Prediction of Homogeneous Azeotropes by the UNIFAC Method for Binary Refrigerant Mixtures

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In this work, four approaches based on the UNIFAC model are proposed to predict the azeotropes without any experimental data. 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 a binary system. If the vapor phase of the binary mixture is considered as an ideal gas, only the UNIFAC model is used; otherwise, the UNIFAC model, Peng−Robinson equation of state (EoS), and one of the Huron−Vidal (HV), Orbey−Sandler modification of Huron−Vidal (HVOS), or modified Huron−Vidal first-order (MHV1) mixing rules are combined to calculate the azeotrope. According to the positive or negative sign of the second derivative of the pressure with respect to the composition, the azeotropic types can be determined. In total, eight binary systems of ethane (R170) + trifluoromethane (R23), pentafluoroethane (R125) + cyclopropane (RC270), cyclopropane (RC270) + 1,1,1,2-tetrafluoroethane (R134a), pentafluoroethane (R125) + propane (R290), 1,1,1,2,3,3,3-heptafluoropropane (R227ea) + dimethyl ether (DME, RE170), 1,1,1-trifluoroethane (R143a) + butane (R600), and pentafluoroethane (R125) + isobutane (R600a) were used to verify the methods. With the results of the prediction, the cost and time of experiments can be saved.

Introduction

The traditional chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants have been or should be phased out in the refrigeration industry because of their ozone depletion potentials (ODPs) and global warming potentials (GWPs). Therefore, searching for the environmentally friendly alternative refrigerants has become one of the most important tasks for refrigeration researchers. Investigations show that it is very hard to find a pure substance that can offer good refrigeration performance and meet the environmental requirements. Therefore, mixed refrigerants, especially the azeotropes, are becoming more and more attractive for their behaviors as very nearly pure substances at their azeotropic compositions. Correlating the VLE data can obtain the azeotropes with accurate compositions, pressures, and temperatures, but the VLE experiments are very expensive and time-consuming. In this case, if there is a theoretical method that can determine the existence of the azeotropes and give the reliable azeotropic compositions, the cost and time of VLE experiments will be saved by narrowing the searching range.

Several models have been proposed to obtain acceptable results for predicting homogeneous azeotropes. Fidkowski et al. described a method to compute all the homogeneous azeotropes using the homotopy continuation technique in a multicomponent mixture.[1] Tolsma and Barton improved Fidkowski's work to compute homogeneous and heterogeneous azeotropes.[2,3] Their approach was extended to predict refrigerant mixtures by Aslam and Sunol.[4] In this method, the interaction parameters correlated from the experimental data were needed. Morrison and McLinden used the CSD equation of state (EoS) to predict the azeotropes for the binary refrigerant mixtures, but the compositions of the azeotropes were not obtained from their model.[5] Artemenko and Mazur presented an approach that employed neural networks and EoS to verify the existence of azeotropes in the binary natural and synthetic refrigerant mixtures.[6] The compositions of the azeotropes could not be obtained from their approach either.

In our previous work, a simple model based on Newton's method using the Wilson activity coefficient equation was proposed to determine the binary homogeneous azeotropes, in which one point of the measured VLE data was required.[7] Unfortunately, it is hard to obtain the VLE data of new mixtures in most circumstances. In another work, the UNIFAC model which had been widely used in the prediction of vapor−liquid equilibrium was used to optimize the parameters of the Wilson activity coefficient model, and then the azeotropes could be calculated by the Wilson model.[8] No experimental data were needed in the calculation, but the vapor phase had to be assumed to be ideal gas.

In this work, according to the thermodynamic criterion of the first derivative of the pressure with respect to the composition equal to zero at the azeotropic point for the binary system, four methods based on the UNIFAC model were developed to predict the azeotropes. For the mixtures at low to moderate pressures, the vapor phase can be considered as an ideal gas, and only the UNIFAC model was used; for the mixtures at high pressures, the vapor phase must be considered as a real gas, and so the UNIFAC model needs to combine the EoS and mixing rules to calculate the azeotrope. As with the UNIFAC−Wilson model in our earlier work, no experimental data were used in these four methods, and only a few calculations of phase equilibrium were needed. In addition, the types of the azeotropes were determined according to the positive or negative sign of

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the second derivative of the pressure with respect to the composition.

