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Prediction method of both azeotropic and critical points of the binary refrigerant mixtures

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Abstract: The prediction of the azeotropic point and the determination of the critical point in binary mixtures is very important in refrigerating industry. In this task, a simple method is presented in order to predict and determine both azeotropic and critical points. Our method employs experimental data and a thermodynamic model. 1,1,1,2-tetrafluoroethane (R134a) in the mixture presents the possibility of inventing the azeotropic and critical properties. The mixtures studied in this work are: Cyclopropane (RC270), Propylene (R1270), Hexafluoroethane (R116) and Carbon dioxide (R744) based on 1,1,1,2-tetrafluoroethane (R134a). The model consists of the Peng–Robinson equation of state (EoS), the Mathias–Copeman alph a function and the Wong-Sandler mixing rules involving the NRTL model. The results proved that there is a good agreement between the predicted values and the experimental data. The presented methods are able to predict the azeotropic and determine critical positions.

1. Introduction

To overcome the problem of lack of the given binary mixtures on an industrial scale, the researchers propose the use of numerical methods with thermodynamic developed models which are very reliable in solving many problems under temperature and pressure conditions. The choice of the appropriate method for estimating the different properties is one of the most important steps that guide the simulation. The need for a precise knowledge of azeotropic and critical point's behavior is essential for binary, ternary mixtures and refrigerating equipments. For a continuing research purpose, the prediction of azeotropic and critical points proprieties and behaviors has been studied. Instead of the experimental work which doesn't lead to accurate values, an extensive research using theoretical methods was used for the prediction and determination of both azeotropic and critical points (Loannidis et al. 1997; Alvarado et al. 1998; Segura et al. 1999; Heidemann and Khalil 1980; Qua et al .2009).

The aim of this study is to correctly predict the azeotropic property and critical endpoint of binary mixtures. In addition, apply them in the refrigerating machines in order to avoid several problems during the cycle of refrigeration such as overheating or under-cooling, owing to the lag thermodynamic. Furthermore, we aim to determine the upper limit of the vapor-liquid equilibrium curve. This paper is organized as follows. Section 2 presents the model. Section 3 presents the results and discussion. Finally, a conclusion is given.

2. Model

The determination of both azeotropic and critical endpoints of phase behavior in the mixtures has been the subject of many theoretical and experimental studies. In this task, we build a model based on the knowledge of physical and thermodynamic properties of mixture refrigerants. This model focuses on two approaches (Fedali et al. 2014). A schematic diagram of our model is presented in figure 1. In the first approach, we use the experimental data of binary mixtures, with calculated volatility to find the most volatile component. Afterwards, we utilize Microsoft Excel as a powerful tool to meet the major needs of data analysis and modeling. In the second approach, in order to estimate and describe the behavior of both azeotropic and critical point, it is important to carefully consider the choice of equations namely: the Peng and Robinson (1976) equation of state (PR) with the Mathias-Copeman (1983) alpha function (MC) and the NonRandom Two-Liquid model (NRTL) (Renon and Prausnitz 1968), using the Wong-Sandler (1992) mixing rules (WS) on which the thermodynamic model is based.

The goal is to develop reliable prediction methods, which can predict the azeotropic point and determine the critical point. Because, it is rare to find experimental data covering a wide range of operating conditions for refrigerants used in industrial refrigeration with air conditioning and which can be measured.

3. Results and discussions

From the following procedure, we can calculate the location of the critical point and azeotrope point: In the first step, we judge if an azeotropic and critical property can or cannot be obtained in binary refrigerant mixtures. In the second step, we will determine the critical points and predict the azeotropic points. We will apply the method based on experimental data for calculating and predicting azeotrope points and critical points, and later will be validated by using a thermodynamic model.

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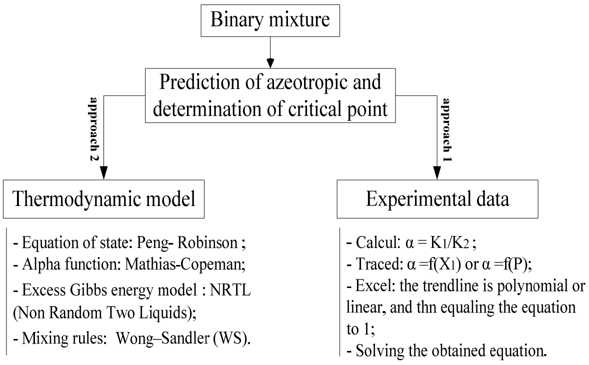

Fig. 1. Diagram of the prediction model.

