Modeling of the thermodynamic properties of the mixtures: Prediction of the position of azeotropes for binary mixtures

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ABSTRACT

In this paper, we present a novel approach to predict the location of azeotropes for binary mixtures by two methods: from the experimental data and the thermodynamic model. The model composed of the Peng–Robinson equation of state, the Mathias–Copeman alpha function, the Wong–Sandler mixing rules involving the NRTL model. The binary mixtures of refrigerants selected are: propane (R290) + 1,1,1,2-tetrafluoroethane (R134a) [1], propane (R290) + difluoromethane (R32) [2] and hexafluoroethane (R116) + ethane (R170) [3], hexafluoroethane (R116) + carbon dioxide (R744) [4] and hexafluoroethane (R116) + propane (R290) [5], to be favorable to the environment with a null ODP (ozone depletion potential) and a low GWP (global warming).

The results prove that there is an agreement between the predicted values and the experimental data and the relative error does not exceed 2.76% for the molar fraction and 3.23% for the pressure. The presented methods are able to predict the azeotropic position and the performances of the models change from one mixture to another.

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1. Introduction

Our world is always changing; we need to preserve the global environment. The phenomenon of the impoverishment of the ozone layer and the climatic reheating are the two problems very discussed of these last years. To solve these problems, various protocols, of with those Montreal Protocol 1987 (ozone depletion) and Kyoto Protocol 1997 (Global Warming: (effective on Feb. 16, 2005)/EU F-gas Regulation (Directive 2006/40/EC)) specified the refrigerant regulation. In the field of the refrigeration, many researches are undertaken to find new refrigeration mixtures with minimal environmental impact (ozone depletion and global warming).

In industry, the presence of azeotropes in mixtures has value is interesting because they behave very nearly as pure materials and when it is a mixture of chemicals in solution and not a compound where those chemicals exhibit strong molecular bonds that are not easily broken. The mixtures show azeotropic behavior and calculation of such property is particularly important in designing of azeotropic distillation.

Many numbers of researches in our group [6–14] have been studied. Our main objective is to develop a new and sample method for the prediction of the position of azeotrope in the binary mixtures. In this study, we presented a new approach for determination of azeotropy directly from the experimental data and theoretically from the thermodynamic model. We studied five binary systems of refrigerants: propane + R134a, propane + R32, R116 + R170, R116 + R744 and R116 + propane.

2. Mathematical modeling

Recently, many methods and approaches have been used to predict the location of azeotropes for vapor–liquid equilibrium of binary mixtures.

We have developed a model for the position of azeotropic mixture refrigerant. We applied the method which is based on experimental data for calculation and prediction of azeotropes and then we confirmed our method by using a thermodynamic model.

2.1. From the experimental data

The azeotropic position is determined for each system (x_{az}: azeotropic composition, P_{az}: azeotropic pressure). With the experimental values, plotting the value of relative volatility (α) according to the molar fraction of the most volatile pure substance, and then

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Table 1
Critical parameters from data[a]

Compound	P_c (MPa)	T_c (K)
R290	4.192	369.83
R134a	4.064	374.30
R32	5.753	351.60
R116	2.941	292.80
R170	4.872	305.32
R744	7.286	304.21

[a] From [21].

Table 2
Mathias–Copeman coefficients.

Coefficients	C_1	C_2	C_3
R290[a]	0.892	−1.936	8.815
R134a[b]	0.849	0.006	−0.053
R32[c]	1.034	−1.454	4.038
R116[d]	0.875	−3.243	0.254
R170[e]	0.531	−0.062	0.214
R744[f]	0.704	−0.314	1.890

[a] Adjusted.
[b] [15].
[c] [2].
[d] [16].
[e] [21].
[f] [15].

we equalizing the obtained curve (α) to 1 (the same principle for the pressure).

2.1.1. Algorithm

- For each isotherm, we trace either the relative volatility (α) according to the molar fraction of the most volatile pure substance x_1, or according to the pressure.
- Using the Excel, plotted points either to a curve (trendline) of a second-degree polynomial (or linear) is adjusted.

Table 3
Azeotropes preaching.

T (K)	X_o	K_1	X_e	K_1	Possibility of having an azeotrope
R290 + R134a					
273.15	0.0991	3.63	0.9149	0.89	Yes
283.15	0.1153	3.02	0.9445	0.92	Yes
293.15	0.0490	3.70	0.9897	0.98	Yes
303.15	0.0850	2.72	0.9707	0.96	Yes
313.15	0.0505	2.95	0.9293	0.94	Yes
R290 + R32					
278.10	0.0430	5.49	0.9750	0.94	Yes
294.83	0.0080	6.13	0.9570	0.94	Yes
303.23	0.0270	4.67	0.9530	0.96	Yes
R116 + R170					
183.31	0.2547	2.21	0.7874	0.93	Yes
192.63	0.2352	2.28	0.7518	0.95	Yes
247.63	0.1572	1.81	0.7340	0.96	Yes
252.80	0.1264	1.88	0.7432	0.96	Yes
R116 + R744					
253.29	0.0284	1.78	0.9477	0.92	Yes
273.27	0.0281	1.37	0.9327	0.94	Yes
283.24	0.0592	1.16	0.9732	0.98	Yes
R116 + R290					
263.30	0.019	11.470	0.961	1.002	No
283.25	0.020	8.400	0.946	1.003	No
291.22	0.020	7.450	0.941	1.004	No
296.23	0.018	7.060	0.808	1.010	No
308.21	0.029	5.241	0.569	1.056	No
323.10	0.030	4.167	0.392	1.074	No