Method Formulation

Azeotropy. Harding et al. mentioned the thermodynamic conditions that must be satisfied for a homogeneous azeotrope system in their article.[9] The conditions are that at thermodynamic equilibrium the composition of each component in the liquid phase must be the same as that in the vapor phase.

For the binary homogeneous azeotrope, the phase equilibrium condition can be written in terms of the equality of fugacity

$$f_i^{V} = f_i^{L} \qquad i = 1, 2 \tag{1}$$

where f_i^V and f_i^L refer to the fugacity of composition i in the vapor and liquid phases, respectively. With the thermodynamic relationship, eq 1 can be written as

$$y_i P = \frac{x_i \gamma_i P_i^{sat} \phi_i^{sat} (PF)_i}{\phi_i^{V}} \tag{2}$$

where x_i is the mole fraction of component i in the liquid phase; y_i is the mole fraction of component i in the vapor phase; P is the pressure of the mixture at the equilibrium state; P_i^{sat} is the saturated vapor pressure; ϕ_i^{sat} is the fugacity coefficient of pure component i; γ_i is the activity coefficient; ϕ_i^{V} is the mixture fugacity coefficient of component i; and $(PF)_i$ is the Poynting factor which can be written as

$$(PF)_i = \exp\left[\frac{V_i^{l}(P - P_i^{sat})}{RT}\right] \tag{3}$$

The symbol V_i^l represents the liquid-phase molar volume of component i, and R is the gas constant.

For a binary system

$$x_1 + x_2 = y_1 + y_2 = 1 \tag{4}$$

we can obtain

$$P = \frac{x_1 \gamma_1 P_1^{sat} \phi_1^{sat} (PF)_1}{\phi_2^{V}} + \frac{x_2 \gamma_2 P_2^{sat} \phi_2^{sat} (PF)_2}{\phi_2^{V}} \tag{5}$$

For the low-pressure system, the vapor phase can be considered as an ideal gas, and as a result

$$P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \tag{6}$$

The Gibbs−Duhem relation gives[10]

$$S\mathrm{d}T - V\mathrm{d}p + \sum_i n_i \mathrm{d}\mu_i = 0 \tag{7}$$

At the binary vapor−liquid equilibrium state

$$s^{v}\mathrm{d}T - v^{v}\mathrm{d}p + y_1 \mathrm{d}\mu_1 + y_2 \mathrm{d}\mu_2 = 0 \tag{8}$$

$$s^{l}\mathrm{d}T - v^{l}\mathrm{d}p + x_1 \mathrm{d}\mu_1 + x_2 \mathrm{d}\mu_2 = 0 \tag{9}$$

The symbol s refers to the molar entropy, and v refers to the molar volume. The superscript v represents vapor phase, and superscript l represents liquid phase. Using eq 4 and subtracting eq 9 from eq 8, we obtain

$$(s^{v} - s^{l})\mathrm{d}T - (v^{v} - v^{l})\mathrm{d}p + (y_1 - x_1)(\mathrm{d}\mu_1 - \mathrm{d}\mu_2) = 0 \tag{10}$$

At an isothermal state, eq 10 can be written as

$$\frac{\mathrm{d}p}{\mathrm{d}x_1} = \frac{(y_1 - x_1)}{(v^{v} - v^{l})} \frac{(\mathrm{d}\mu_1 - \mathrm{d}\mu_2)}{\mathrm{d}x_1} \tag{11}$$