3.1 Azeotropic point

3.1.1 From experimental data

Experimental data are necessary for predicting the existence of an azeotrope. Therefore, for each isotherm in a binary mixture, we calculate the value of partition coefficient K_1 of the most volatile pure substance. Table 1 shows the mixtures which have azeotropic property. One of the characteristics of our model is the relative volatility (α) that depends on experimental measurements PTxy. As it is well known, the relative volatility ($\alpha = K_i/K_j$) represents the ratio of the equilibrium constants of species i to species j. It should be noted that this ratio is not constant but changes with the concentrations of the species in vapor and liquid phases, as well as with temperature and pressure. The PTxy data have been imported from the literatures (Fedele et al. 2007; Ho et al. 2004). An example of calculating relative volatility is given in Table 2 (R1270 + R134a) and Table 3 (RC270 + R134a).

Table 1. Prediction of azetrope for the RC270 + R134a and R1270 + R134a systems.

	T/K	x_i	K_1	x_f	K_1
RC270+R134	253.15	0.1150	4.3805	0.9710	0.9310
	273.15	0.0580	2.6552	0.9780	0.9550
	293.15	0.0670	2.2687	0.9660	0.9420
R1270+R134a	273.15	0.1280	2.6797	0.9230	0.9783
	283.15	0.1200	2.4917	0.9030	0.9779
	293.15	0.1140	2.4123	0.9260	0.9784
	303.15	0.0890	2.3483	0.9050	0.9768
	313.15	0.1060	2.0755	0.8960	0.9766

Table 2 . Calculation example of relative volatility value for the R1270 + R134a system at temperature 253.15 K.

x_1	y_1	x_2	y_2	K_1	K_2	α_{12}
0.000	0.000					
0.115	0.308	0.885	0.692	2.6783	0.7819	3.4252
0.189	0.406	0.811	0.594	2.1481	0.7324	2.9329
0.299	0.488	0.701	0.512	1.6321	0.7304	2.2346
0.388	0.533	0.612	0.467	1.3737	0.7631	1.8002
0.504	0.579	0.496	0.421	1.1488	0.8488	1.3535
0.617	0.616	0.383	0.384	0.9984	1.0026	0.9958
0.674	0.638	0.326	0.362	0.9466	1.1104	0.8525
0.730	0.660	0.270	0.340	0.9041	1.2593	0.7180
0.870	0.745	0.130	0.255	0.8563	1.9615	0.4366
0.971	0.904	0.029	0.096	0.9310	3.3103	0.2812
1.000	1.000					

Table 3. Calculation example of relative volatility value for the RC270 + R134a system at temperature 273.15 K.

x_1	y_1	x_2	y_2	K_1	K_2	α_{12}
0.000	0.000					
0.128	0.343	0.872	0.657	2.6797	0.7534	3.5566
0.213	0.452	0.787	0.548	2.1221	0.6963	3.0476
0.301	0.525	0.699	0.475	1.7442	0.6795	2.5667
0.380	0.578	0.620	0.422	1.5211	0.6806	2.2347
0.445	0.614	0.555	0.386	1.3798	0.6955	1.9839
0.508	0.646	0.492	0.354	1.2717	0.7195	1.7674
0.564	0.674	0.436	0.326	1.1950	0.7477	1.5983
0.618	0.706	0.382	0.294	1.1424	0.7696	1.4843
0.665	0.730	0.335	0.270	1.0977	0.8060	1.3620
0.721	0.755	0.279	0.245	1.0472	0.8781	1.1925
0.814	0.813	0.186	0.187	0.9988	1.0054	0.9934
0.847	0.838	0.153	0.162	0.9894	1.0588	0.9344
0.895	0.877	0.105	0.123	0.9799	1.1714	0.8365
0.923	0.903	0.077	0.097	0.9783	1.2597	0.7766
1.000	1.000					

The results for both binary mixtures are plotted in Figures 2 and 3 which indicate an azeotropic behavior of the RC270 + R134a and R1270 + R134a systems. Furthermore, the positions of azeotrope in binary mixtures can be determined using the relative volatility equation. It is interesting to observe that the model accurately predict azeotropic points at α_{12} = 1.

