RESEARCH OF NEW REFRIGERANTS: PREDICTION OF THE POSITION OF AZEOTROPES FOR BINARY MIXTURES

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RESUME

The aim of this paper is to predict the location of azeotropes for binary mixtures using two methods: firstly from the experimental data and secondly with a thermodynamic model. The model is composed of the Peng–Robinson equation of state, the Mathias–Copeman alpha function and the Wong–Sandler mixing rules involving the NRTL model. The binary systems of refrigerants considered in this paper are: Pentafluoroethane (R125) + Propane (R290) [1], 1,1,1-Trifluoroéthane (R143a) + Propane (R290) [2] and Carbon Dioxide (R744) + Propane (R290) [3]. The mixtures mentioned above have been chosen because they are environment friendly with a null ODP and a low GWP.

The results proved that there is a good agreement between the predicted values and the experimental data. The presented methods are able of predicting the azeotropic positions.

INTRODUCTION

The problems affecting the environment and more particularly the ozone layer and increasing the greenhouse effect are known to be highly topical. Our main objective is to develop a method for the prediction of the position of azeotrope in the binary mixtures in order to use them in the refrigerating machines. In such machines, it is needed to avoid various problems during the cycle of refrigeration which may be induced by the lag of liquid-vapor equilibrium such as overheating or under- cooling.

NOMENCLATURE

a	[J. ^{3}.mol^{-2}])	Parameter of the PR equation of state (energy parameter)
b	[[m^3.mol^{-1}]	Parameter of the PR equation of state (molar co-volume parameter)
c		Numerical constant equal to -0.62323 (equation (6))
g	[J. mol^{-1}]	Molar Gibbs energy
G	[J]	Gibbs energy
P	[MPa]	Pressure
R	[J.mol^{-1}.K^{-1}]	Gas constant
T	[K]	Temperature
v	[m^3.mol^{-1}]	Molar volume
x		Liquid mole fraction

y		Vapor mole fraction
Greek letters		
$a(T)$		Alpha function (equations (4) and (5))
Subscripts		
c		Critical property
az		Azeotrope property
r		Reduced
i,j		Molecular species
γ		Calculated by the model of activity coefficient
Superscript		
E		Excess property

MODEL TO PREDICT AZEOTROPE

In this work, propane is associated with other pure substances like R125, R143a and R744 to form binary mixtures. The organization chart shown below illustrates our model to predict and determine the azeotrope position.
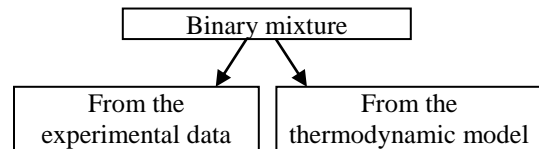
FROM THE EXPERIMENTAL DATA

The azeotropes position is determined for each mixture (x_{az}: azeotropic composition, P_{az}: azeotropic pressure).

ALGORITHM

- As it is well known, the relative volatility ($\alpha = K_i/K_j$), represents the ratio of the equilibrium constants of the (i) and (j) species. For each isotherm, the values of the partition coefficients have been calculated and the value of the relative volatility (α) is deduced. At first, (α) is plotted versus the molar fraction of the most volatile pure substance (x_1).
  For each isotherm, the relative volatility (α) is also plotted versus the pressure.
- Using Excel software, the plotted points are either fitted using a second order polynomial curve or a linear trendline.
- The equation of the curve of tendency is equalized to 1.

- By solving the obtained equation, values the azeotropic composition (x_{az}) and azeotropic pressure (P_{az}) are obtained.

We applied the method which is based on experimental data for calculation and prediction of azeotropes, and then the developed method is validated using a thermodynamic model.

FROM THE THERMODYNAMIC MODEL

The developed model is based on a simple correlation schema. Such model allows knowing if an azeotrope may be obtained or not in binary refrigerant mixtures.

The PR EoS [1] has been used together with the Mathias–Copeman alpha function (equations (4) and (5)) [5] for an accurate representation of the pure component vapor pressures.

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

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, [5]:

$$\alpha(T) = \left[1 + c_1\left(1 - T_r^{0,5}\right) + c_2\left(1 - T_r^{0,5}\right)^2 + c_3\left(1 - T_r^{0,5}\right)^3\right]^2 \tag{4}$$

If $T > T_C$

$$\alpha(T) = \left[1 + c_1\left(1 - T_r^{0,5}\right)\right]^2 \tag{5}$$

Where c_1, c_2 and c_3 are adjustable parameters.