Using the second condition of the homogeneous azeotrope system, at the azeotropic composition

$$x_1 = y_1 \tag{12}$$

we get

$$\frac{\mathrm{d}p}{\mathrm{d}x_1} = 0 \tag{13}$$

Equation 13 shows that there is a pressure extremum at the azeotropic point in the phase equilibrium envelope curve. The mixture with the positive pressure extremum at the isothermal state is called a positive azeotrope, and the mixture with the negative pressure extremum is called a negative azeotrope.[5]

For the positive azeotrope, the pressure is the concave function of the composition. So the relationship of pressure and composition at the azeotropic point is given as

$$\frac{\mathrm{d}^2 p}{\mathrm{d}x_1^2} < 0 \tag{14}$$

For the negative azeotrope, the pressure is the convex function of the composition, that is

$$\frac{\mathrm{d}^2 p}{\mathrm{d}x_1^2} > 0 \tag{15}$$

In this work, eq 13 is the criterion to determine the existence and the location of the azeotrope. It can be solved by the bisection method, which repeatedly divides the interval into two subintervals and selects the one which includes the root. If the composition of x_1 locates between 0 and 1, that indicates the binary system is azeotropic; otherwise, it is zeotropic. Equation 14 and eq 15 can be used to determine if the system is positive azeotrope or negative azeotrope.

Thermodynamic Models. If the vapor phase of the system is considered as a real gas, eq 5 is needed. A few calculations of phase equilibrium are involved in eq 5, and so the suitable equations of state and mixing rules should be chosen. The saturated vapor pressures and activity coefficients in eq 5 can be computed by the Antoine equation and UNIFAC model, respectively. If the vapor phase of the system is considered as an ideal gas, eq 5 can be simplified to eq 6. Thus, only the Antoine equation and UNIFAC model are needed to calculate the azeotrope.

The Peng−Robinson equation of state (PR EoS) is used in this form[11]

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{16}$$

where p is the pressure; R is the gas constant; v is the mole volume; T is the temperature; and a and b are constants of EoS.

In the PR EoS, constants a and b can be given as

$$a(T) = 0.457235 \frac{R^2 T_c^2 \alpha(T)}{p_c} \tag{17}$$

$$b = 0.077796 \frac{RT_c}{p_c} \tag{18}$$

where

$$\alpha(T) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2 \qquad (19)$$

$$T_r = \frac{T}{T_c} \qquad (20)$$

p_c and T_c are the critical pressure and temperature, respectively, and ω is the acentric factor.

The Huron−Vidal (HV),[12] HVOS,[13] and MHV1[14,15] mixing rules are used to calculate the azeotropes combined with the PR EoS, respectively.

The HV mixing rule is employed in the form

$$a = b\left[\sum_i x_i\left(\frac{a_{ii}}{b_{ii}}\right) + \frac{G^E}{C}\right] \qquad (21)$$

$$b = \sum_i x_i b_{ii} \qquad (22)$$

where G^E is the excess Gibbs free energy at infinite pressure and C is a constant. For the PR EoS, C is −0.623225.

In the HVOS mixing rule, the expression for the parameter b is the same as that in the HV mixing rule, and the expression for the parameter a is

$$a = b\left[\sum_i x_i\left(\frac{a_{ii}}{b_{ii}}\right) + \frac{A^E}{C} + \frac{RT}{C}\sum_i x_i \ln\left(\frac{b}{b_{ii}}\right)\right] \qquad (23)$$

where A_E is the excess Helmholtz free energy at infinite pressure and C is −0.623225.

In the MHV1 mixing rule, the expression for the parameter b is the same as that in the HV mixing rule, and the expression for the parameter a is

$$a = b\left[\sum_i x_i\left(\frac{a_{ii}}{b_{ii}}\right) + \frac{G^E}{q_1} + \frac{RT}{q_1}\sum_i x_i \ln\left(\frac{b}{b_{ii}}\right)\right] \qquad (24)$$

where G^E is the excess Gibbs free energy at zero pressure and q_1 is a constant. For the PR EoS, q_1 is −0.53.

