+R1234yf) and (R32+R152a), respectively at different isotherms, where the symbol curves represent the results values obtained with the relative volatility model and the dashed red line represents where the relative volatility is equal to unity (α_{12}= 1) .

It can be seen that the relative volatility for studied mixtures decreases when the temperature and the molar fraction of the most volatile pure substance increase (Figure 6-11), this is predictable because the model of relative volatility is a function of compositions and pressure. Additionally, since an increase in the pressure requires an increase in the temperature, this also affects the relative volatility.

Moreover, it can be seen from the results of the relative volatility displayed in figures 6-11, that the two blends (R1234yf+R600a) and (R1234yf+R290) indicate an azeotropic behavior (mixtures behaves like a pure fluid and then its components cannot be separated by simple distillation) for the all investigated temperature range studied: T= (283.15; 293.15; 303.15; 313.15 and 313.15) K and T= (253.15; 263.15; 273.15; 283.15 and 293.15) K, respectively, where it is observed that the calculated α_{12} values of both mixtures cross the line of constant relative volatility (α_{12}= 1) for all studied temperatures which can be expected due to the stronger molecular interactions and close values of the vapor pressures of the pure compounds of the studied refrigerant blends.

The azeotropic phenomena is located at high molar fractions of the most volatile pure substance for (R1234yf+R600a) and at low molar fractions of the most volatile pure substance for (R1234yf+R290), respectively.

The model of relative volatility accurately predicts the azeotropic behavior at (α_{12}= 1) in each isotherm (Figures 6-7). At the azeotropes, the compositions in the liquid phase and the vapor phase are identical, leading to a relative volatility (α_{12}= 1).In addition, it was also found from the results of the relative volatility of (R1234yf+R600a and R1234yf+R290) blends that systems composed of R1234yf mixed with hydrocarbons (HCs) like isobutane (R600a) and propane (R290), leading to the formation of azeotropes in the binary mixtures. These facts should be taken into account when designing new low GWP refrigerants since azeotropic mixtures are preferred among different types of refrigerant mixtures.

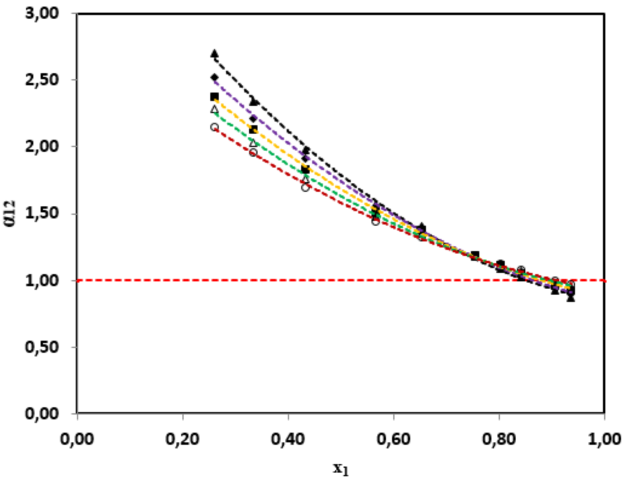


Figure 6. Plot of relative volatility (α_{12}) daigram for R1234yf+R600a system.((▲) 283.15K ;(♦) 293.15K; (■) 303.15 K; (△) 313.15 K; (○) 313.15 K; (…) line of constant relative volatility (α_{12} = 1)).

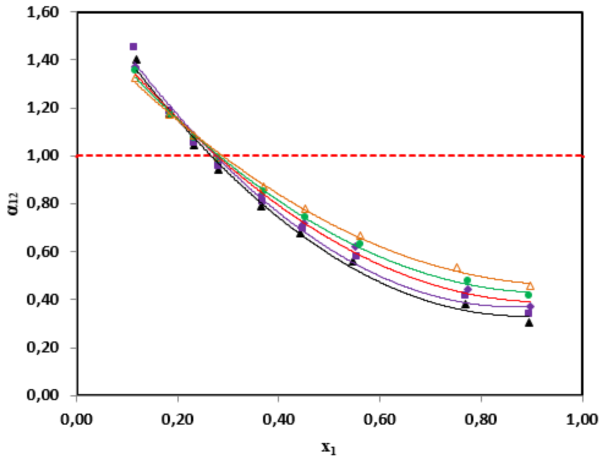


Figure 7. Plot of relative volatility (α_{12}) diagram for R1234yf+R290 system. ((▲) 253.15 K; (■) 263.15 K ;(♦) 273.15 K ;(●) 283.15 K; (△) 293.15 K; (…) line of constant relative volatility (α_{12} = 1)).

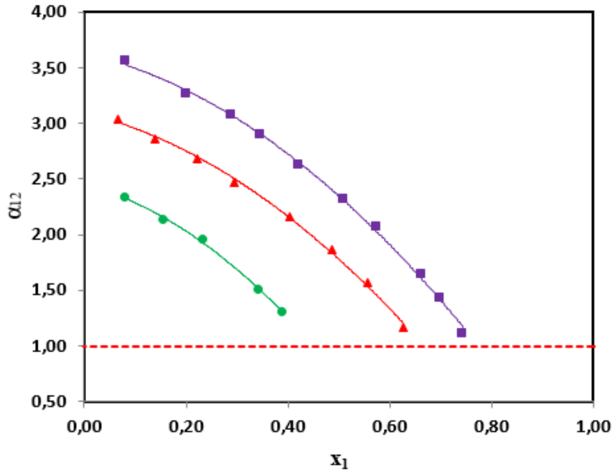


Figure 8.Plot of relative volatility (α_{12}) diagram for R744+R134a system. ((■) 329.60 K; (▲) 339.1 K; (●) 354 K; (…) line of constant relative volatility (α_{12} = 1)).