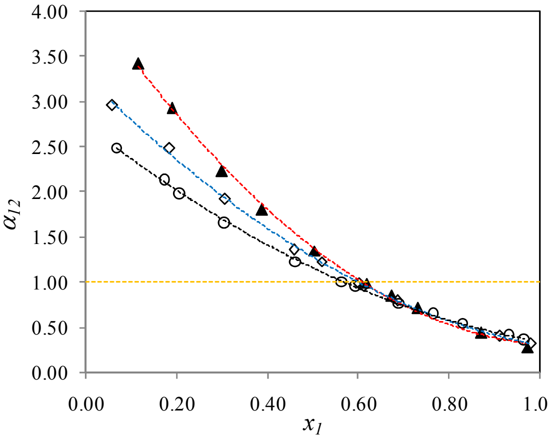

Fig. 2. Relative volatility (α) for the system RC270 + R134a at different molar fraction (x_1): (▲) 253.15 K, (◇) 273.15 K and (○) 293.15 K.

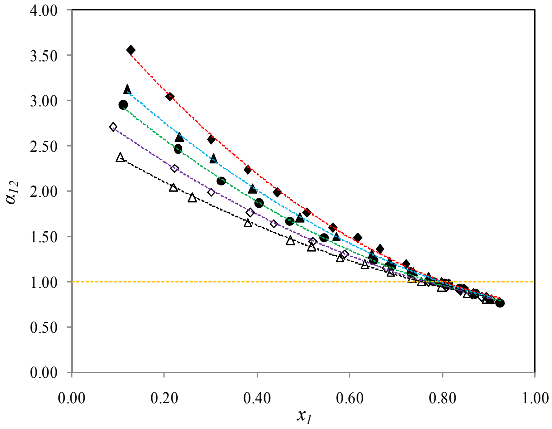

Fig. 3. Relative volatility (α) for the system R1270 + R134a at different molar fraction (x_1): (♦) 273.15 K, (▲) 283.15 K, (●) 293.15 K, (◇) 303.15 K and (Δ) 313.15 K.

3.1.2 From thermodynamic model

The results obtained by using this method from experimental data, predict precisely the existence and locations of an azeotrope. To justify the effectiveness of our method, we confirmed the obtained results by a thermodynamic model. Figures 4 and 5 illustrate the thermodynamic model predictions. They show a good agreement between the results of the two approaches (experimental data and thermodynamic model).

3.2 Critical point

3.2.1 From experimental data

Besides predicting accurately the existence and location of azeotrope, our method is able to predict and determine critical point of binary mixtures applying the same considerations as above. The PTxy data have been imported from the literatures (Madani et al. 2004; Silva-Oliver and Galcia-Luna 2002). Figures 6 and 7 illustrate very well the variation of relative volatility versus different molar fractions. They represent curves with a precision of high degree. It is remarkable to observe that the model accurately predict the critical points and therefore, the limit of the instability phase domain.

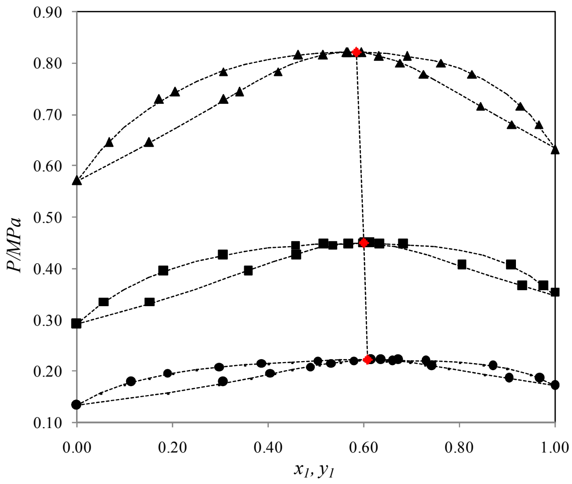

Fig. 4. VLE for the system RC270 + R134a at different temperatures: (■) 258 K, (▲) 278 K, (●) 298 K and (◆) azeotropic point.