X_o, X_e: the experimental molar fractions of initial and final azeotropes, respectively.
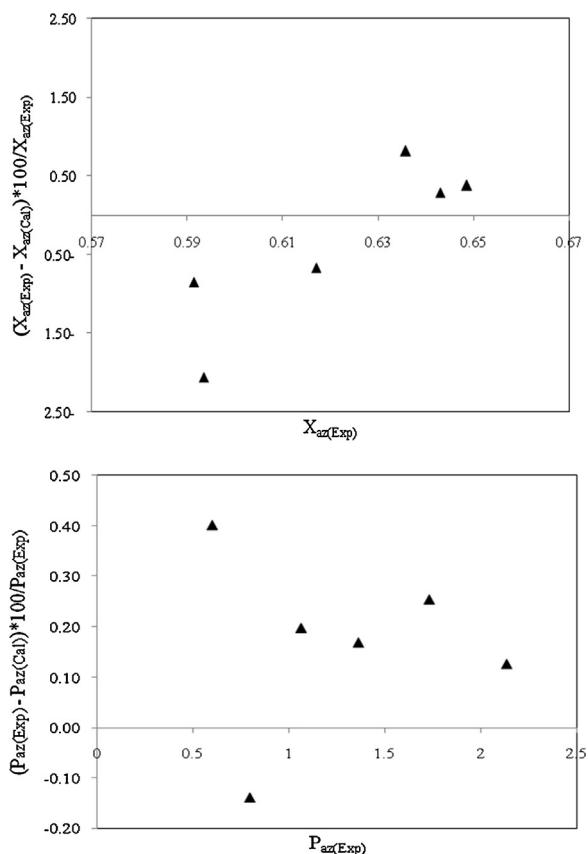
Fig. 1. Deviation of pressure and vapor-phase composition for R290 + R134a system.

- Equalizing the equation of the curve of tendency to 1.
- Solving the obtained equation, where values are obtained x_{az} and P_{az}.

2.2. From the thermodynamic model

Our thermodynamic model based on a simple correlative scheme that allows one to judge if can be obtained or not

Table 4
Experimental and calculated compositions and pressures of the azeotrope at each temperature of R290 + R134a, R290 + R32, R116 + R170 and R116 + R744.

| T (K)	$X_{az(exp)}$	$X_{az(cal)}$	$P_{az(exp)}$	$P_{az(cal)}$
R290 + R134a				
273.15	0.6486	0.6461	0.5972	0.5948
283.15	0.6430	0.6411	0.7939	0.7950
293.15	0.6358	0.6306	1.0603	1.0582
303.15	0.6171	0.6211	1.3595	1.3572
313.15	0.5935	0.6057	1.7289	1.7245
323.15	0.5914	0.5964	2.1318	2.1291
R290 + R32				
278.10	0.6610	0.6593	1.2193	1.2217
294.83	06746	0.6748	1.9211	1.9006
303.23	0.6838	0.6827	2.3498	2.3517
313.26	0.6964	0.6903	2.9903	2.9603
R116 + R170				
189.31	0.7027	0.6979	0.1688	0.1634
192.63	0.6958	0.6986	0.1937	0.1926
247.63	0.6662	0.6674	1.4652	1.4636
252.80	0.6630	0.6634	1.7160	1.6902
R116 + R744				
253.29	0.2051	0.1996	2.1640	2.1796
273.27	0.1822	0.1821	3.7280	3.7458
283.24	0.1790	0.1735	4.7740	4.8050
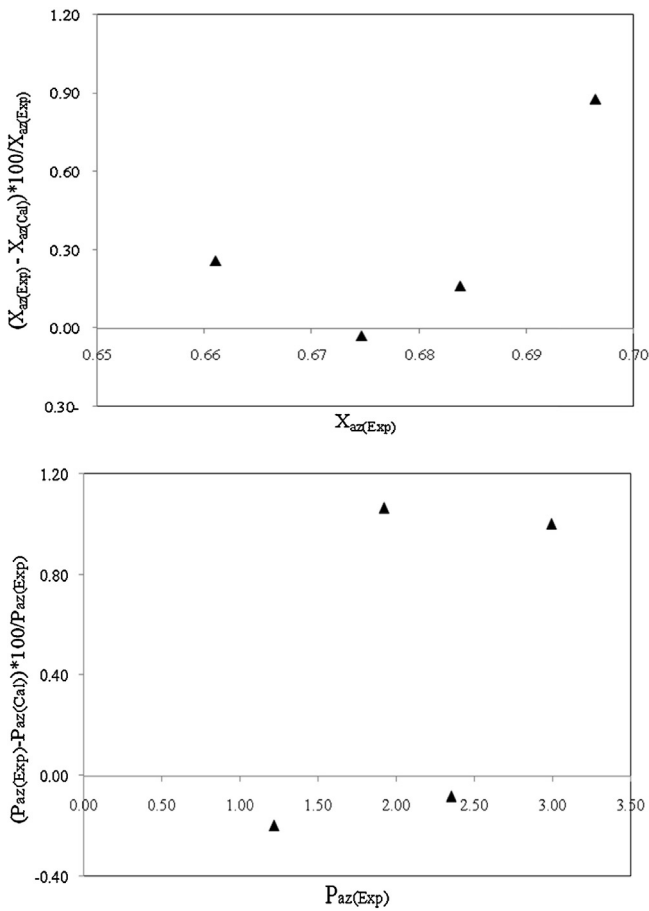
Fig. 2. Deviation of pressure and vapor-phase composition for R290 + R32 system.
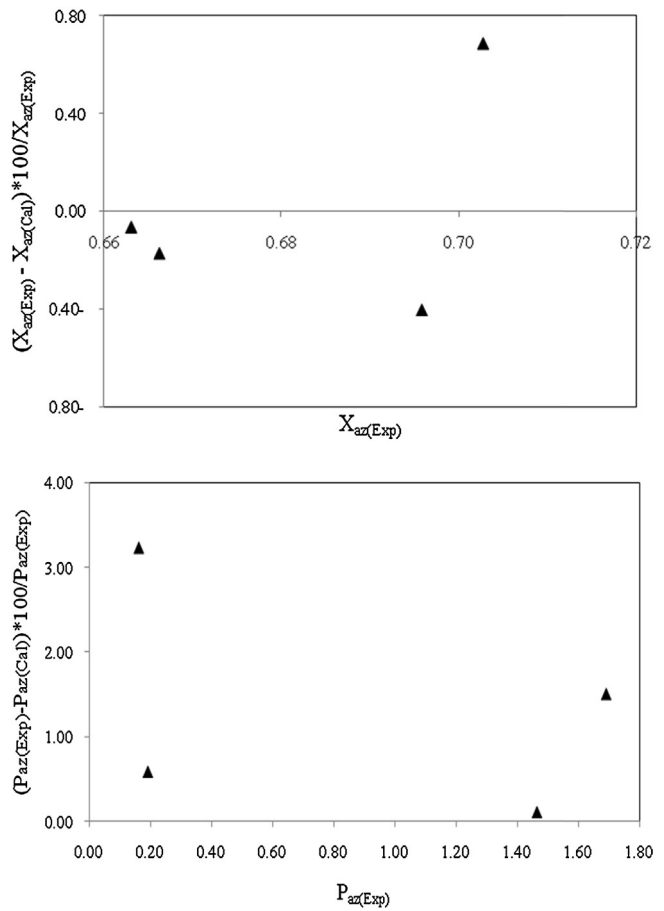

