Isothermal Vapor−Liquid Equilibria for 1,1-Difluoroethane (R152a) + Propane (R290) at Temperatures between (254.31 and 287.94) K

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The vapor−liquid equilibrium (VLE) data for the binary system of R152a + R290 were measured with a recirculation method at five temperature points from (254.31 to 287.94) K. All of the data were correlated by the Peng−Robinson (PR) EoS with the Huron−Vidal (HV) mixing rule involving the nonrandom two-liquid (NRTL) activity coefficient model. The correlated results show good agreement with the experimental data at each temperature. The data were also compared with the results obtained from the literature. Azeotropic behavior can be found at the measured temperature range.

Introduction

The traditional chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants have been or should be phased out because of their ozone depletion potential (ODP) and high global warming potential (GWP). Therefore, searching for environmentally friendly alternative refrigerants becomes very important in the refrigeration industry. Former investigations show that it is very hard to find pure substance candidates with appropriate properties. Therefore, mixed refrigerants are becoming more and more attractive. Mixtures of hydrocarbons (HCs) and hydrofluorocarbons (HFCs) are considered as promising alternative refrigerants because of their zero ODP and low GWP. The potential refrigeration performance of these mixtures as alternative refrigerants can be estimated by their thermodynamic parameters. Vapor−liquid equilibrium (VLE) data is one of the most important fundamental parameters. In this work, VLE data for the binary system of 1,1-difluoroethane (R152a) + propane (R290) were measured with a recirculation method at the temperature range of (254.31 to 287.94) K and correlated with the Peng−Robinson[1] equation of state (PR EoS) incorporating the Huron−Vidal (HV) mixing rule[2] utilizing the nonrandom two-liquid (NRTL)[3] activity coefficient model. Meanwhile, the present measured data were also compared with the results obtained from the literature, and details will be presented in the following sections.

Experimental Section

Materials. R152a was supplied by Changshu 3F Fluorochemical Industry Co with a declared mole fraction purity of > 0.999. R290 was provided by Dalian Special Gas Industry Company with a declared mole fraction of > 0.999. Both of the materials were used without further purification.

Apparatus. The VLE data of R152a + R290 were measured with an apparatus based on the vapor-phase recirculation method which has been introduced in our previous work.[4−6] A stainless steel equilibrium cell with a volume of 300 cm^3 was immerged in the liquid bath. The liquid bath was filled with R12 (dichlorodifluoromethane). It was cooled by the liquid nitrogen coil and heated by an electric heater. A stirrer was located in the liquid bath to obtain a uniform temperature distribution. The liquid bath was placed in a vacuum vessel to prevent the heat transfer to the environment. A self-made electromagnetic pump outside of the vacuum vessel was used to drive the vapor phase into the liquid phase in the cell. The liquid bath temperature fluctuation was controlled to less than ± 0.01 K by a Shimaden SR 253 digital controller. A gas chromatograph (Beifen SP3400) equipped with a thermal conductivity detector (TCD) was used to measure the phase composition at the equilibrium state. The uncertainty of the composition measurement is estimated to be ± 0.003 in mole fraction after careful calibration (different from previous data due to the difference of the material purity and chromatographic column). The temperature in the equilibrium cell was measured by a 25 Ω standard platinum resistance thermometer which was inserted in the cell. The thermometer was calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences with an uncertainty of ± 0.003 K. The combined standard uncertainty of the temperature measurement is estimated to be ± 0.01 K. The pressure in the cell was measured by a pressure transducer (Druck PMP 4010) with a full scale of 6 MPa and an uncertainty of ± 0.002 MPa. The combined standard uncertainty of the pressure measurement is estimated to be within ± 0.005 MPa.

Experimental Procedure. The cell and the recirculation loop were first evacuated to remove the impurities at room temperature. While the temperature of the liquid bath was decreasing, the pure less volatile component (R152a in this work) was driven into the equilibrium cell. After the desired temperature was reached and maintained constant for 1 h, the saturated vapor pressure of the pure component was measured. The more volatile component (R290 in this work) was then charged to the cell and mixed with R152a sufficiently through the circulation of the vapor phase. After the pump worked for at least 2 h and the fluctuation of the pressure was less than ± 0.001 MPa in 0.5 h, the equilibrium state was considered to be established. After

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that, the pressure in the cell was measured. The vapor and liquid mole fractions were measured respectively by the gas chromatograph at least three times, and then the average value was recorded. Repeating this process by adding the more volatile component step by step, the VLE data of other compositions were measured. At last, the system was evacuated again, and the pure R290 was charged to measure its saturated vapor pressure.