In this work, the excess Helmholtz free energy A^E and excess Gibbs free energy G^E are approximatively estimated using the following formula

$$A^E \approx G^E = RT\sum_i x_i \ln \gamma_i \qquad (25)$$

The activity coefficient can be calculated by the UNIFAC model in which the activity coefficient is separated into two parts

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad (26)$$

where $\ln \gamma_i^C$ is the combinatorial part and $\ln \gamma_i^R$ is the residual part. The combinatorial part provides the contribution due to differences in molecular size and shape, and the residual part provides the contribution due to molecular interactions. The temperature-independent group interaction parameter ψ_{mn} is given by

$$\psi_{mn} = \exp\left(-\frac{a_{mn}}{T}\right) \qquad (27)$$

where a_{mn} is the group interaction parameter with units of kelvin.[16]

The Antoine equation is used to calculate the saturated vapor pressure

$$\log_{10}\frac{P_i^{\text{sat}}}{10^5} = A_i - \frac{B_i}{T + C_i} \qquad (28)$$

where P_i^{sat} is in Pa and T is in K, and symbols A_i, B_i, and C_i are constants.

Table 1. Antoine Parameters Used in This Work

names	A	B	C
R170	3.95405	663.720	256.68
R23	4.22140	707.396	249.84
R125	4.13392	800.869	242.09
RC270	4.03084	866.150	248.00
R134a	4.11874	850.881	232.99
R290	3.92828	803.997	247.04
RE170	4.44136	1025.560	256.05
R600	3.93266	935.773	238.79
R143a	4.06800	801.340	244.55
R600a	4.00272	947.540	248.87

Mathematical Formulation. The difference quotients used in this work were given by

$$P'(x) = \frac{P(x+h) - P(x)}{h} \qquad (29)$$

$$P''(x) = \frac{P(x+h) - 2P(x) + P(x-h)}{h^2} \qquad (30)$$

where $P'(x)$ and $P''(x)$ represent the first and second derivatives of pressure with respect to composition, respectively, and h represents the step length. Equation 13 shows that the sign of $P'(x)$ will change at the azeotropic composition, which can help to search the root of eq 13 from 0 to 1 using the bisection method. A few calculations of phase equilibrium are needed in the process of searching the root. A root between 0 and 1 indicates the existence of the azeotropy, which is just the azeotropic composition. According to eq 14 and eq 15, the type of the azeotrope can be determined by judging the sign of $P''(x)$ at the azeotropic composition.

Results and Discussion

Several binary systems of ethane (R170) + trifluoromethane (R23),[17] pentafluoroethane (R125) + cyclopropane (RC270),[18] cyclopropane (RC270) + 1,1,1,2-tetrafluoroethane (R134a),[18] pentafluoroethane (R125) + propane (R290),[19] 1,1,1,2,3,3,3-heptafluoropropane (R227ea) + dimethyl ether (DME, RE170),[20] 1,1,1-trifluoroethane (R143a) + butane (R600),[21] and pentafluoroethane (R125) + isobutane (R600a)[22] were used to verify the methods in this work. Every system was calculated by four methods which were the UNIFAC model (when the vapor phase of the system was considered as an ideal gas), the PR−HV−UNIFAC model, the PR−HVOS-UNIFAC model, and the PR−MHV1−UNIFAC model. These methods are called the UNIFAC, HV, HVOS, and MHV1 methods, respectively, in the following sections. Antoine parameters used in the methods are shown in Table 1.[23] Group interaction parameters can be obtained from refs 24 and 25. The predicted results and the experimental data at different temperatures for these systems are listed in Table 2. The deviations between the experimental data and the calculated data computed by the UNIFAC−Wilson method are also shown in Table 2. The symbol $x_{1,\text{exp}}$ refers to the azeotropic composition obtained from experiment. The symbols $x_{1,\text{U}}$, $x_{1,\text{HV}}$, $x_{1,\text{HVOS}}$, and x_{MHV1} refer to the azeotropic compositions computed by UNIFAC, HV, HVOS, and MHV1 methods, respectively. The symbols Δx_{U}, Δx_{HV}, Δx_{HVOS}, and Δx_{MHV1} represent the deviations between the data calculated by these four models and the experimental data. The deviations are also plotted in Figure 1. The symbol Δx_{UW} refers to the