Fig. 3. Deviation of pressure and vapor-phase composition for R116 + R170 system.

an azeotrope is probable in binary refrigerant mixtures. We have used the Peng Robinson (PR) EoS [17] together with the Mathias–Copeman alpha function (Eqs. (4) and (5)) [18] for accurate representation of the pure component vapor pressures. The critical temperature (T_c) and critical pressure (P_c) for each pure component is given in Table 1.

$$P = \frac{RT}{v-b} - \frac{a(T)}{(v^2 + 2vb - v^2)} \tag{1}$$

with

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

$$b = 0.07780 \frac{RT_c}{P_c} \tag{3}$$

Mathias–Copeman alpha function

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3]^2 \tag{4}$$

If $T > T_c$

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5})]^2 \tag{5}$$

where c_1, c_2 and c_3 are adjustable parameters (see Table 2).- The Wong–Sandler (WS) mixing rules are chosen here from the good representation of vapor–liquid equilibria [19]

$$b = \frac{\sum_i \sum_j x_i x_j (b - a/RT)}{1 - (\sum_i x_i (a_i/b_i)/RT + g_\gamma^E(T, P = \infty, x)/CRT)} \tag{6}$$

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{7}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b - \frac{a}{RT}\right)_i + \left(b - \frac{a}{RT}\right)_j\right](1 - k_{ij}) \tag{8}$$

where k_{ij} is an adjustable binary interaction parameter and C is a numerical constant which depends on the EoS.- The component activity parameters of binary mixture system are calculated with model NRTL (non-random two liquids) [20]

$$Ln\gamma_i = \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{k=1}^n G_{ki} x_k} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n G_{ki} x_k}\left(\tau_{ij} - \frac{\sum_{k=1}^n x_k \tau_{kj} G_{kj}}{\sum_{k=1}^n G_{ki} x_k}\right) \tag{9}$$

Table 5
The equations of the curve of tendency of the binary mixtures $P_{az} = f(T)$ and $X_{az} = f(T)$.