Results and Correlation

VLE data for the binary system of R152a + R290 were measured at five temperature points of (254.31, 259.27, 269.26, 279.47, and 287.94) K. All of the experimental data were correlated by the PR EoS with the HV mixing rule involving the NRTL activity coefficient model (PR−HV−NRTL model).

The PR EoS is given below:

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{1}$$

where p is the pressure, R is the gas constant ($R = 8.314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ in this work), 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 are defined as:

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

$$b = 0.077796\frac{RT_c}{p_c} \tag{3}$$

where

$$\alpha(T) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2 \tag{4}$$

$$T_r = \frac{T}{T_c} \tag{5}$$

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

The HV mixing rule is used in the form:

$$a = b\left[\sum_i x_i\left(\frac{a_{ii}}{b_{ii}}\right) - \frac{g_\infty^E}{C}\right] \tag{6}$$

$$b = \sum_i x_i b_{ii} \tag{7}$$

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

The NRTL activity coefficient model is used to calculate the excess Gibbs energy in the form:

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji}G_{ji}x_j}{\sum_l G_{li}x_l} \tag{8}$$

$$\tau_{ji} = \frac{\Delta g_{ji}}{RT} \tag{9}$$

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{10}$$

$$\alpha_{ji} = \alpha_{ij} \tag{11}$$

where $\tau_{ii} = 0$, $\alpha_{ii} = 0$, and α_{ji}, τ_{ji}, and τ_{ij} are adjustable parameters. In this work, $\alpha_{ji} = 0.3$.

Table 1. Critical Parameters and Acentric Factors for R152a and R290

compound	T_c/K	p_c/MPa	ω
R152a	386.41	4.5168	0.27521
R290	369.89	4.2512	0.15210

Table 2. Experimental and Calculated Vapor Pressure of R152a and R290

T/K	p_{exp}/MPa	p_{ref}/MPa	Δp^a/MPa	$\Delta p/p^b$
		R152a		
254.31	0.127	0.127	0.000	0.000
259.27	0.156	0.156	0.000	0.000
269.26	0.231	0.229	0.002	0.866
279.47	0.331	0.329	0.002	0.604
287.94	0.437	0.436	0.001	0.229
		R290		
254.31	0.257	0.255	0.002	0.778
259.27	0.303	0.303	0.000	0.000
269.26	0.422	0.420	0.002	0.474
279.47	0.574	0.573	0.001	0.174
287.94	0.727	0.727	0.000	0.000

[a] $\Delta p = p_{exp} - p_{ref}$. [b] $\Delta p/p = 100((p_{exp} - p_{ref})/p_{exp})$.

The gradient method is used to calculate the adjustable parameters τ_{ji} and τ_{ij} from the experimental data by minimizing the following objective function:

$$F = \sum_{i=1}^{N}\left(\frac{|p_{exp} - p_{cal}|}{p_{exp}}\right) \tag{12}$$

where N is the number of the experimental data points and p_{exp} and p_{cal} are the pressures obtained from the experiment and calculation, respectively.

The critical temperatures, critical pressures, and acentric factors for R152a and R290 used in the correlation are listed in Table 1.[7] The vapor pressure data of R152a and R290 were compared with the data calculated from REFPROP 8.0,[7] and the results are shown in Table 2. Good agreement can be observed.