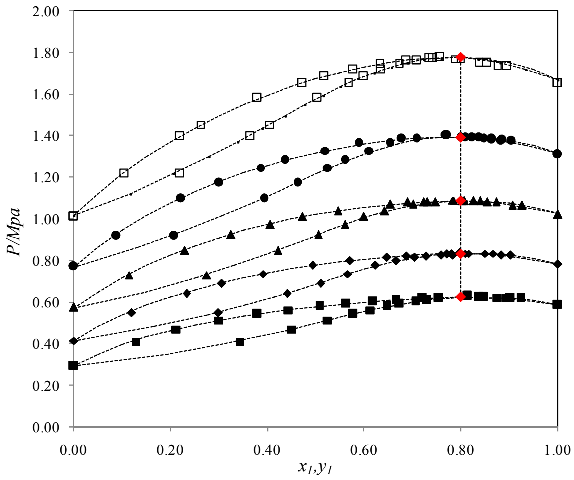

Fig. 5. VLE for the system R1270 + R134a at different temperatures: (■) 273.15 K, (♦) 283.15 K, (▲) 293.15 K, (●) 303.15 K, (□) 313.15 K and (◆) azeotropic point.

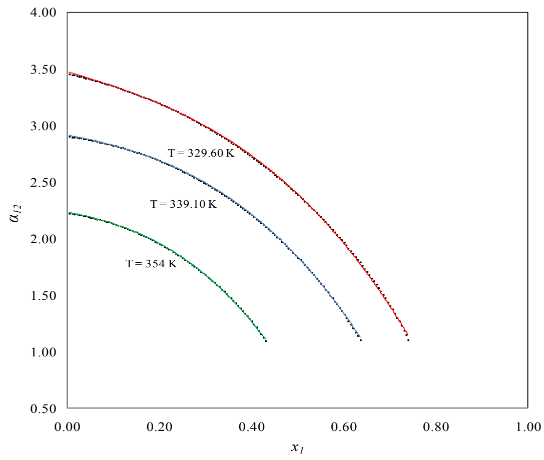

Fig. 6. Relative volatility (α) for the system R744 + R134a at different molar fraction (x_1).

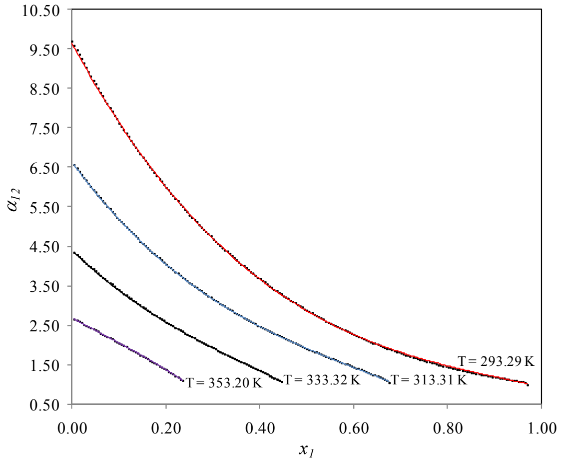

Fig. 7. Relative volatility (α) for the system R116+ R134a at different molar fraction (x_1).

3.2.2 From thermodynamic model

The thermodynamic model shows the critical point pressure versus molar fraction for each of the two components. In the same graph (Figures 8 and 9), we plotted the thermodynamic model as well as we presented the critical point locus. Figures 8 & 9 show a good agreement between the two models is observed. After we have determined the position of the azeotropes and the locations of critical points from experimental data, these values were confirmed using a thermodynamic model.

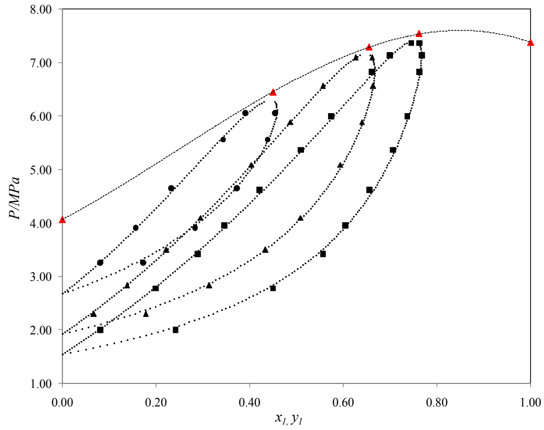

Fig. 8. VLE for the system R744 + R134a at different temperatures: (■) 329.60 K, (▲) 339.10 K, (●) 354 K and (▲) critical point.