The Wong–Sandler (WS) mixing rules are chosen from the good representation of the vapor-liquid equilibrium [6], for EoS Peng-Robinson which are given by:

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

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

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

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 systems are calculated with the NRTL (Non Random Two Liquids) model [7]:

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

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

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

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

$$\tau_{ii} = \tau_{jj} = 0 \tag{12}$$

The chosen excess Gibbs energy model is the NRTL:

$$g^E = \sum_i x_i \sum_j \frac{x_j \exp\left(-\alpha_{ji} \frac{\tau_{ji}}{RT}\right)}{\sum_k x_k \exp\left(-\alpha_{ki} \frac{\tau_{ki}}{RT}\right)} \tau_{ji} \tag{13}$$

α_{ji}, τ_{ji} and τ_{ij} are adjustable parameters. It is recommended to use $\alpha_{ij} = 0.3$ [8].

RESULTATS AND DISCUSSION

EXPERIMENTAL DATA

The results are shown in tables 1, 2 and 3.

Table 1: Prediction of azeotrope for the (R125 + R290) system

T/K	x_0	K_1	x_f	K_1
263.15	0.0538	4.0595	0.9360	0.9154
278.15	0.0836	3.0287	0.9546	0.9529
293.15	0.0425	3.0071	0.9519	0.9704
308.15	0.1424	2.0077	0.9603	0.9854
323.15	0.1333	1.8207	0.9072	0.9781

Table 2: Prediction of azeotrope for the (R143a + R290) system

T/K	x_0	K_1	x_f	K_1
268.15	0.2000	1.7900	0.946	0.9831
278.15	0.2000	1.8000	0.922	0.9512
288.15	0.2150	1.6930	0.928	0.9580
298.15	0.2120	1.6604	0.924	0.9589
308.15	0.1930	1.6736	0.891	0.9652
318.15	0.1830	1.6339	0.906	0,9702

Table 3: Prediction of azeotrope for the (R744 + R290) system

T/K	x_0	K_1	x_f	K_1
253.15	0.0160	11.9375	0.8700	1.0747
263.15	0.0170	10.4118	0.8200	1.1195
273.15	0.0200	8.6500	0.8140	1.1241
283.15	0.0210	7.5238	0.8080	1.1101
293.15	0.0220	6.3182	0.8510	1.0693
303.15	0.0250	5.3600	0.8590	1.0361
313.15	0.0260	4.7308	0.7030	1.0697
323.15	0.0210	4.1905	0.5590	1.1377