All of the experimental and correlated results are presented in Table 3 and plotted in Figure 1. The symbols x_{1exp} and y_{1exp} refer to the mole fractions of the liquid and vapor phases for R152a. y_{1cal} refers to the mole fraction of the vapor phase obtained from the calculation. Δp and Δy represent the deviations between the experimental data and the calculated data. They are also shown in Figures 2 and 3, respectively. As shown in Figure 1, the correlated results agree well with the experimental data at each temperature. The average absolute deviations (AAD) of vapor phase mole fraction, the average relative deviations (ARD) of pressure, and root-mean-square (rms) deviations of pressure and vapor-phase mole fraction are presented in Table 4. The adjustable parameters τ_{ji} and τ_{ij} were regressed as functions of the temperature to ensure that they can be used in the entire temperature range, which can be written as:

$$\tau_{ij} = -0.430584 + \frac{212.64}{T} + \frac{20330.5}{T^2} \tag{13}$$

$$\tau_{ji} = -0.353811 + \frac{329.677}{T} + \frac{40323.9}{T^2} \tag{14}$$

VLE data of the R152a + R290 system at temperatures ranging from (273.15 to 313.15) K at 10 K intervals were reported in the literature.[8] The temperature points of (273.15

Table 3. Experimental Data and Correlated Data for the Binary System of R152a (1) + R290 (2)

experimental data			calculated data with the PR−HV−NRTL model			
p_{exp}			p_{cal}		Δp^a	
MPa	$X_{1\text{exp}}$	$y_{1\text{exp}}$	MPa	$y_{1\text{cal}}$	MPa	Δy^b
254.31 K						
0.257	0.000	0.000	0.254	0.000	0.003	0.000
0.293	0.190	0.222	0.292	0.232	0.001	−0.010
0.293	0.244	0.248	0.293	0.256	0.000	−0.008
0.293	0.257	0.252	0.293	0.261	0.000	−0.009
0.293	0.265	0.256	0.293	0.263	0.000	−0.007
0.292	0.333	0.277	0.292	0.284	0.000	−0.007
0.274	0.615	0.367	0.275	0.360	−0.001	0.007
0.251	0.756	0.433	0.251	0.428	0.000	0.005
0.127	1.000	1.000	0.126	1.000	0.001	0.000
259.27 K						
0.303	0.000	0.000	0.302	0.000	0.001	0.000
0.347	0.190	0.223	0.346	0.233	0.001	−0.010
0.348	0.246	0.250	0.348	0.259	0.000	−0.009
0.348	0.257	0.255	0.348	0.263	0.000	−0.008
0.348	0.262	0.2531	0.348	0.265	0.000	−0.012
0.345	0.330	0.284	0.347	0.288	−0.002	−0.004
0.325	0.621	0.366	0.325	0.375	0.000	−0.009
0.297	0.756	0.457	0.297	0.444	0.000	0.013
0.156	1.000	1.000	0.155	1.000	0.001	0.000
269.26 K						
0.422	0.000	0.000	0.420	0.000	0.002	0.000
0.480	0.190	0.224	0.479	0.233	0.001	−0.009
0.482	0.242	0.253	0.481	0.260	0.001	−0.007
0.482	0.258	0.260	0.482	0.268	0.000	−0.008
0.481	0.262	0.254	0.482	0.269	−0.001	−0.015
0.480	0.326	0.292	0.481	0.295	−0.001	−0.003
0.449	0.621	0.400	0.449	0.399	0.000	0.001
0.409	0.758	0.484	0.409	0.477	0.000	0.007
0.231	1.000	1.000	0.228	1.000	0.003	0.000
279.47 K						
0.574	0.000	0.000	0.572	0.000	0.002	0.000
0.650	0.190	0.226	0.650	0.232	0.000	−0.006
0.655	0.242	0.257	0.654	0.263	0.001	−0.006
0.655	0.258	0.264	0.655	0.271	0.000	−0.007
0.655	0.262	0.265	0.655	0.273	0.000	−0.008
0.655	0.281	0.277	0.655	0.282	0.000	−0.005
0.654	0.333	0.312	0.654	0.305	0.000	0.007
0.610	0.618	0.420	0.611	0.421	−0.001	−0.001
0.556	0.762	0.508	0.554	0.511	0.002	−0.003
0.331	1.000	1.000	0.328	1.000	0.003	0.000
287.94 K						
0.727	0.000	0.000	0.726	0.000	0.001	0.000
0.825	0.193	0.227	0.825	0.233	0.000	−0.006
0.829	0.241	0.259	0.830	0.263	−0.001	−0.004
0.831	0.258	0.268	0.831	0.273	0.000	−0.005
0.831	0.262	0.266	0.831	0.275	0.000	−0.009
0.831	0.282	0.280	0.831	0.286	0.000	−0.006
0.830	0.334	0.308	0.830	0.311	0.000	−0.003
0.773	0.612	0.440	0.776	0.436	−0.003	0.004
0.437	1.000	1.000	0.435	1.000	0.002	0.000