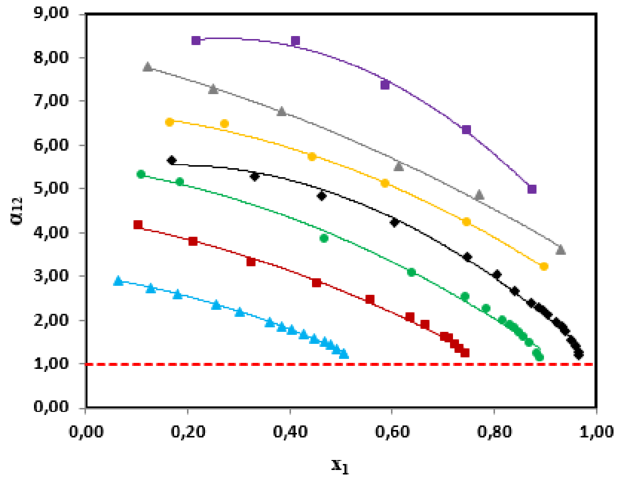


Figure 9.Plot of relative volatility (α_{12}) diagram for R744+R1234ze system.((■) 283.32 K; (▲) 293.15 K; (●) 298.15 K; (♦) 308.15 K; (●) 318.11 K; (■) 333.01 K;(▲) 353.02 K; (…) line of constant relative volatility (α_{12} = 1)).

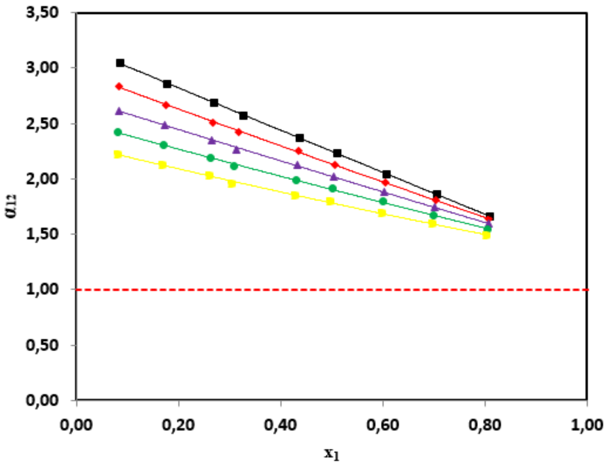


Figure 10.Plot of relative volatility (α_{12}) diagram for R32+R1234yf system. ((■) 283.15 K ;(♦) 293.15 K ;(▲) 303.15 K; (●) 313.15 K; (■) 323.15 K; (…) line of constant relative volatility (α_{12} = 1)).

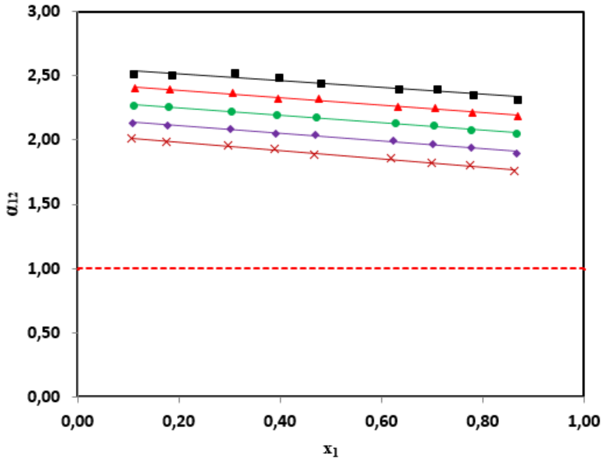


Figure 11.Plot of relative volatility (α_{12}) diagram for R32+R152a system.((■) 283.15 K;(▲) 293.15 K ;(●) 303.15 K; (♦) 313.15 K; (×) 323.15 K; (…) line of constant relative volatility (α_{12} = 1)).

In the case of the two binary systems (R744+R1234ze) and (R744+R134a), it was found that both systems exhibit a critical behavior (Figures 8-9) at temperatures higher than the critical temperature of pure carbon dioxide (Tc (R744) = 304.13 K), where it was observed that the calculated α_{12} values of both mixtures accurately predict the critical behavior and therefore, the limit of the instability phase domain (critical point corresponds to the limit of stability).

The critical behavior was observed between the temperature interval, which corresponds to four isotherms T= (308.15; 318.11; 333.01 and 353.02) K for R744+R1234ze system and three isotherms for T= (329.60; 339.1 and 354) K for the R744+R134a system. This last feature is the consequence of the stronger intermolecular interactions occurring in the systems (R744+R1234ze and R744+R134a). Thus, for temperatures higher than the critical temperature of the most volatile pure substance (carbon dioxide (R744)), the binary systems conventionally has a critical point.

On other hand, a zeotropic behavior (behavior differs from pure fluids (mixtures having gliding temperature and the intermolecular interactions could be neglected) it can be found for all isotherms investigated T= (283.15; 293.15; 303.15; 313.15 and 323.15) K in binary refrigerant systems (R32+R1234yf) and (R32+R152a) (Figures 10-11),where is clearly observed that the calculated α_{12} values do not cross the line of constant relative volatility (α_{12}= 1) for all studied temperatures. Additionally, the values of relative volatility are all greater than 1, which indicates that the components of mixtures can be separated by ordinary distillation.

It fully indicates that the relative volatility model can satisfactorily predict the isothermal (VLE) properties of binary refrigerant mixtures. Overall, results show that the relative volatility model can be used as a computational tool to know the behavior VLE properties and the thermodynamic behavior (subcritical and critical phase behavior) of these mixtures.

3.2 Determination of Azeotropic and Critical Properties

The values of the molar fraction and the pressure calculated of the data experimental ones and those obtained from the model are illustrated in Tables 3-4.

Table 3. Comparison between experimental data and theoretical calculations of azeotropic properties.

T [K]	$x_{az,exp}$	$x_{az,cal}$	$p_{az,exp}$	$p_{az,cal}$
R1234yf+R290				
253.15	0.2800	0.2759	0.2672	0.2655
263.15	0.2810	0.2750	0.3776	0.3741
273.15	0.2800	0.2781	0.5184	0.5134
283.15	0.2810	0.2818	0.6949	0.6881
293.15	0.2810	0.2885	0.9121	0.9018
R1234yf+R600a				
283.15	0.8413	0.8521	0.4465	0.4454
293.15	0.8463	0.8620	0.6011	0.6013
303.15	0.8484	0.8747	0.7925	0.7930
313.15	0.9038	0.8937	1.0230	1.0260
323.15	0.9059	0.8979	1.3108	1.3115

Table 4. Comparison between experimental data and theoretical calculations of critical properties.