Table 2. Experimental Data and the Results of the Prediction[a]

systems	T/K	$x_{1,\mathrm{exp}}$	$x_{1,\mathrm{U}}$	$x_{1,\mathrm{HV}}$	$x_{1,\mathrm{HVOS}}$	$x_{1,\mathrm{MHV1}}$	Δx_{U}	Δx_{HV}	Δx_{HVOS}	Δx_{MHV1}	Δx_{UW}
R170 (1) + R23 (2)	188.31	0.585	0.610	0.612	0.612	0.612	0.025	0.027	0.027	0.027	0.036
	193.28	0.580	0.601	0.602	0.602	0.602	0.021	0.022	0.022	0.022	0.033
	198.66	0.573	0.592	0.591	0.591	0.592	0.019	0.018	0.018	0.019	0.030
	212.84	0.554	0.568	0.567	0.567	0.567	0.014	0.013	0.013	0.013	0.022
	228.50	0.534	0.545	0.543	0.543	0.543	0.011	0.009	0.009	0.009	0.017
	243.76	0.517	0.523	0.524	0.524	0.524	0.006	0.007	0.007	0.007	0.011
R125 (1) + RC270 (2)	253.15	0.755	0.916	0.882	0.883	0.884	0.161	0.127	0.128	0.129	0.152
	273.15	0.779	0.938	0.885	0.886	0.889	0.159	0.106	0.107	0.110	0.149
	293.15	0.792	0.958	0.877	0.878	0.884	0.166	0.085	0.086	0.092	0.155
RC270 (1) + R134a (2)	253.15	0.620	0.626	0.608	0.608	0.608	0.006	−0.012	−0.012	−0.012	0.040
	273.15	0.599	0.605	0.579	0.579	0.580	0.006	−0.020	−0.020	−0.019	0.033
	293.15	0.573	0.586	0.551	0.551	0.552	0.013	−0.022	−0.022	−0.021	0.036
R125 (1) + R290 (2)	273.15	0.802	0.696	0.672	0.672	0.673	−0.106	−0.130	−0.130	−0.129	−0.103
	283.15	0.770	0.710	0.679	0.679	0.681	−0.06	−0.091	−0.091	−0.089	−0.057
	293.15	0.772	0.725	0.685	0.685	0.687	−0.047	−0.087	−0.087	−0.085	−0.045
	303.15	0.767	0.739	0.688	0.688	0.692	−0.028	−0.079	−0.079	−0.075	−0.026
	313.15	0.779	0.753	0.689	0.689	0.694	−0.026	−0.090	−0.090	−0.085	−0.024
R227ea (1) + RE170 (2)	278.15	0.616	0.607	0.599	0.599	0.599	−0.009	−0.017	−0.017	−0.017	
	293.15	0.620	0.599	0.578	0.578	0.578	−0.021	−0.042	−0.042	−0.042	
	308.15	0.647	0.598	0.562	0.562	0.562	−0.049	−0.085	−0.085	−0.085	

[a] $\Delta x_{\mathrm{U}} = x_{1,\mathrm{U}} - x_{1,\mathrm{exp}}$; $\Delta x_{\mathrm{HV}} = x_{1,\mathrm{HV}} - x_{1,\mathrm{exp}}$; $\Delta x_{\mathrm{HVOS}} = x_{1,\mathrm{HVOS}} - x_{1,\mathrm{exp}}$; $\Delta x_{\mathrm{MHV1}} = x_{1,\mathrm{MHV1}} - x_{1,\mathrm{exp}}$.