[a] $\Delta p = p_{\text{exp}} - p_{\text{cal}}$. [b] $\Delta y = y_{1\text{exp}} - y_{1\text{cal}}$.

and 283.15) K are located in the measured temperature range of this work. The comparisons between the data in literature and those of this work at these two temperature points are shown in Figure 4. In Figure 4, the solid lines represent the results calculated using the PR−HV−NRTL with the adjustable parameters correlated by eqs 13 and 14 at (273.15 and 283.15) K, respectively, and the points indicated by filled circles and squares represent VLE data from the literature. The rms deviations of pressure and vapor-phase mole fraction in the literature are 0.0210 and 0.0390 at 273.15 K and 0.0210 and 0.0320 at 283.15 K, respectively. The maximum rms deviations of pressure and vapor-phase mole fraction in this work are 0.0052 and 0.0127, respectively.

Azeotropic behavior can be found from Figure 1. The azeotropic pressure and composition for each temperature can be determined by fitting the condition:[9]

$$\frac{dp}{dx_1} = 0 \tag{15}$$

The results are shown in Table 5. The symbols $x_{1,\text{az}}$ and p_{az} represent the calculated azeotropic compositions of R152a and pressures, respectively.

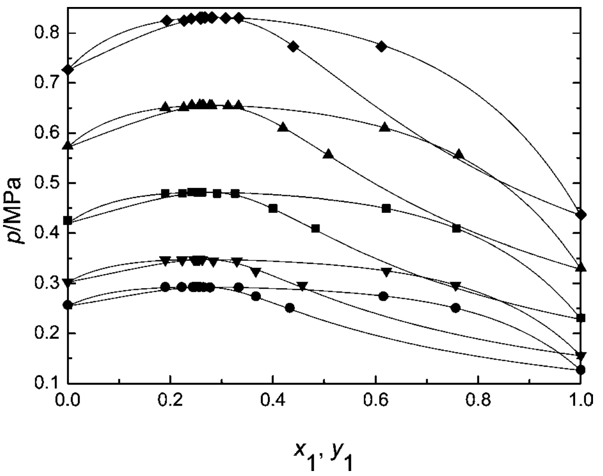

Figure 1. VLE data for the R152a (1) + R290 (2) system at four temperatures: ●, 254.31 K; ▼, 259.27 K; ■, 269.26 K; ▲, 279.47 K; ◆, 287.94 K; solid line, calculated using the PR−HV−NRTL model.

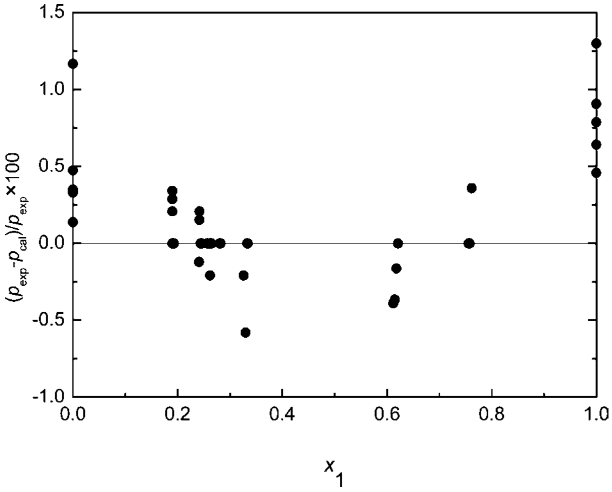

Figure 2. Deviations of the pressure between the experimental data and the calculated data.