T [K]	$x_{c,exp}$	$x_{c,cal}$	$p_{c,exp}$	$p_{c,cal}$
R744+R134a				
329.60	0.7640	0.7746	7.3690	7.4470
339.10	0.6612	0.6678	7.0980	7.1299
354	0.4560	0.4509	6.0430	6.1617
R744+R1234ze				
308.13	0.9790	1.0000	7.6480	7.7676
318.11	0.8970	0.9344	7.6030	8.0978
333.01	0.7650	0.7985	7.3990	7.9549
353.02	0.5400	0.5580	6.4520	6.8139

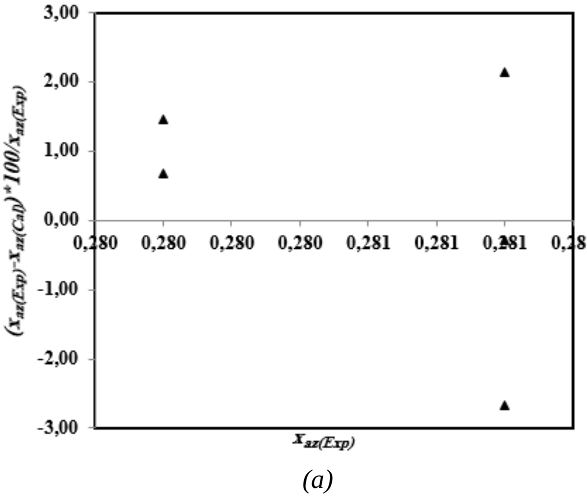
Indeed, the calculated values of the *x* (molar fraction) and *P* (pressure in MPa) for each blend are compared to the experimental ones as folows:

$$\Delta x(\%) = \frac{\left(x^{Exp} - x^{Cal}\right)}{x_{Exp}} * 100 \qquad (13)$$

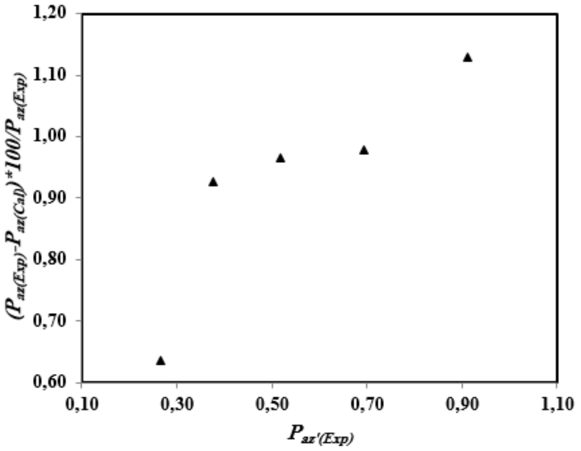
$$\Delta P(\%) = \frac{\left(P^{Exp} - P^{Cal}\right)}{P^{Exp}} * 100 \qquad (14)$$

The comparison of the calculated results with the relative volatility model and the experimental data demonstrates a high consistency between the two.

The relative error values plotted in Figures 12-15 indicate that this method gives good computational of both critical and azeotrope locations. It can be seen that the relative error does not exceed 4.3 % for the molar fraction (*x*) and 7.5 % for the pressure (*P*).

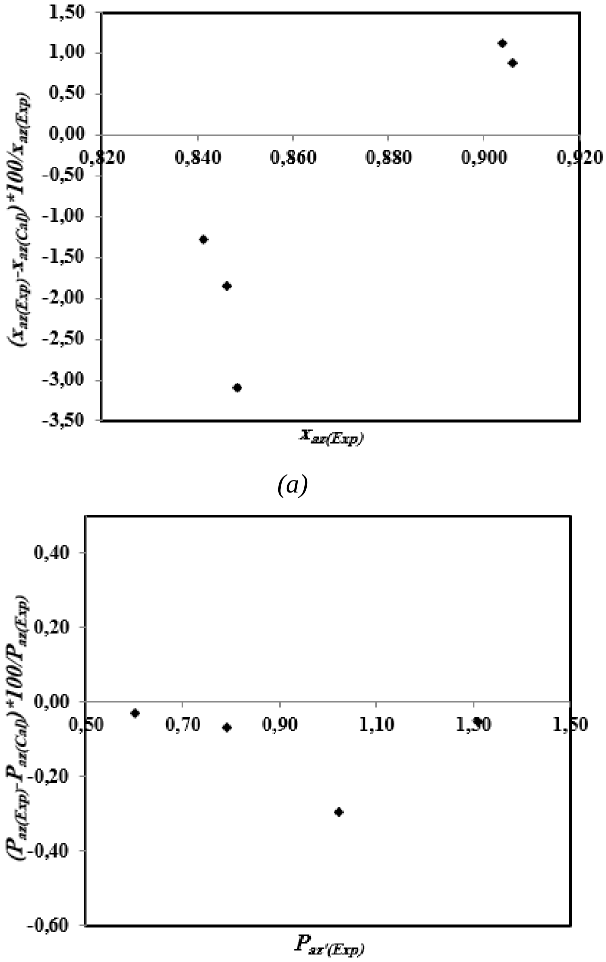


(a)



(b)

Figure 12.Relative error of mole fractions (a) and pressures (b) of R1234yf+R290 system.

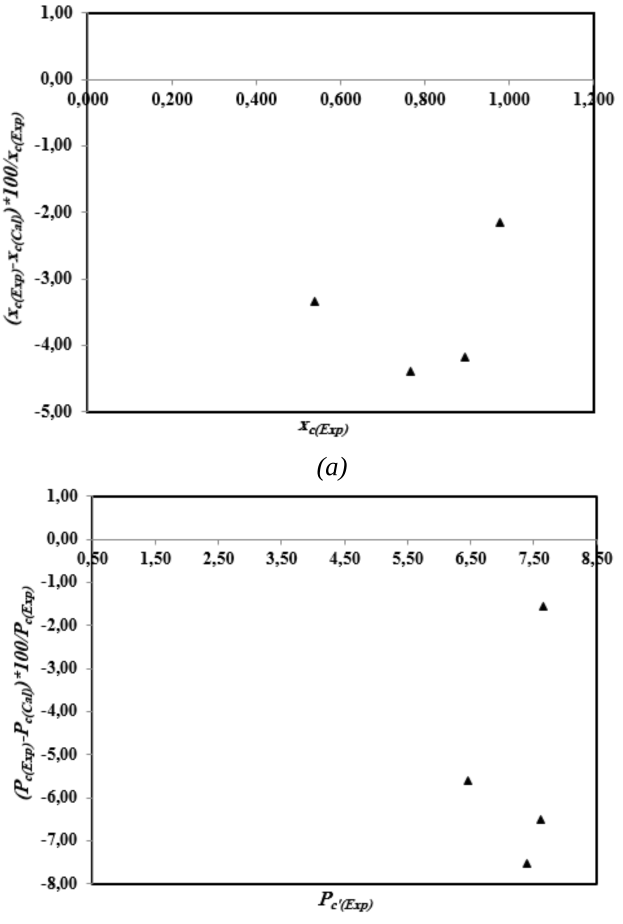


(b)

Figure 13. Relative error of mole fractions (a) and pressures (b) of R1234yf+R600a system.