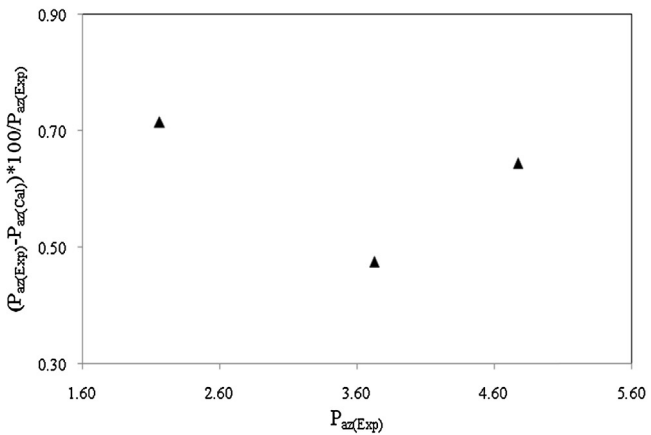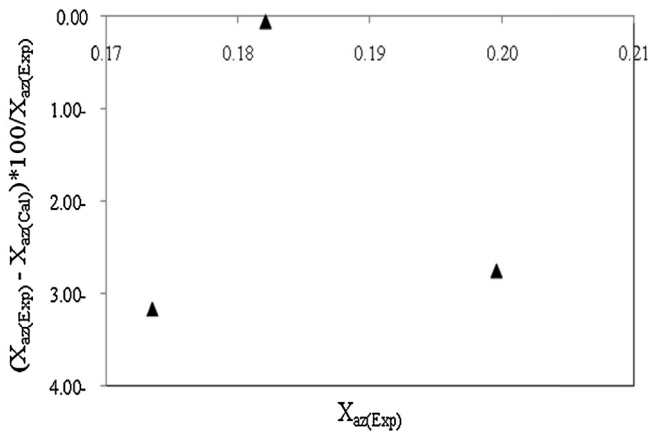|	$P_{az} = f(T)$	$X_{az} = f(T)$
R134a + R290	$P_{az} = 0.0002T^2 - 0.0638T + 5.8777$	$X_{az} = -0.00003T^2 + 0.018T - 1.882$
R290 + R32	$P_{az} = 0.0005T^2 - 0.2358T + 29.3971$	$X_{az} = 0.00001T^2 - 0.005T + 1.279$
R116 + R170	$P_{az} = 0.0004T^2 - 0.1420T + 13.5902$	$X_{az} = 0.000007T^2 - 0.003T + 1.145$
R116 + R744	$P_{az} = 0.0009T^2 - 0.4113T + 46.6887$	$X_{az} = 0.0000004T^2 - 0.001T + 0.452$

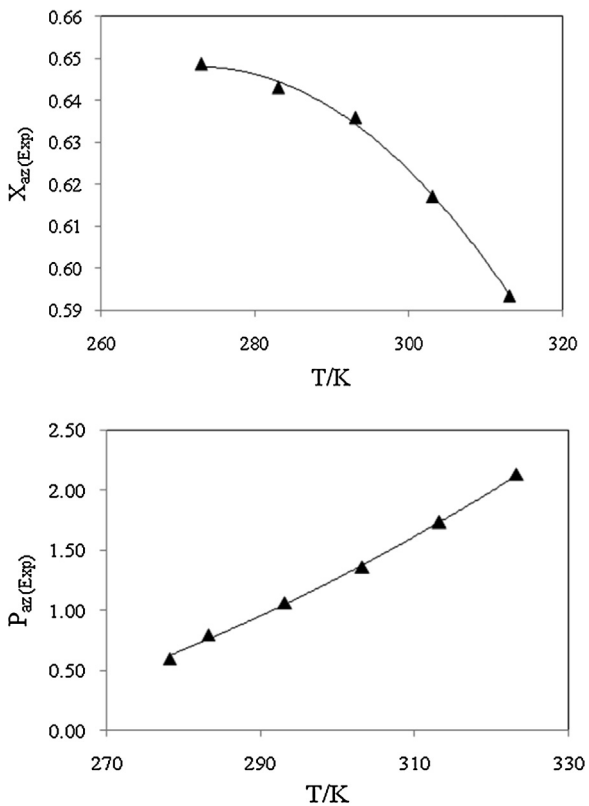**Fig. 4.** Deviation of pressure and vapor-phase composition for R116 + R744 system.

Fig. 5. Azeotropic composition and pressure versus temperature for R290 + R134a system.
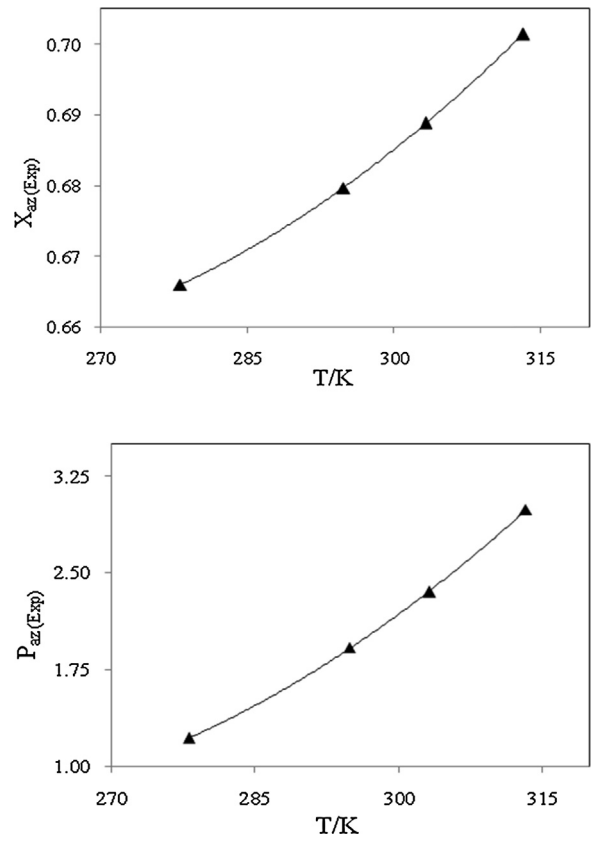