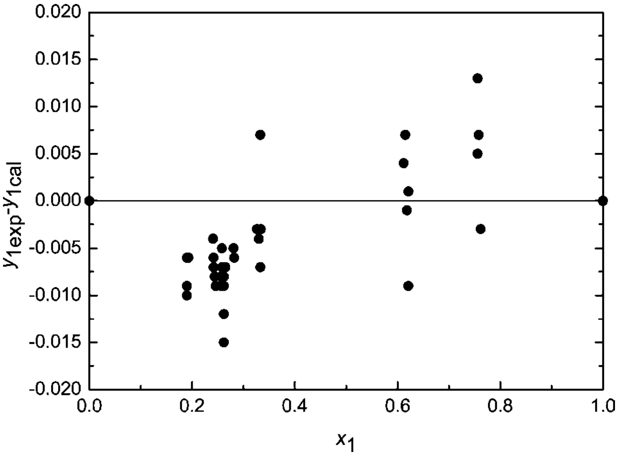

Figure 3. Deviations of the mole fraction of the vapor phase between the experimental data and the calculated data.

Table 4. Deviations of Pressures and Vapor Phase Mole Fraction for R152a + R290

T / K	254.31	259.27	269.26	279.47	287.94
ARD p/%[a]	0.3597	0.2346	0.3038	0.2020	0.1433
AAD y[b]	0.0059	0.0072	0.0055	0.0043	0.0040
rms p[c]	0.0052	0.0032	0.0049	0.0034	0.0022
rms y_2[d]	0.0094	0.0127	0.0102	0.0073	0.0066

[a] ARD $p/\% = (100/N)\sum_{i=1}^{N}((|p_{i\mathrm{exp}} - p_{i\mathrm{cal}}|)/p_{i\mathrm{exp}})$. [b] AAD $y = \sum_{i=1}^{N}((|y_{i\mathrm{exp}} - y_{i\mathrm{cal}}|)/N)$. [c] rms $p = ((1/N)\sum_{i=1}^{N}((p_{i\mathrm{exp}} - p_{i\mathrm{cal}})/p_{i\mathrm{exp}})^2)(1/2)$. [d] rms $y_2 = ((1/N)\sum_{i=1}^{N}((y_{2,i\mathrm{exp}} - y_{2,i\mathrm{cal}})/y_{2,i\mathrm{exp}})^2)(1/2)$.

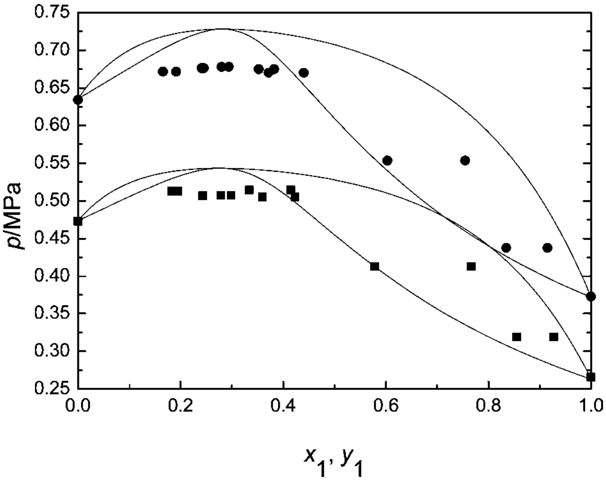

Figure 4. Comparisons between the calculated VLE data and the experimental data in ref 8: ■, 273.15 K; ●, 283.15 K; solid line, calculated using the PR−HV−NRTL model regressed in this work.

Table 5. Azeotropic Composition $x_{1,\mathrm{az}}$ and Pressure p_{az} for the R152a + R290 System at Each Experimental Temperature

T / K	$x_{1,\mathrm{az}}$	p_{az} / MPa	T / K	$x_{1,\mathrm{az}}$	p_{az} / MPa
254.31	0.262	0.293	279.47	0.282	0.655
259.27	0.266	0.348	287.94	0.288	0.831
269.26	0.274	0.482			

Conclusions

In this work, VLE data for the binary system R152a + R290 were measured with a recirculation method at five temperature points from (254.31 to 287.94) K. All of the data were correlated by the PR EoS with the HV mixing rule involving the NRTL activity coefficient model. The correlated results show good agreement with the experimental data at each temperature. The maximum ARD of pressure is 0.36 %, while the maximum AAD of vapor-phase mole fraction is 0.0072. The azeotropic behavior can be found at the measured temperature range. Therefore, this system has good potential to be a refrigerant alternative, since the azeotropes behave like pure substances at their azeotropic compositions.

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