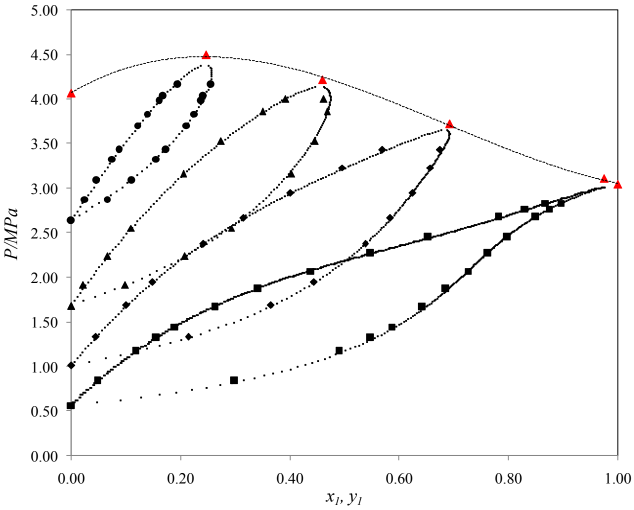

Fig. 9. VLE for the system R116 + R134a at different temperatures: (■) 293.29 K, (♦) 313.31 K, (▲) 333.32 K, (●) 353.20 K and (▲) critical point.

3.3 Model evaluation

There are differences between results obtained by both approaches presented in Figure 1. To facilitate comparison between these results, which have been listed or traced, and in order to illustrate the reliability of this model, we calculated the deviation of pressure and molar fraction for the studied systems in this work. For azetropic behaviour, we plotted the deviation, while for critical behavior we listed the values of deviation in Table 4.

Table 4. Relative deviations for the systems: R744 + R134a and R116 + R134a.

	T/K	Pc (Exp)	xc (Exp)	Pc (cal)	xc (cal)
R744 + R134a	329.60	7.3690	0.7540	7.5395	0.7614
	339.10	7.0980	0.6612	7.2862	0.6546
	354.00	6.0430	0.4560	6.4533	0.4495
R116 + R134a	293.29	2.8317	0.8953	3.0158	0.9752
	313.31	3.4302	0.6741	3.6503	0.6920
	333.32	3.9955	0.4615	4.1343	0.4586
	353.20	4.1610	0.2560	4.3706	0.2470

Figure 10 show pressure and molar fraction deviations for both Cyclopropane + 1,1,2-tetrafluoroethane and Propylene + 1,1,2-tetrafluoroethane. Relative error for both systems does not exceed 1.5 % and 2% for pressure and molar fraction respectively in the azeotropic study.

For Hexafluoroethane + 1,1,2-tetrafluoroethane and Carbon dioxide + 1,1,1,2-tetrafluoroethane, deviations obtained are presented in Table 4. For R744 + R134a relative error does not exceed 4 % and 1.5% for pressure and molar fraction respectively while for R116 + R134a they don't exceed 6% and 4% in the critical behavior study. The fitting results can be judged as evidence that our model is capable of predicting azeotropic and critical points.

3.4 Comparison with literature data

This comparison is of great interest in predicting the liquid-vapor equilibrium properties in the refrigeration industry. Results obtained with our model are compared in Table 4 for RC270 + R134a (azeotropic point) and Figure 12 for R116 + R134a (critical point).

The experimental of Fedele et al. (2007) and calculated data are reported in Table 5. We can see that the good agreement between model and experimental results.

We have plotted the experimental data (Madani et al. (2008)) on a PT diagram in which we have calculated the critical lines. The predicted critical locus is in good agreement with an error that does not exeed 3% (Figure 11).

This study provides the ability of this model to predict the azeotrope point and determine the critical point.

The binary systems involving R134a were studied with simple method to predict the azeotropic point and determine the critical point. According to our results, this method can be applied to other binary mixtures. Besides, we try to apply it to ternary mixtures.