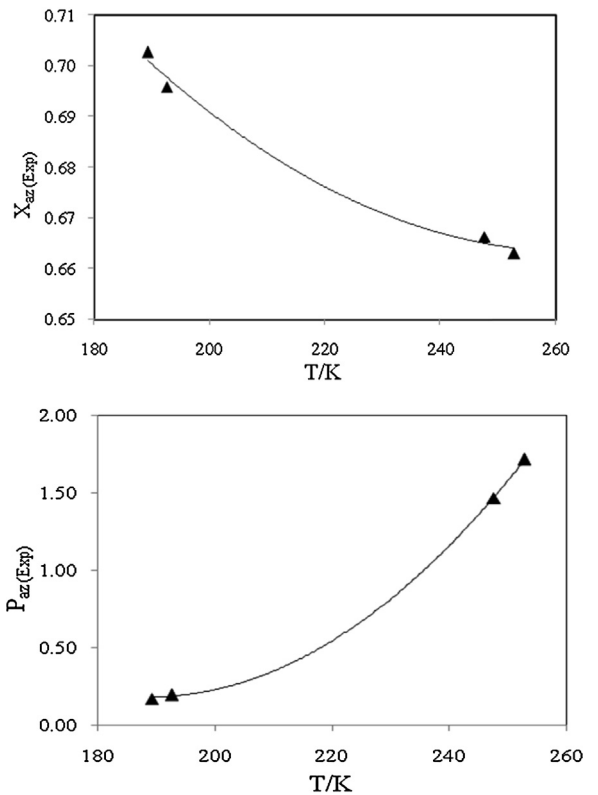**Fig. 6.** Azeotropic composition and pressure versus temperature for R290 + R32 system.

Fig. 7. Azeotropic composition and pressure versus temperature for R116 + R170 system.
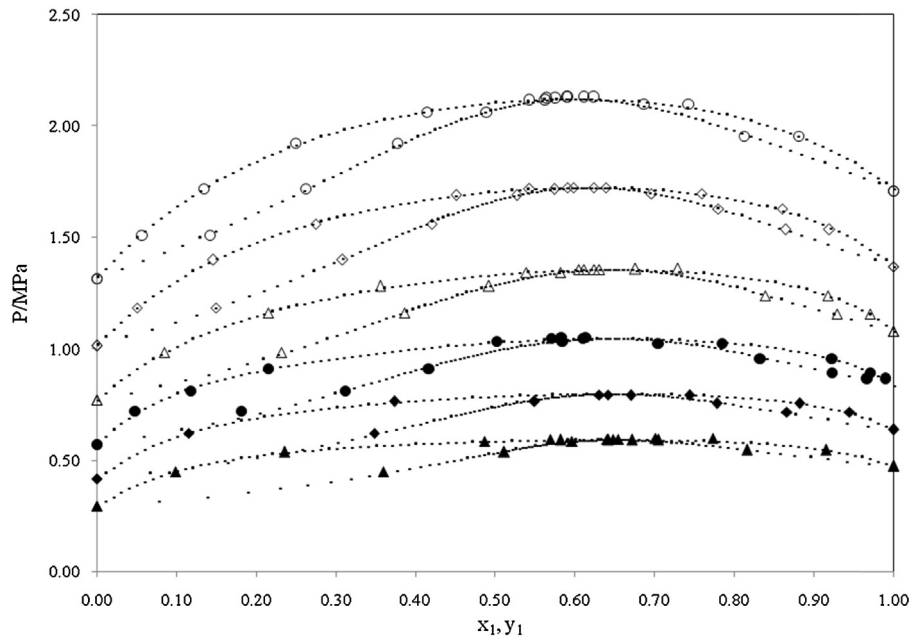
Fig. 8. VLE for the system R290 + R134a at different temperatures: (▲) 273.15 K, (◆) 283.15 K, (●) 293.15 K, (△) 303.15 K, (◇) 313.15 K, (○) 323.15 K.
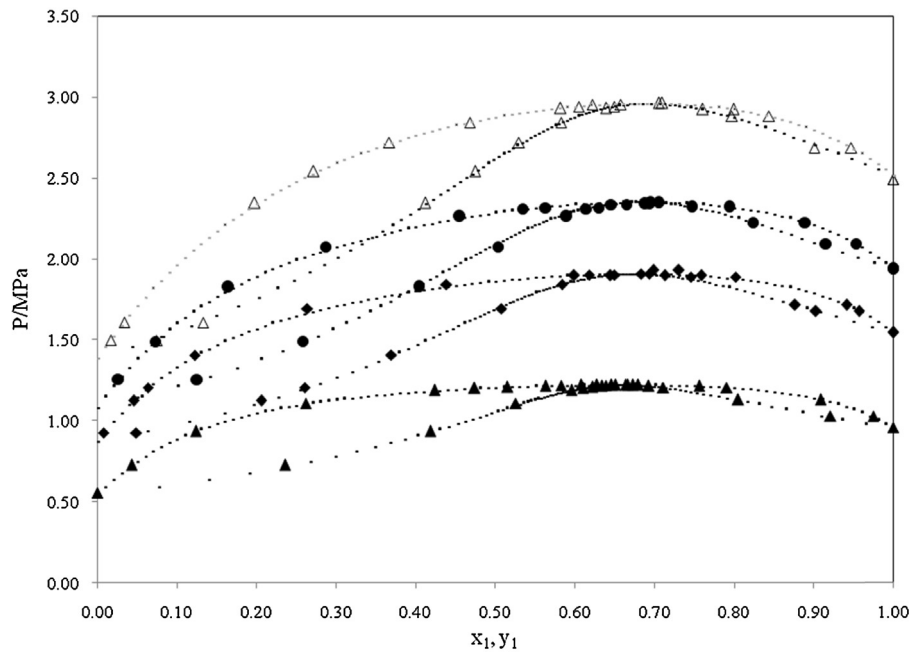