3.3 Phase Behavior of Binary Refrigerant Systems

Figures 16-21 present the (P-x-y) relationship between the isothermal dew and bubble curves of the binary refrigerant systems: R744+R134a, R744+R1234ze, R1234yf+R290, R1234yf+R600a, R32+R1234yf and R32+R152a at different temperatures. The symbol curves denote the isothermal experimental (VLE) data taken from the literature and the dashed line curves are the results of predictions and modeled data using the cubic equation of state of (PR–EoS) associated with the (MC) alpha function and coupled with the (WS) mixing rule and the NRTL G^E model. From the variation of the bubble and dew point pressure curves in the phase diagram (P-x-y), different thermodynamic behaviors can be observed, when the molar fraction of the mixture changes.



(a)

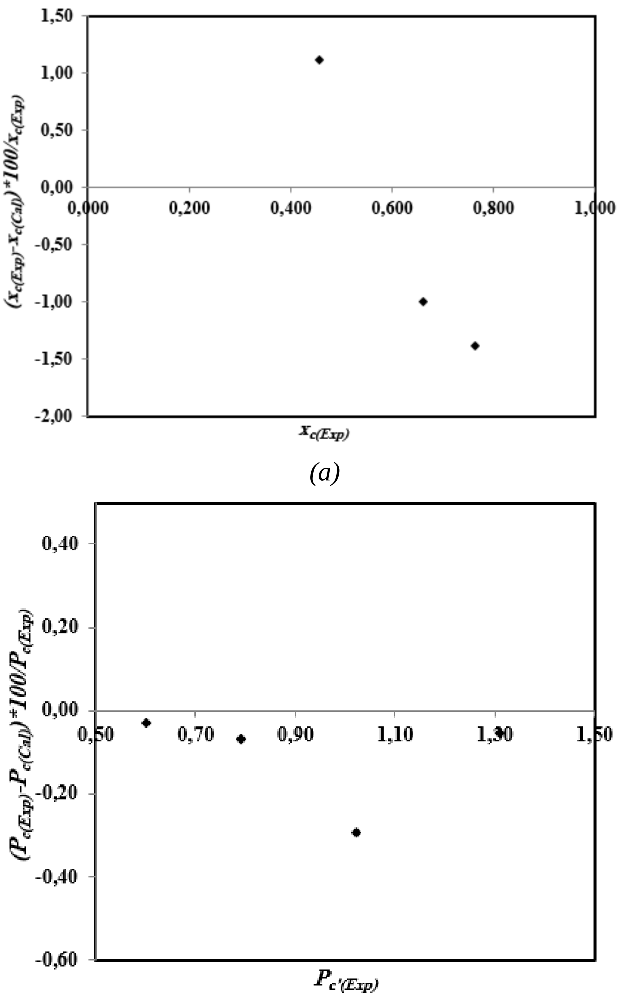
(b)

Figure 14.Relative error of mole fractions (a) and pressures (b) of R744+R1234ze system.

As can be seen from the figures 16-21, the model: "PR–MC–WS–NRTL" is able to perfectly accurately predicts the phase behavior and the location of the both critical and azeotropes points of the blends, where the results show that there is excellent agreement between the computation values obtained with our prediction model and the published isothermal VLE data, where it found that the relative deviation is less than 2.60 % and 2.58 % for the liquid and vapor mole fractions, respectively (see Table 5)).

The binary mixture (R744+R1234ze) was studied at seven different isotherms ranging from 283.32 to 353.02 K, whereas the binary mixture (R744+R134a) was studied at three different isotherms ranging from 329.60 to 354 K.

It can be found that both mixtures exhibits a critical behavior, due to the intermolecular interactions occurring in these systems. The critical behavior was observed for the three isotherms (329.60; 339.1 and 354 K) above the critical temperature (Tc) of the carbon dioxide (Tc (R744) = 304.13 K) for the blend R744+R134a (Figure 16). Whereas, for the blend R744+R1234ze, the critical behavior was observed for the four isotherms (308.15; 318.11; 333.01 and 353.02 K) above the critical temperature (Tc) of the carbon dioxide (Tc (R744) = 304.13 K) (Figure 17).This last feature is the consequence for temperatures higher than the critical temperature of the most volatile pure substance (carbon dioxide), the binary systems conventionally has a critical point.



(a)

(b)

Figure 15.Relative error of mole fractions (a) and pressures (b) of R744+R134a system.

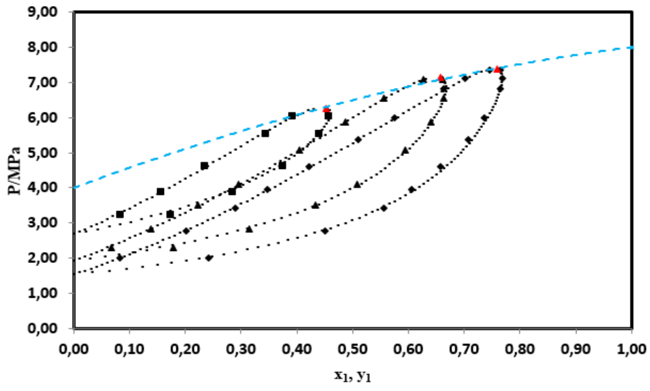


Figure 16.P-x-y diagram for the isothermal vapor-liquid equilibria of R744+R134a system. (Experimental data at various isotherms [23]*: (♦) 329.60 K; (▲) 339.10 K; (■) 354 K; (▲) locus of critical points; (…) critical line; (…): Calculated (VLE) properties using the proposed model).*