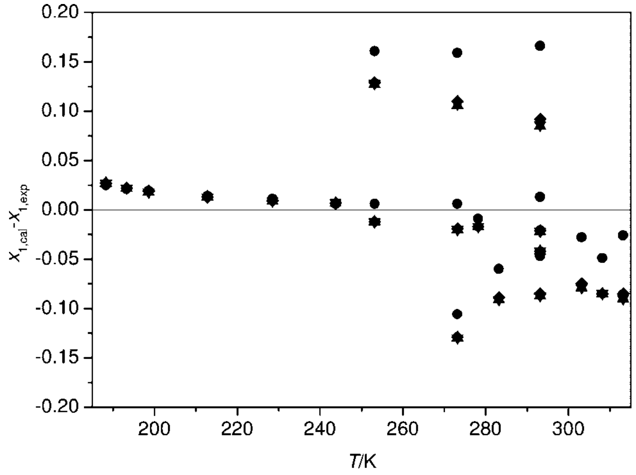

Figure 1. Deviations of azeotropic composition between the calculated data and the experimental data: ●, UNIFAC model; ▲, PR−HV−UNIFAC model; ▼, PR−HVOS−UNIFAC model; ◆, PR−MHV1−UNIFAC model.

deviations between the data calculated by the UNIFAC−Wilson method[8] and the experimental data. The azeotropic types of the five azeotropic systems were determined by computing the second derivatives of the pressures with respect to compositions. The results are listed in Table 3. The symbols $P''(x_{\mathrm{u}})$, $P''(x_{\mathrm{HV}})$, $P''(x_{\mathrm{HVOS}})$, and $P''(x_{\mathrm{MHV1}})$ refer to the second derivatives of the pressures calculated by those four methods at the azeotropic compositions.

Ethane (R170) + Trifluoromethane (R23) System. The results of calculation at six temperatures are shown in Table 2 and Table 3. All the methods show similar results that give good agreement with the experimental data. They all perform better than the UNIFAC−Wilson method that is mentioned in our previous work. The calculations using HV and HVOS methods give the same results at six temperatures. The largest deviations of the four methods all emerged at the lowest temperature 188.31 K.

Pentafluoroethane (R125) + Cyclopropane (RC270) System. The results for the pentafluoroethane (R125) and cyclopropane (RC270) binary system at (253.15, 273.15, and 293.15) K are shown in Table 2. The direct use of the UNIFAC method (the vapor phase of the system was considered as an ideal gas) behaves differently with the other methods and gives the worst results. The HV, HVOS, and MHV1 methods give similar results, and the HV method is the best. The results of the UNIFAC−Wilson method are better than that of the UNIFAC method but worse than those by the HV, HVOS, and MHV1 methods.

Cyclopropane (RC270) + 1,1,1,2-Tetrafluoroethane (R134a) System. As shown in Table 2, the binary mixtures of cyclopropane (RC270) and 1,1,1,2-tetrafluoroethane (R134a) were calculated by four methods at (253.15, 273.15, and 293.15) K. All the calculated results agree well with the experimental data. The UNIFAC method gives the best results, and the largest positive deviation is 0.013 at 293.15 K. The HV method and HVOS method obtain the same results, and they both give the negative deviations. The MHV1 method also gives the negative deviations, and the largest deviation is −0.021 at 293.15 K. The smallest deviations of these four methods all emerged at 253.15 K. All the methods performed better than the UNIFAC−Wilson method.

Pentafluoroethane (R125) + Propane (R290) System. The mixtures of pentafluoroethane (R125) and propane (R290) were calculated by four methods at five temperatures, and the results are shown in Table 2. For this system, all the methods give the negative deviations. The UNIFAC method performs much better than the other methods (including the UNIFAC−Wilson method) at all five temperatures. The MHV1 method behaves a little better than HV and HVOS methods. The largest deviation of this system is −0.130 which is presented by HV and HVOS methods at 273.15 K. The MHV1, HV, and HVOS methods all perform worse than the UNIFAC−Wilson method.

