Fluid Phase Equilibria 379 (2014) 120–127

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

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

Saida Fedali*, Hakim Madani, Cherif Bougriou

Laboratoire d'étude des systèmes Energétiques Industriels, Département de Mécanique, Faculté de Technologie, Université Hadj Lakhdar Batna, Algeria

ARTICLE INFO

Article history:
Received 28 February 2014
Received in revised form 6 July 2014
Accepted 16 July 2014
Available online 24 July 2014

Keywords:
Azeotrope
Binary mixture
Vapor–liquid equilibrium
Equation of state

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.

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

* Corresponding author.
E-mail addresses: saida_fedali@yahoo.fr (S. Fedali), madani_hakim@yahoo.fr (H. Madani).

http://dx.doi.org/10.1016/j.fluid.2014.07.018
0378-3812/

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.

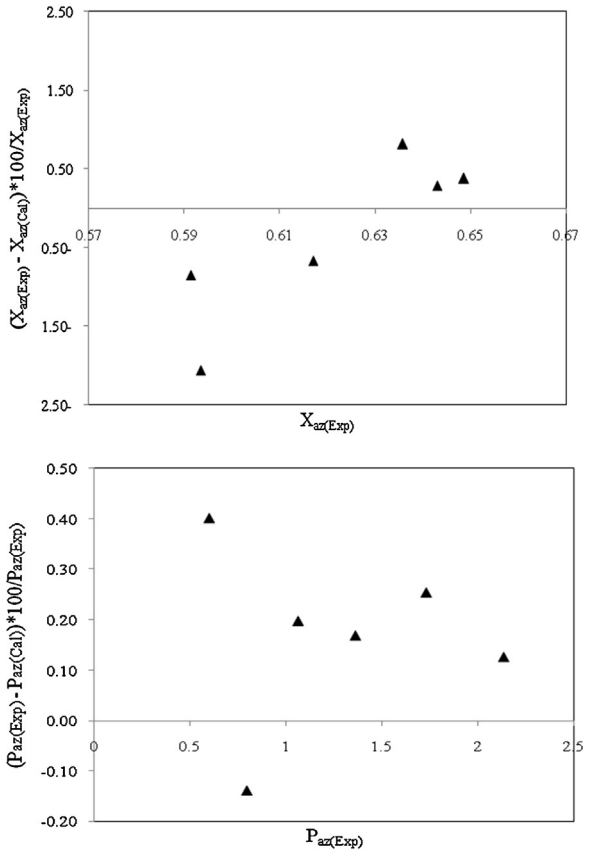

Fig. 1. Deviation of pressure and vapor-phase composition for R290 + R134a system.

- 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