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Vapor−Liquid Equilibria for 1,1,2,2-Tetrafluoroethane (R134) + Fluoroethane (R161) at Temperatures between (263.15 and 288.15) K

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Isothermal vapor−liquid equilibrium data of the 1,1,2,2-tetrafluoroethane (R134) + fluoroethane (R161) system were measured at temperatures ranging from (263.15 to 288.15) K with an apparatus using a recirculation method. The experimental data including temperatures, pressures, and compositions were regressed using the Peng−Robinson equation of state with the Huron−Vidal mixing rule involving the nonrandom two-liquid (NRTL) model. No azeotropic behavior was found in the measured temperature points.

Introduction

Traditional chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants have been or will be phased out since most of them have high ozone depletion potentials (ODPs) and global warming potentials (GWPs). Even some hydrofluorocarbons (HFCs) will be phased out in the coming few years because of their high GWP values. Therefore, searching for the highly efficient alternative refrigerants which are essentially friendly to the environment becomes one of the most important tasks for the refrigeration and air-conditioning industry. The former investigations show that it is very hard to find appropriate pure substance candidates. Therefore, a mixed fluid is one good choice to meet the requirements. The study of binary vapor−liquid equilibrium (VLE) is very important for the mixed refrigerants study since the VLE data are crucial data for evaluating the performance of the mixed refrigerants and optimizing mixture compositions. Some binary VLE data have been measured in our previous work.[1−6] In this study, isothermal VLE data for the 1,1,2,2-tetrafluoroethane (R134) + fluoroethane (R161) system were measured with a recirculation method at a temperature range from (263.15 to 288.15) K. The experimental data were also correlated by the Peng−Robinson[7] equation of state (PR EoS) with the Huron−Vidal (HV) mixing rule[8] utilizing the nonrandom two-liquid (NRTL)[9] activity coefficient model. R161 is a good component in some mixtures for refrigeration applications.[10] R134 has a lower GWP value than 1,1,1,2-tetrafluoroethane (R134a). The GWP values of R134a, R134, and R161 are shown in Table 1.[11] No VLE data of this system were found in previous literature.

Table 1. GWP Values of R134a, R134, and R161[11]

name	chemical name	GWP
R134a	1,1,1,2-tetrafluoroethane	1300
R134	1,1,2,2-tetrafluoroethane	1000
R161	fluoroethane	12

Experimental Section

Materials. R134 was supplied by Nanjing Yuji Tuohao Co. with a declared mole fraction purity of 0.995. R161 was supplied by Zhejiang Lantian Co. with a declared mole fraction purity of 0.997. Both materials were used without further purification.

Apparatus. The VLE data of R134 + R161 were measured by an apparatus based on the vapor-phase recirculation method which has been introduced in the previous work.[1] An equilibrium cell made by stainless steel was immerged in the liquid bath which was filled with dichlorodifluoromethane (R12). The bath was cooled by a liquid nitrogen coil and heated with an electric heater. The volume of the cell is estimated to be 300 cm^3. A self-made electromagnetic pump was used to circulate the vapor phase from the top of the cell into the liquid phase at the bottom of the cell. A stirrer in the liquid bath was used to obtain a uniform temperature distribution. The temperature fluctuation of the liquid bath controlled by a Shimaden SR 253 digital controller reaches a range within ± 0.01 K. The mole fractions of vapor and liquid phases were measured by a gas chromatograph (Beifen SP3400) equipped with a thermal conductivity detector (TCD). The gas chromatograph was calibrated using mixtures with known compositions, which were gravimetrically prepared with a Sartorius BS4000S precise balance. The uncertainty of the composition measurement is estimated to be less than ± 0.005 in mole fraction. The temperature of the cell was measured by a 25 Ω standard platinum resistance thermometer with an uncertainty of ± 0.003 K. It was calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences based on the 1990 International Temperature Scale (ITS90). The combined standard uncertainty of the temperature measurement is estimated to be ± 0.01 K. The pressure in the cell was measured by a Druck PMP 4010 pressure transducer 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 system with the cell and the connecting tubes was evacuated at first to remove the residual gas. Then, small amounts of pure R134 were charged into the equilibrium cell and evacuated by the vacuum pump three times to purge the total system. After that about 100 g of R134 was introduced to the equilibrium cell while the bath was cooled down to a desired temperature. When the desired temperature was reached and maintained for at least 1 h and the fluctuation of the temperature was within ± 0.01 K, the saturated vapor

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Table 2. Critical Parameters and Acentric Factors for R134 and R161[12]

compound	T_c/K	p_c/MPa	ω
R134	391.74	4.640	0.293
R161	375.28	5.027	0.217

Table 3. Experimental and Literature Vapor Pressure of R161[13]