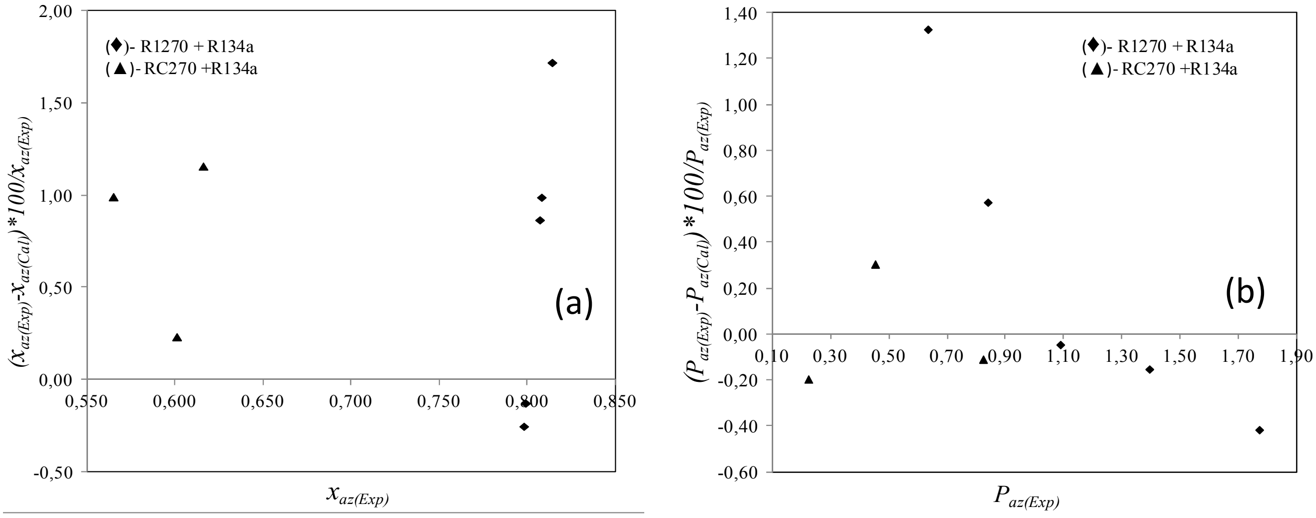

Fig. 10. Deviations in vapor composition (a) and pressure (b) of experimental data and our model.

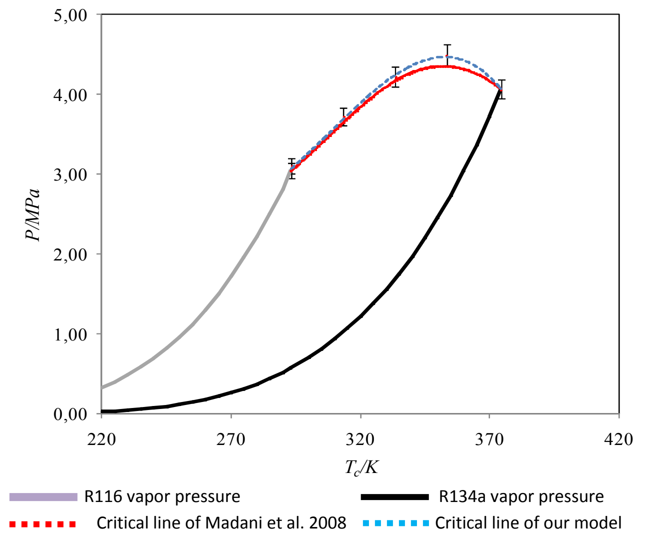

Fig. 11. PT diagram of R116 + R134a binary system:

Table 5. Comparison of molar fraction and pressure of the azeotrope for the system RC270+R134a.

T/K	x_{az}	P_{az}	x_{az}	P_{az}	$\Delta x_{az}\%$	$\Delta P_{az}\%$
	Fedele et al. (2007)		Our model			
253.15	0.620	0.221	0.617	0.222	-0.486	-0.375
273.15	0.599	0.450	0.596	0.449	-0.503	0.196
293.15	0.573	0.821	0.572	0.822	-0.112	-0.119

5. Conclusion

The prediction of azeotropic point and determination of critical point for four binary mixtures: RC270 + R134a, R1270 + R134a, R116 + R134a and R744 + R134a were studied with one method. Two approaches are presented, in the first we use experimental data to predict the existence of an azeotrope and determine the critical point. In the second, we evaluate (confirm) the reliability of the first approach with thermodynamic model. The present thermodynamic model combines Peng-Robinson equation of state with Mathias-Copeman alpha function and the NRTL excess free energy model, using the Wong–Sandler mixing rules.

The results obtained in this study are in many cases very accurate in both the azotropic point and critical point. This paper present proof that by using simple method, it is possible to predict with high accuracy: (i) the critical locus of binary systems; and (ii) the azeotrope behavior of systems.

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