On the other hand, it can be directly observed that the two binary systems (R1234yf+R290) and (R1234yf+R600a) show an azeotropic behavior (mixtures have the same behavior as a pure substance during the change of state (condensation or evaporation) in the all temperatures range studied, where the bubble and dew curve are tangent to each other and these two curves do not intersect (Figures 18-19).This azeotrope is a homogeneous azeotrope at maximum pressure, where the composition of the phases of the liquid and the vapor are identical (x_1=y_1) and the relationship between P and x_1 at azeotropic point satisfying this condition (dP/dx_1=0).The azeotropes phenomenon was observed between the mole fractions (0.2 and 0.4) and (0.8 and 0.9) for both binary mixtures (R1234yf+R290) and (R1234yf+R600a) in the isothermal range between 253.15 to 293.15 K and 283.15 to 323.15 K, respectively.

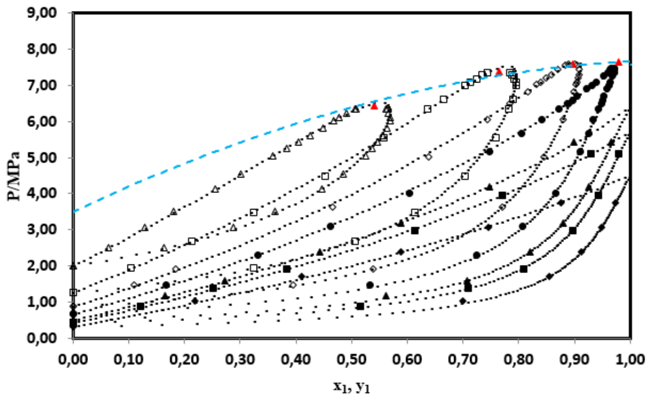


Figure 17.P-x-y diagram for the isothermal vapor-liquid equilibria of R744+R1234ze system.(Experimental data at various isotherms [29]*: (♦) 283.32 K ; (■) 293.15 K ; (▲) 298.15 K ; (●) 308.13 K ; (◊) 318.11 K ; (□) 333.01 K ; (Δ) 353.02 K ; (▲) locus of critical points; (…) critical line; (…): Calculated (VLE) properties using the proposed model).*

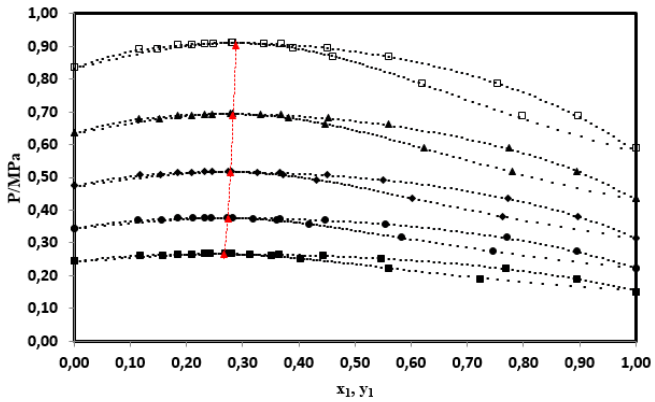


Figure 18.P-x-y diagram for the isothermal vapor-liquid equilibria of R1234yf+R290 system.(Experimental data at various isotherms [30]*: (■) 253.15 K ; (●) 263.15 K ; (♦) 273.15 K ; (▲) 283.15 K ; (□) 293.15 K ; (▲) locus of azeotropic points;(…) azeotropic line; (…) : Calculated (VLE) properties using the proposed model).*

The azeotropes occur in the blends with compounds having similar molecular properties, which are reflected on their thermodynamic properties by having close values of the vapor pressures and the critical temperatures. These blends could be useful for refrigeration applications, where with the same evaporation pressure; the binary systems will have a constant evaporation temperature in the evaporator of the cooling unit.

In the case of the two blends (R32+R1234yf and R32+R152a), it can be found obviously from the graphical VLE representations that the refrigerant blends shows a zeotropic behavior (Figures 20-21) (the bubble and dew curve are not tangent to each other) over the whole ranges of temperature (283.15 to 323.15 K), where these systems have an almost ideal behavior and the intermolecular interactions could be neglected.

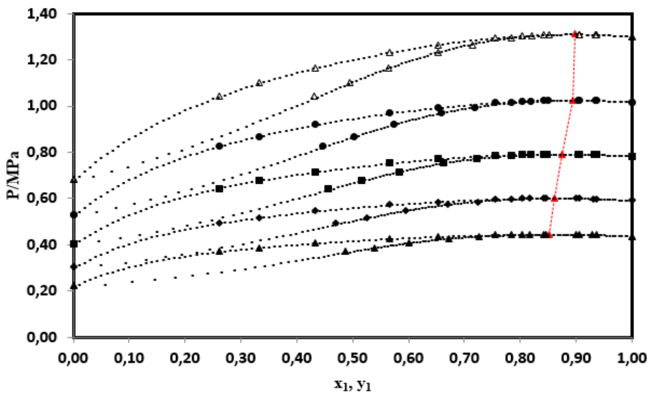


Figure 19.P-x-ydiagram for the isothermal vapor-liquid equilibria of R1234yf+R600a system.(Experimental data at various isotherms [31]*: (▲) 283.15 K ;(♦) 293.15 K ;(■) 303.15 K; (●) 313.15 K; (Δ) 323.15 K; (▲) locus of azeotropic points; (…) azeotropic line; (…): Calculated (VLE) properties using the proposed model).*