1,1,1,2,3,3,3-Heptafluoropropane (R227ea) + Dimethyl Ether (DME, RE170) System. The results of the calculations for the binary system of 1,1,1,2,3,3,3-heptafluoropropane (R227ea) and dimethyl ether (DME, RE170) at (278.15, 293.15, and 308.15) K are shown in Table 2. Because of the lack of the Antoine parameters, the saturated vapor pressures of R227ea were used directly from the experimental data of the literature in the calculation. The UNIFAC method obtains the best results which show good agreement with the experimental data. The

Table 3. Results of the Second Derivatives of the Pressures with Respect to Compositions

systems	T/K	P''/Pa (x_u)	P''/Pa (x_{HV})	P''/Pa (x_{HVOS})	P''/Pa(x_{MHV1})
R170 + R23	188.31	−78426	−88392	−88392	−88913
	193.28	−109291	−124849	−124849	−125626
	198.66	−152628	−177766	−177766	−178918
	212.84	−331175	−416648	−416647	−419321
	228.50	−676194	−967778	−967780	−971430
	243.76	−1215340	−2119548	−2115876	−2102405
R125 + RC270	253.15	−345125	−374270	−373916	−372584
	273.15	−644192	−806819	−804730	−798011
	293.15	−1085884	−1635682	−1626975	−1598328
RC270 + R134a	253.15	−157286	−177157	−177117	−177477
	273.15	−386703	−469529	−469465	−469570
	293.15	−778006	−1059147	−1057093	−1052734
R125 + R290	273.15	−766639	−948052	−948002	−942162
	283.15	−1020711	−1348195	−1347823	−1335355
	293.15	−1327430	−1908239	−1907711	−1880393
	303.15	−1690781	−2727248	−2725740	−2662942
	313.15	−2114110	−4079711	−4075874	−3890769
R227ea + RE170	278.15	345387	367755	368726	367905
	293.15	585810	661555	663890	661992
	308.15	921594	1119673	1123211	367905

other three methods give similar results and perform worse. All the methods give the negative deviations for this system. The smallest deviation is presented by the UNIFAC method at 278.15 K. This system was not calculated with the UNIFAC−Wilson method in our previous work,[8] so the deviations obtained from this method are absent in Table 2.

1,1,1-Trifluoroethane (R143a) + Butane (R600) and Pentafluoroethane (R125) + Isobutane (R600a) Systems. As shown in Table 2, no root is found in the range of 0 to 1 by the four methods for these two binary systems at their experimental temperatures, respectively. This indicates that there is no azeotrope at the tested temperatures for these two systems, just as shown in the literature.[21,22]

As shown in Table 3, the systems of ethane (R170) + trifluoromethane (R23), pentafluoroethane (R125) + cyclopropane (RC270), cyclopropane (RC270) + 1,1,1,2-tetrafluoroethane (R134a), and pentafluoroethane (R125) + propane (R290) are positive azeotropes since the second derivatives of the pressures at the azeotropic compositions are negative. The system of 1,1,1,2,3,3,3-heptafluoropropane (R227ea) + dimethyl ether (DME, RE170) is negative azeotrope. These conclusions agree well with the results of the literature.

Conclusions

On the basis of the thermodynamic criteria that the first derivative of the pressure with respect to the composition equals zero at the azeotropic point for the binary system, four methods are proposed to predict the azeotropes. All of these methods were developed based on the UNIFAC model, which had been widely used in the prediction of vapor−liquid equilibrium. No experimental data were used, and only a few calculations of phase equilibrium were needed. If the vapor phase of the binary mixture was considered as an ideal gas, only the UNIFAC model was used; otherwise, the UNIFAC model combined with the PR EoS and one of the HV, HVOS, and MHV1 mixing rules was used to calculate the azeotrope. By computing the second derivative of the pressure with respect to the composition, the azeotropic types can be determined to be positive or negative. Several binary systems were used to verify these methods. Comparing the experimental data and our previous work, we find that these methods could give reliable results in prediction of the azeotropes and could predict the azeotropic types. With the results of the prediction, the cost and time of the experiment can be saved.

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