K_1: Partition coefficient of the most volatile pure substance.
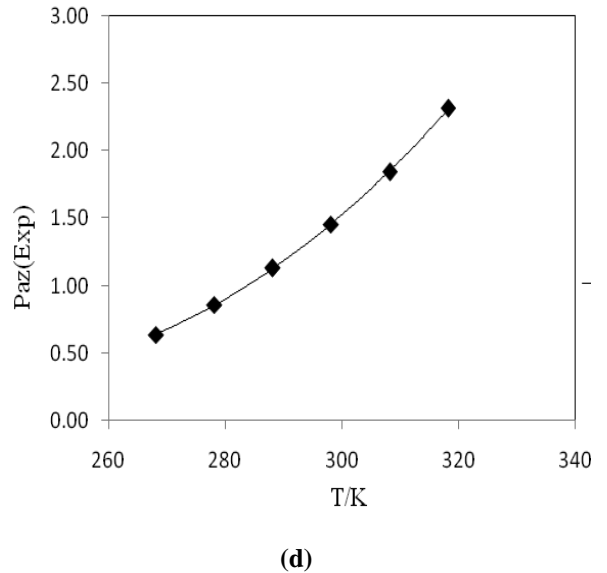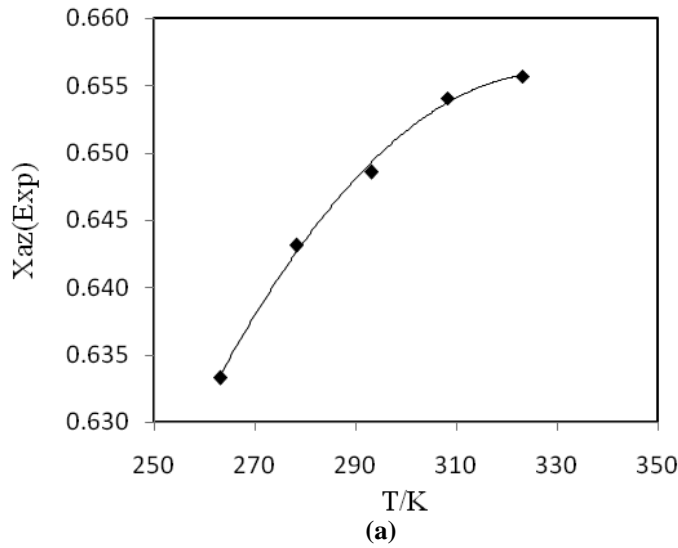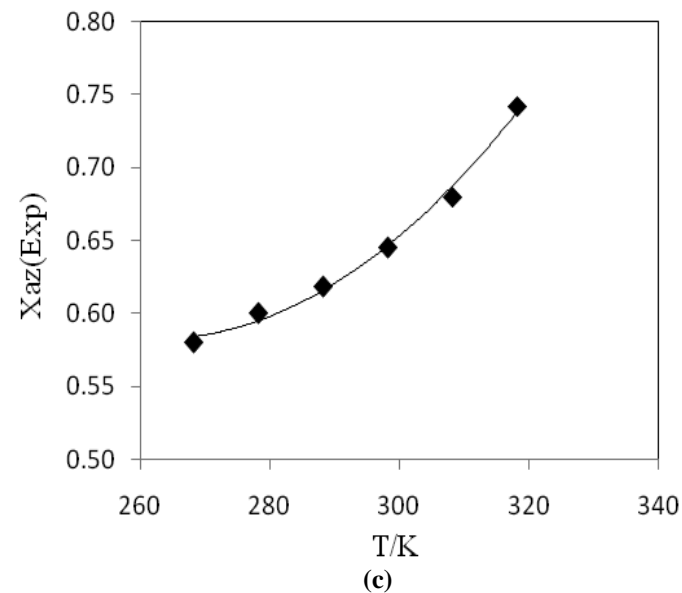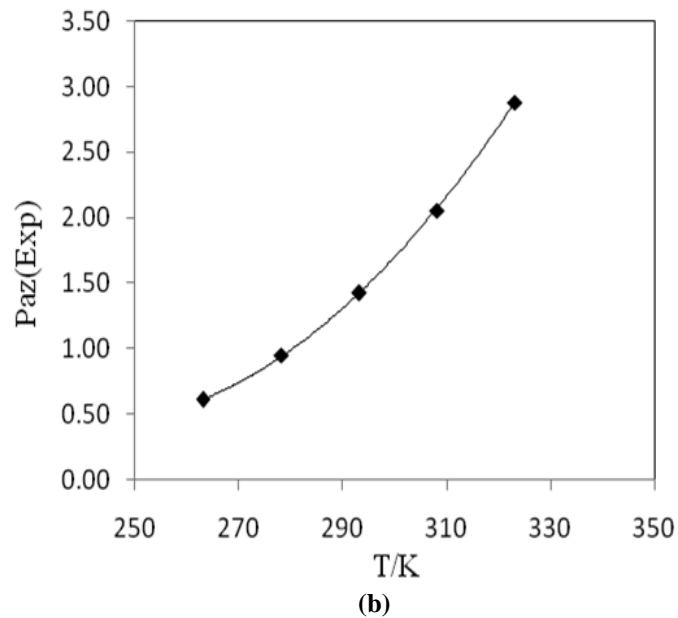
(a)

(d)

Figure 1 Azeotropic composition and pressure versus temperature. (a) and (b) (R125+R290) mixture, (c) and (d) (R143a+R290) mixture.

In Tables 1-2, it can be concluded that all systems display azeotropic mixtures except the last one (R744 + R290). The compositions of the vapor and liquid phases are the same when we are in the presence of an azeotrope.

To extend our study, the molar fractions and pressures of azeotropes are plotted versus temperature for the (R125+R290) and (R143a+R290) mixtures (Fig.1).

The values of the molar fraction and the pressure (azeotrope) versus temperature of the (R125 + R290) can be correlated by the following equation:

$$P_{az} (MPa)= 0.001*T^2 - 0.171*T + 21.07 \tag{14}$$

$$X_{az}= -0.000005*T^2 + 0.003*T + 0.093 \tag{15}$$

For the (R143a + R290) system, the correlation equations are given by:

$$P_{az} (MPa)= 0.001*T^2 - 0.144*T + 17.57 \tag{16}$$

$$X_{az} = 0.00005*T^2 - 0.026*T + 3.993 \tag{17}$$

THERMODYNAMIC MODEL

In figs 2 and 3, the (R125 + R290) and (R143a + R290) systems form azeotropes at all temperatures between molar fractions ranging from 0.5 to 0.8. This azeotrope is a homogeneous azeotrope at maximum pressure. The (R744 + R290) system (fig 4) does not present any azeotrope for all temperatures.
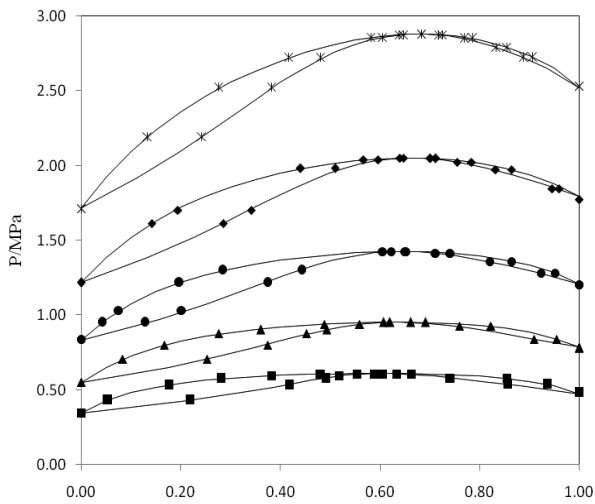

(b)

(c)

Figure 2 VLE for the system (R125 + R290) for various temperatures: (■) 263.15 K, (●) 293.15 K, (♦) 308.15 K, (✳) 323.15 K
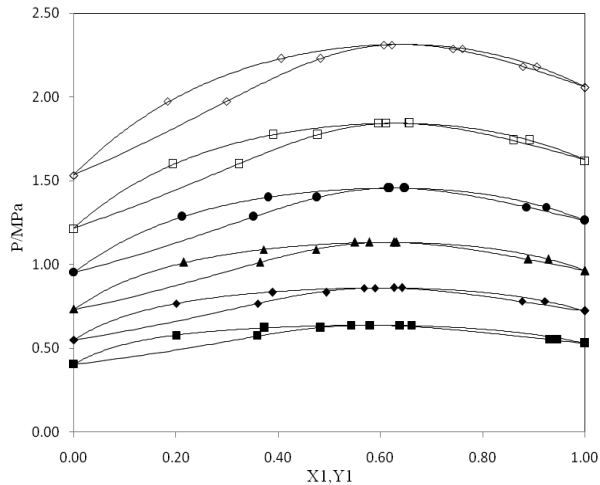

Figure 3 VLE for the system R143a + R290 for various temperatures: (■) 268.15 K, (▲) 288. 15 K, (♦) 278. 15 K, (●) 298. 15 K, (□) 308. 15 K, (◊) 318. 15 K

The results proved that there is a good agreement between the predicted values and the experimental data. Indeed, the calculated values of the x_{azeo} (molar fraction) and P_{azeo} (pressure in MPa) for each mixture are compared to the experimental ones as folows:

Molar fraction X_{azeo}

$$\Delta X_{azeo} = \frac{(X_{azeo\ (Exp)} - X_{azeo\ (Cal)})}{X_{azeo\ (Exp)}} * 100$$

Pressure P_{azeo}

$$\Delta P_{azeo} = \frac{(P_{azeo\ (Exp)} - P_{azeo\ (Cal)})}{P_{azeo\ (Exp)}} * 100$$

The relative error does not exceed 3% for the molar fraction and 2 % for the pressure for this study.
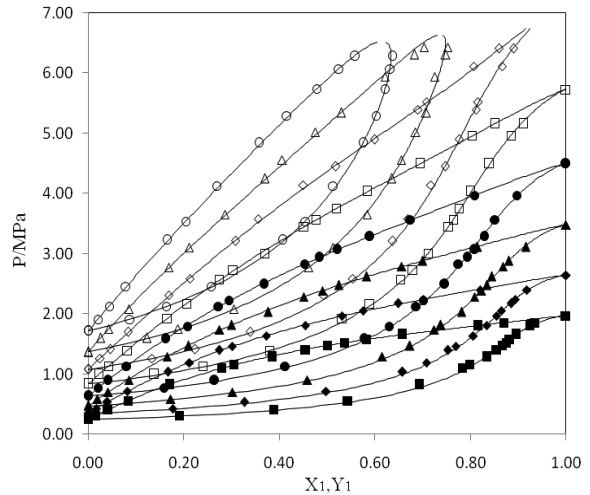

Figure 4 VLE for the system R744 + R290 for versus temperatures: (■) 252.15 K, (♦) 263.15 K, (▲) 273.15 K, (●) 283.15 K, (□) 293.15 K, (◊) 303.15 K, (Δ) 313.15 K, (○) 323.15K

CONCLUSION

In this study, we studied three refrigerants R125, R143a and R744 associated with R290. The (R125 + R290) and (R143a + R290) systems have azeotropes. The approach provided reasonably good fits to the measured values. The obtained results using the developed model for the binary mixtures proved that it described accurately such binary mixtures. Therefore, this model is expected to be useful to other binary refrigerant mixtures.

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