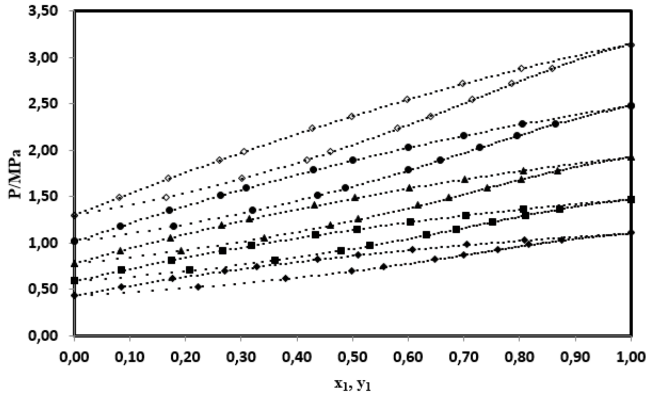


Figure 20.P-x-y diagram for the isothermal vapor-liquid equilibria of R32+R1234yf system.(Experimental data at various isotherms [32]*: (♦) 283.15K; (■) 293.15 K ;(▲) 303.15 K; (●) 313.15 K; (◊) 323.15 K; (…): Calculated (VLE) properties using the proposed model).*

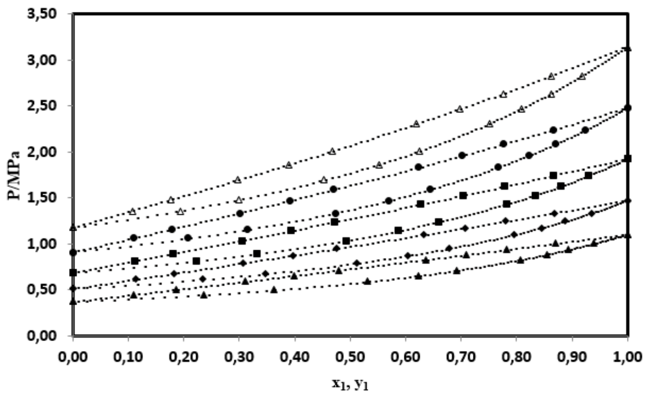


Figure 21.P-x-y diagram for the isothermal vapor-liquid equilibria of R32+R152a system.(Experimental data at various isotherms [33]*: (▲) 283.15 K; (♦) 293.15 K ;(■) 303.15 K; (●) 313.15 K; (Δ) 323.15 K; (…): Calculated (VLE) properties using the proposed model).*

To check the accuracy of our thermodynamic model «PR–MC–WS–NRTL» used in this study to correlate the isothermal (VLE) data of the binary refrigerant blends, the deviations, MRDU, and the BIASU [34] between the experimental data available in literature and the results of mathematical modeling of binary refrigerant systems are applied for both vapor and liquid phases mole fractions, respectively by Eqs. (15) and (16):

$$\text{BIASU} = \left(\frac{100}{N}\right)\sum\left(\frac{U_{Cal} - U_{Exp}}{U_{Exp}}\right) \tag{15}$$

$$\text{MRDU} = \left(\frac{100}{N}\right)\sum\left|\frac{U_{Cal} - U_{Exp}}{U_{Exp}}\right| \tag{16}$$

Where N is the number of data points, U=$x_1$or y_1 and the subscripts Exp, and Cal denote the measured and calculated quantities.

These indicators give information about the agreement between model and experimental results. The deviations between the published experimental values and the results of computation of the liquid and vapor compositions are reported in Table 5.

Table 5. The MRDU and BIASU obtained in fitting experimental isothermal (VLE) data with the proposed model for the binary refrigerant systems.

T [K]	**Bias** *x %*	*MRD x %*	*Bias y %*	*MRD y %*
R744+R134a				
329.60	2.60	2.61	0.78	0.88
339.10	2.52	2.54	1.18	1.24
354	1.42	1.48	2.58	2.70
329.60	2.60	2.61	0.78	0.88
R744+R1234ze				
283.32	-1.13	1.77	-0.52	0.72
293.15	-0.89	1.45	-0.05	0.37
298.15	-0.80	1.25	-0.64	0.84
308.13	0.01	0.57	-0.27	0.31
318.11	-0.64	1.03	-0.37	0.39
333.01	0.03	0.80	0.01	0.25
353.02	-0.53	0.53	-0.48	0.59
R1234yf+R290				
253.15	1.17	0.78	0.24	0.66
263.15	1.12	1.75	0.66	0.78
273.15	0.37	0.98	-0.17	0.76
283.15	0.34	0.83	-0.08	0.57
293.15	-0.84	1.24	-0.99	1.08
R1234yf+R600a				
283.15	-0.21	0.64	-0.06	0.41
293.15	-0.32	0.57	0.03	0.59
303.15	-0.14	0.27	-0.10	0.40
313.15	-0.12	0.29	0.00	0.26
323.15	-0.03	0.14	-0.02	0.33
R32+R1234yf				
283.15	-0.04	0.07	0.03	0.09
293.15	-0.05	0.05	0.07	0.15
303.15	0.01	0.08	0.14	0.20
313.15	-0.02	0.12	0.18	0.27
323.15	-0.12	0.24	0.22	0.44
R32+R152a				
283.15	0.11	0.24	-0.80	0.80
293.15	0.12	0.22	-0.50	0.54
303.15	0.16	0.18	-0.33	0.34
313.15	0.19	0.26	-0.24	0.24
323.15	0.18	0.28	-0.09	0.09

4. Conclusions

In the present study, six binary refrigerant systems have been studied with the aim to predict their phase behavior and determine the thermodynamic properties (critical and azeotropic points) in isothermal (VLE) using two models: “Relative volatility model” and the thermodynamic model “PR–MC–WS–NRTL”.

In the first part of this work, the possibility of presence of azeotropic or critical states in the binary working fluids has been verified and computing their properties (compositions and pressures) in each isotherm was made. It can be seen that the relative error does not exceed 4.3 % for the molar fraction and 7.5 % for the pressure.

In the second part, the thermodynamic model, which combines the cubic equation of state of Peng–Robinson (PR-EoS) with the (MC) alpha function, and the NRTL G^E model, using the WS mixing rules has been employing to correlate the data of isothermal (VLE) properties of this blends and describe their phase behavior.

The results of mathematical modeling showed that the isothermal VLE of the studied binary working fluids is well correlated using the proposed model. The obtained results for the binary refrigerant systems proved that the model described accurately their behavior in both subcritical and supercritical regions, where the relative deviation is less than 2.60 % and 2.58 %, respectively for the liquid and vapor mole fractions.