Fig. 9. VLE for the system R290 + R32 at different temperatures: (▲) 278.10 K, (◆) 294.83 K, (●) 303.23 K, (△) 313.66 K.

where the model parameters C_{ij} and G_{ij} are defined as follows:

$$C_{ji} = \frac{\tau_{ij}}{RT} \tag{10}$$

$$G_{ij} = \exp\left(-\alpha_{ji}\frac{\tau_{ji}}{RT}\right) \tag{11}$$

The excess Gibbs energy model chosen is the NRTL [17]

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

Table 6
Values of the binary parameters at each temperature for R290 + R134a.

T (K)	τ_{12}	τ_{21}	K_{12}
273.15	4144	3953	−0.0001
283.15	5305	4553	−0.1146
293.15	6332	5500	−0.2322
303.15	5858	3874	−0.1164
313.15	3948	2999	0.0626
323.15	2113	2563	0.1903

where α_{ji}, τ_{ji} and τ_{ij} are adjustable parameters. It is recommended [15] to use $\alpha_{ij} = 0.3$ for systems like the current one. Where $\tau_{ii} = \tau_{jj} = 0$ and $\alpha_{ii} = 0$.
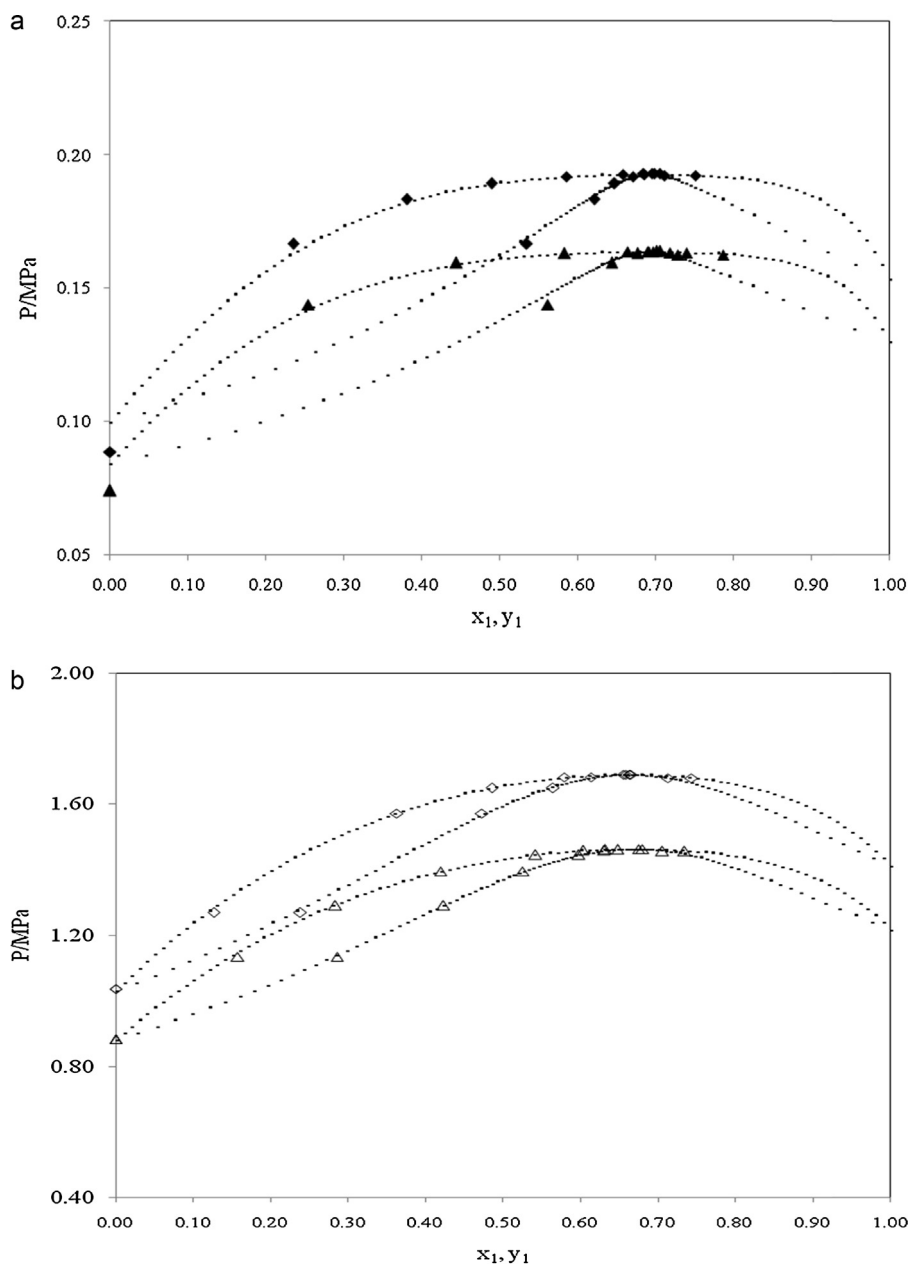
Fig. 10. VLE for the system R116 + R170 at different temperatures: (a) (▲) 189.31 K, (♦) 192.63 K, (b) (△) 247.63 K, (◊) 252.80 K.