From the discussion of the obtained results in this work, the main conclusions are:

- The computation model “Relative volatility” gives good predictions of azeotropic and critical behavior of binary refrigerant systems;
- the relative volatility model has the ability to determine the thermodynamic properties;
- The (PR-MC-WS-NRTL) model has high accuracy in the prediction of isothermal (VLE) properties;
- The binary blends (R744+R134a and R744+R1234ze) exhibits critical behavior;
- The refrigerant blends: (R1234yf+R290 and R1234yf+R600a) have exhibited azeotropic behavior;
- The blends R32+R1234yf and R32+R152a have showed zeotropic behavior.

Nomenclature

Symbols

a	Energy parameter (J m^3 mol^{-2})
b	Molar co volume parameter (m^3 mol^{-1})
c_1,c_2 ,c_3	Mathias-Copeman coefficient
C	Numerical constant equal to -0.62323
N	Number of experimental points
g	Gibbs energy (J)
G	Molar Gibbs energy (J mol^{-1})
K_{ij}	Binary interaction parameter
K_1	Partition coefficient
P	Pressure (MPa)
R	Universal gas constant (J mol^{-1} K^{-1})
T	Temperature (K)
v	Molar volume (m^3mol^{-1})
x	Liquid mole fraction
y	Vapor mole fraction

Greek symbols

$\alpha(T)$	Alpha function
α_{ij}	Relative volatility between component *i* and *j*
γ_i	Activity coefficient of component *i*
∞	Infinite pressure reference state

τ	Binary interaction coefficients in NRTL activity model

Subscripts

az	Azeotrope property
c	Critical property
i,j	Molecular species
1	Most volatile pure substance
2	Less volatile pure substance
Cal	Calculated property
Exp	Experimental property

Superscript

E	Excess property

Abbreviations

GWP	Global warming potential
ODP	Ozone depleting potential
VLE	Vapor liquid equilibria
EoS	Equation of state
PR	Peng–Robinson
MC	Mathias–Copeman
WS	Wong–Sandler
NRTL	Non Random Two Liquids

Refrigerants

R744	Carbon dioxide
R134a	1,1,1,2-tetrafluoroethane
R1234yf	2,3,3,3-tetrafluoroprop-1-ene
R1234ze	Trans-1,3,3,3-tetrafluoropropene
R290	Propane
R600a	Isobutane
R32	Difluoromethane
R152a	1,1-Difluoroethane

References:

[1] C. Coquelet, A. Chareton, and D. Richon, “Vapour–liquid equilibrium measurements and correlation of the difluoromethane (R32) + propane (R290) + 1,1,1,2,3,3,3-heptafluoropropane (R227ea) ternary mixture at temperatures from 269.85 to 328.35K,” *Fluid Phase Equilib*., 218, 209–214, 2004, doi:10.1016/j.fluid.2003.12.009.

[2] Y. Maalem, A. Zarfa, Y. Tamene, S. Fedali, and H. Madani, “Prediction of thermodynamic properties of the ternary azeotropic mixtures,” *Fluid Phase Equilib*., 517, 112613, 2020, doi:10.1016/j.fluid.2020.112613.

[3] JM. Calm, “The next generation of refrigerants – Historical review, considerations, and outlook,” *Int. J. Refrig*., 31,1123–1133, 2008, doi:10.1016/j.ijrefrig.2008.01.013.

[4] S. Kato and D. Bluck, “Practical Applications of a Pure Prediction Method for Binary VLE to the Establishment of a High-Precision UNIFAC,” *J. Chem. Eng. Data*., 61, 4236–4244, 2016, doi:10.1021/acs.jced.6b00593.

[5] A. Jakob, H. Grensemann, J. Lohmann, and J. Gmehling, “Further Development of Modified UNIFAC (Dortmund): Revision and Extension 5,” *Ind. Eng. Chem. Res*., 45,7924–7933, 2006, doi:10.1021/ie060355c.

[6] K. Zheng, H. Wu, C. Geng, G. Wang, Y. Yang, and Y. Li, “ A Comparative Study of the Perturbed-Chain Statistical Associating Fluid Theory Equation of State and Activity Coefficient Models in Phase Equilibria Calculations for Mixtures Containing Associating and Polar Components,” *Ind. Eng. Chem. Res*., 57, 3014–3030, 2018, doi:10.1021/acs.iecr.7b04758.

[7] P. Anila, K. Rayapa Reddy, G. Srinivasa Rao, PVS. Sai Ram, D. Ramachandran, and C. Rambabu, “ Activity coefficients and excess Gibbs energy functions of acetophenone with 1,2-dichloroethane and 1,1,2,2-tetrachloroethane binary mixtures by using NRTL, UNIQUAC, UNIFAC and VAN LAAR models at a local atmospheric pressure of 95.3 kPa,” *Karbala Int. J. Mod Sci* ., 2, 211–218, 2016, doi:10.1016/j.kijoms.2016.07.001.

[8] H. Mokarizadeh, S. Moayedfard, and M. Mozaffarian, “Comparison of MOSCED (NRTL) model results with regular correlative and predictive models based on vapor-liquid equilibrium calculations for azeotropic systems,” *Fluid Phase Equilib*., 516, 112592, 2020, doi:10.1016/j.fluid.2020.112592.

[9] G. Yu, C. Dai, and Z. Lei, “Modified UNIFAC-Lei Model for Ionic Liquid–CH4 Systems,” *Ind. Eng. Chem. Res*., 57, 7064–7076, 2018, doi:10.1021/acs.iecr.8b00986.

[10] AS. Teja and JS. Rowlinson, “The prediction of the thermodynamic properties of fluids and fluid mixtures — IV. Critical and azeotropic states,” *Chem. Eng. Sci*., 28, 529–538, 1973, doi:10.1016/0009-2509(73)80050-8.

[11] S. Artemenko and V. Mazur, “Azeotropy in the natural and synthetic refrigerant mixtures,” *Int. J. Refrig*.,30,831839,2007,doi:10.1016/j.ijrefrig.2006.11.010.

[12] ZT. Fidkowski, MF. Malone, and MF. Doherty, “Computing azeotropes in multicomponent mixtures,” *Comput. Chem. Eng*.,17,1141–1155, 1993, doi:10.1016/0098-1354(93)80095-5.

[13] JE. Tolsma and PI. Barton, “Computation of heteroazeotropes. Part I: Theory,” *Chem. Eng. Sci*., 55, 3817–3834, 2000, doi:10.1016/S0009-2509(00)00032-4.

[14] P. Kolář and K. Kojima, “Prediction of critical points in multicomponent systems using the PSRK group contribution equation of state,” *Fluid Phase Equilib*., 118,175–200,1996, doi:10.1016/0378 3812(95)02850-1.

[15] XQ. Dong, MQ. Gong, Y. Zhang, and JF. Wu, “Prediction of homogeneous azeotropes by Wilson equation for binary HFCs and HCs refrigerant mixtures,” *Fluid Phase Equilib*., 269, 6–11, 2008, doi:10.1016/j.fluid.2008.04.012.

[16] RA. Heidemann and AM. Khalil, “The calculation of critical points,” *AIChE .J* ., 26, 769–779, 1980, doi:10.1002/aic.690260510.

[17] DV. Nichita, “Calculation of critical points using a reduction method,” *Fluid Phase Equilib*., 228–229, 223–231,2005, doi:10.1016/j.fluid.2004.09.036.

[18] RW. Maier, JF. Brennecke, and MA. Stadtherr, “Reliable computation of homogeneous azeotropes,” *AIChE. J*., 44,1745–1755,1998, doi:10.1002/aic.690440806.

[19] M. He, Y. Liu, and X. Liu, “Prediction of critical temperature and critical pressure of multi-component mixtures,” *Fluid Phase Equilib.*, 441, 2–8,2017, doi:10.1016/j.fluid.2016.11.017.

[20] P. Hu, Z-S. Chen, and W-L. Cheng, “Prediction of vapor–liquid equilibria properties of several HFC binary refrigerant mixtures,” *Fluid Phase Equilib.*, 204,75–84, 2003, doi: 10.1016/S0378-3812(02)00216-9.

[21] X. Dong, M. Gong, Y. Zhang, J. Liu, and J. Wu, “Prediction of Homogeneous Azeotropes by the UNIFAC Method for Binary Refrigerant Mixtures,” *J. Chem \& Eng. Data.*, 55, 52–57, 2010, doi:10.1021/je900693q.

[22] S. Fedali, H. Madani, and C. Bougriou, “Prediction method of both azeotropic and critical points of the binary refrigerant mixtures,” *J. Appl. Eng. Sci. & Technol.*, Vol 3 No 1, 2017.

[23] G. Silva-Oliver and LA. Galicia-Luna, “Vapor–liquid equilibria for carbon dioxide + 1,1,1,2-tetrafluoroethane (R-134a) systems at temperatures from 329 to 354 K and pressures upto 7.37 MPa,” *Fluid Phase Equilib.*, 199, 213–222, 2002, doi:10.1016/S0378-3812(01)00816-0.

[24] D-Y. Peng and DB. Robinson, “A New Two-Constant Equation of State,” *Ind. Eng. Chem. Fundam.*, 15, 59–64, 1976, doi:10.1021/i160057a011.

[25] PM. Mathias and TW. Copeman, “Extension of the Peng-Robinson equation of state to complex mixtures: Evaluation of the various forms of the local composition concept,” *Fluid Phase Equilib.*, 13, 91–108, 1983, doi:10.1016/0378-3812(83)80084-3.

[26] Dortmund Data Bank (DDB), Version 97, “DDBST Software and Separation Technology GmbH,” Oldenburg, Germany, 1997.

[27] DSH. Wong and SI. Sandler, “A theoretically correct mixing rule for cubic equations of state,” *AIChE .J.*, 38, 671–680, 1992, doi:10.1002/aic.690380505.

[28] H. Renon and JM. Prausnitz, “Local compositions 1 in thermodynamic excess functions for liquid mixtures,” *AIChE .J.*, 14, 135–144, 1968, doi:10.1002/aic.690140124.

[29] S. Wang, R. Fauve, C. Coquelet, A. Valtz, C. Houriez, P-A. Artola, E. El Ahmar, B. Rousseau, and H. Haitao, “Vapor–liquid equilibrium and molecular simulation data for carbon dioxide (CO2) + trans-1,3,3,3-tetrafluoroprop-1-ene (R-1234ze(E)) mixture at temperatures from 283.32 to 353.02 K and pressures up to 7.6 MPa,” *Int. J. Refrig.*, 98, 362–371, 2019, doi:10.1016/j.ijrefrig.2018.10.032.

[30] Q. Zhong, X. Dong, Y. Zhao, H. Li, H. Zhang, H. Guo,and M. Gong , “Measurements of isothermal vapour–liquid equilibrium for the 2,3,3,3-tetrafluoroprop-1-ene + propane system at temperatures from 253.150 to 293.150 K,” *Int. J. Refrig.*, 81, 26–32, 2017, doi:10.1016/J.IJREFRIG.2017.05.016.

[31] P. Hu, L-X. Chen, and Z-S. Chen, “Vapor–liquid equilibria for binary system of 2,3,3,3-tetrafluoroprop-1-ene (HFO-1234yf) +isobutane (HC-600a),” *Fluid Phase Equilib.*, 365,1–4, 2014, doi:10.1016/j.fluid.2013.12.015.

[32] X. Hu, T. Yang, X. Meng, S. Bi, and J. Wu, “Vapor liquid equilibrium measurements for difluoromethane (R32) + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) and fluoroethane (R161) + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf),” *Fluid Phase Equilib.*, 438, 10–17, 2017, doi:10.1016/j.fluid.2017.01.024.

[33] T. Yang, X. Hu, X. Meng, and J. Wu, “Vapor–Liquid Equilibria for the Binary and Ternary Systems of Difluoromethane (R32), 1,1-Difluoroethane (R152a), and 2,3,3,3-Tetrafluoroprop-1-ene (R1234yf),” *J. Chem. Eng. Data.*, 63, 771–780, 2018, doi:10.1021/acs.jced.7b00950.

[34] H. Madani, A. Valtz, F. Zhang, J. El Abbadi, C. Houriez, P. Paricaud, and C.Coquelet, “Isothermal vapor-liquid equilibrium data for the trifluoromethane (R23) + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) system at temperatures from 254 to 348 K,” *Fluid Phase Equilib.*, 415, 158–165, 2016, doi:10.1016/j.fluid.2016.02.005.