3. Results and discussions

Predicting the composition for an azeotropic is of key importance in fluid-phase equilibrium of the refrigerant mixture is very important before it can be tested for its refrigeration characteristics.

3.1. Prediction of azeotropes

First the value of the partition coefficient $K_1 = x_1/y_1$ of the most volatile pure substance is calculated for each isotherm. Azeotropic behavior of the mixture is predicted using the mole fractions and not pressure.

Table 7
Values of the binary parameters at each temperature for R290 + R32.

T (K)	τ_{12}	τ_{21}	K_{12}
278.10	4019	3731	0.1827
294.83	4160	4045	0.1394
303.23	3951	3793	0.1657
313.66	1566	3341	0.3325

Table 8
Values of the binary parameters at each temperature for R116 + R170.

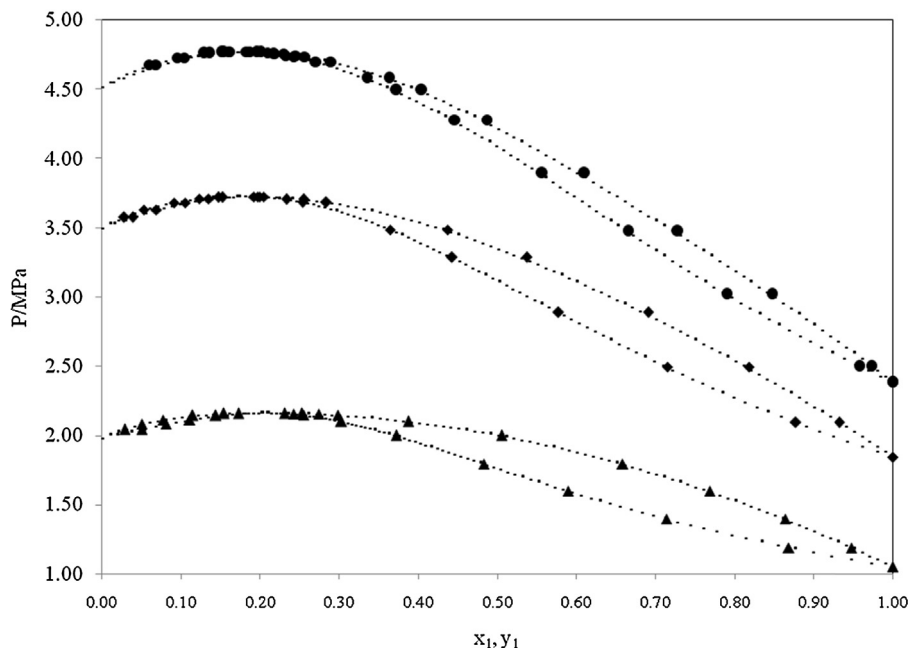| T (K)	τ_{12}	τ_{21}	K_{12}
189.31	3385	237	0.2301
192.63	3396	−110	0.2915
247.63	3401	794	0.1500
252.80	3000	786	0.1800

Fig. 11. VLE for the system R116 + R744 at different temperatures: (▲) 253.29 K, (♦) 273.27 K, (●) 283.24 K.

Table 3 shows the first four mixtures which have azeotropic mixture except the last mixture (R116 + R290).

The compositions of the vapor and liquid phases are the same when we are in the presence of an azeotrope.

3.2. Determination of azeotropes from the experimental data

From the experimental data, we will determine the position of the azeotropes (x_{az}: molar fraction, P_{az}: pressure in MPa) for each mixture, the algorithm is clarified before.

The values of the molar fraction and the azeotrope pressure calculated of the data experimental ones, and those obtained from the model are illustrated in Table 4.

Comparison between the experimental values measured to those of the values computed of azeotropic compositions and pressures by the following relations: _Molar fraction x_{az}_

$$\Delta x_{az}^{c/o} = \frac{x_{az(\exp)} - x_{az(cal)}}{X_{az(\exp)}} * 100 \tag{13}$$

Pressure P_{azeo}

$$\Delta P_{az}^{c/o} = \frac{P_{az(\exp)} - P_{az(cal)}}{P_{az(\exp)}} * 100 \tag{14}$$

The relative error values plotted in Figs. 1–4 indicate that this method gives good predictions of the azeotrope location and the relative error does not exceed 2.76% for the molar fraction and 3.23% for the pressure.
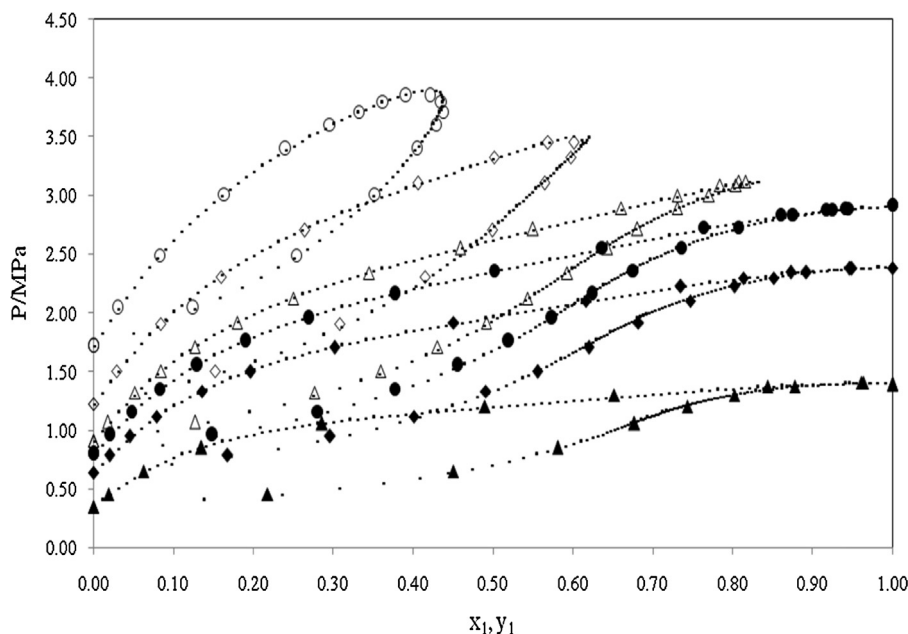

Fig. 12. VLE for the system R116 + R290 at different temperatures: (▲) 263.30 K, (♦) 283.20 K, (●) 291.22 K, (△) 296.23 K, (◇) 308.21 K, (○) 323.19 K.

Table 9
Values of the binary parameters at each temperature for R116 + R744.

T (K)	τ_{12}	τ_{21}	K_{12}
253.29	362	3977	0.2171
273.27	324	4073	0.1917
283.24	287	3650	0.2177

Table 10
Values of the binary parameters at each temperature for R116 + R290.

T (K)	τ_{12}	τ_{21}	K_{12}
263.30	1891	3292	0.1301
283.25	1783	3194	0.1383
291.22	921	3497	0.1910
296.23	596	3691	0.2073
308.21	608	3806	0.1930
323.19	795	3749	0.1756

Collected figures.

To widening our study more in a range of temperature (see Table 4), the molar fractions of azeotropes and those pressures in function to temperature have been traced (Figs. 5–7).

We can have the value of the molar fraction of azeotrope where the pressure according to the temperature of the systems quoted in Table 5.

3.3. Determination of the azeotropes from a thermodynamic model

The vapor pressures of the binary mixtures are presented in the publications [1–5].

The effectiveness of our method, we will justify further, where by using a very robust thermodynamic model which gave its consistency in a large number of articles published (paragraph 2). The experimental and calculated data PTxy are illustrated in Figs. 8–12 according to the system studied.

Figs. 8 to 10 present an azeotrope between 0.6 and 0.8 for the systems (R290 + R134a, R290 + R32 and R116 + R170) and between 0.0 and 0.3 in the system R116 + R290 (Fig. 11). This azeotrope is a homogeneous azeotrope at maximum pressure (for isothermal). Where the composition of the liquid phase and the composition of the vapor phase are identical, the mixture is the same process as a pure substance. R116 + R290 (Fig. 12) does not present an azeotrope, the system presents a quasi-azeotrope, then disappeared above the critical point of R116, which in maid agreements with the experimental values.

The adjusted NRTL (τ_{12} and τ_{21}) parameters for the Wong–Sandler mixing rules (K_{12}) obtained at each temperature are given in Tables 6–10.

4. Conclusion

In this study, isothermal VLE data have been determined for propane + 1,1,1,2-tetrafluoroethane at T = 278.15–313.15 K and propane + difluoromethane at T = 278.10–303.23 K and hexafluoroethane + ethane at T = 189.31–252.80 K and hexafluoroethane + carbone at T = 253.29–283.24 K and hexafluoroethane + propane at T = 263.20–223.19 K using two methods. The results have been correlated with the Peng–Robinson equation of state using the Mathias–Copeman alpha function and Wong–Sandler mixing rules with the NRTL G^E model.

The approach provided reasonably good fits to the values measured. The obtained results of the present model for the binary mixtures prove that the present model works well for these binary mixtures. Therefore, this model can be applicable to the other binary refrigerant mixtures.

List of symbols

a	parameter of the equation of state [energy parameter ($J\,m^3\,mol^{-2}$)]
b	parameter of the equation of state [molar co-volume parameter ($m^3\,mol^{-1}$)]
c	Mathias–Copeman coefficient
C	numerical constant equal to -0.62323
g	molar Gibbs energy ($J\,mol^{-1}$)
k_{ij}	binary interaction parameter
K_1	partition coefficient
N	number of experimental points
P	pressure (MPa)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
T	temperature (K)
x	liquid mole fraction
y	vapor mole fraction

Greek letters

α	alpha function (Eqs. (4) and (5))
α_{ji}	non-randomness NRTL model parameter (Eq. (8))
τ_{ij}	NRTL model binary interaction parameter (Eq. (9)) ($J\,mol^{-1}$)
τ_{ji}	NRTL model binary interaction parameter (Eqs. (8)–(11)) ($J\,mol^{-1}$)
∞	infinite pressure reference state

Superscript

E	excess property

Subscripts

az	azeotropic property
C	critical property
cal	calculated property
e	end
exp	experimental property
i, j	molecular species
r	reduced
1	most volatile pure substance
2	less volatile pure substance

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