T/K	p_{exp}/MPa	p_{ref}/MPa	Δp^a/MPa	$\Delta p/p^b$
263.15	0.311	0.312	−0.001	−0.322
268.15	0.372	0.372	0.000	0.000
278.15	0.517	0.517	0.000	0.000
288.15	0.700	0.699	0.001	0.322

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

pressure of the pure component could be obtained. Then, a desired amount of R161 was driven into the cell. The content of the cell was mixed sufficiently by the electromagnetic circulation pump. After the pump ran for at least 2 h and the fluctuation of the temperature was less than ± 0.01 K for at least 0.5 h, the equilibrium data can be 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 mixture was evacuated, and the saturated vapor pressure of R161 at this temperature was measured with a method similar to the R134 measurement.

Results and Correlation

VLE data for the binary system of R134 + R161 were measured at four temperatures of (263.15, 268.15, 278.15, and 288.15) 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 critical temperatures, critical pressures, and acentric factors for R134 and R161 used in the correlation are provided in Table 2.[12] The saturated vapor pressure data of R161 were compared with the literature data.[13] The results are shown in Table 3.

The PR EoS is employed in the form

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

where p is the pressure in Pa, R is the gas constant ($R = 8.314$ J·mol^{-1}·K^{-1} in this work), v is the mole volume in m^3·mol^{-1}, T is the temperature in K, and a and b are constants of the EoS.

The constants a and b of the PR EoS are defined as

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

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

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 rules take the form

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

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

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 was used to calculate the excess Gibbs energy in the form

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

$$\tau_{ji} = \frac{A_{ji}}{T} \tag{9}$$

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

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

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

Table 4. Experimental Data and Correlated Data for the Binary System of R134 (1) + R161 (2)

experimental data			calculated data with the PR-HV-NRTL model			
p_{exp}/MPa	x_{1exp}	y_{1exp}	p_{cal}/MPa	y_{1cal}	Δp^a/MPa	Δy^b
T/K = 263.15 K						
0.311	0	0	0.309	0	0.002	0
0.303	0.049	0.017	0.298	0.018	0.005	−0.001
0.285	0.116	0.045	0.283	0.047	0.002	−0.003
0.271	0.178	0.078	0.269	0.080	0.002	−0.002
0.225	0.394	0.242	0.225	0.240	0.000	0.001
0.201	0.525	0.383	0.202	0.374	−0.001	0.009
0.184	0.651	0.538	0.185	0.525	−0.001	0.013
0.168	0.819	0.757	0.167	0.750	0.001	0.007
0.155	1	1	0.154	1	0.001	0
T/K = 268.15 K						
0.372	0	0	0.368	0	0.004	0
0.360	0.049	0.018	0.355	0.018	0.005	−0.001
0.340	0.117	0.047	0.337	0.049	0.002	−0.002
0.322	0.179	0.080	0.321	0.083	0.002	−0.003
0.269	0.393	0.248	0.269	0.245	0.000	0.003
0.242	0.522	0.387	0.244	0.377	−0.002	0.010
0.223	0.652	0.543	0.223	0.533	0.000	0.010
0.204	0.820	0.753	0.202	0.756	0.002	−0.003
0.189	1	1	0.187	1	0.002	0
T/K = 278.15 K						
0.517	0	0	0.512	0	0.005	0
0.498	0.049	0.020	0.495	0.020	0.003	0.000
0.472	0.114	0.052	0.471	0.051	0.001	0.001
0.449	0.179	0.085	0.448	0.088	0.000	−0.003
0.379	0.394	0.254	0.380	0.257	−0.001	−0.003
0.344	0.521	0.398	0.346	0.388	−0.002	0.009
0.318	0.652	0.554	0.318	0.544	0.000	0.010
0.294	0.819	0.760	0.291	0.761	0.002	−0.001
0.276	1	1	0.272	1	0.004	0
T/K = 288.15 K						
0.700	0	0	0.695	0	0.005	0
0.675	0.048	0.022	0.672	0.021	0.002	0.001
0.641	0.115	0.056	0.641	0.055	0.001	0.001
0.609	0.172	0.089	0.614	0.089	−0.005	0.000
0.565	0.278	0.156	0.567	0.164	−0.002	−0.009
0.477	0.522	0.403	0.477	0.400	0.000	0.003
0.443	0.654	0.563	0.441	0.557	0.002	0.006
0.411	0.821	0.770	0.407	0.771	0.004	0.000
0.386	1	1	0.383	1	0.003	0

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

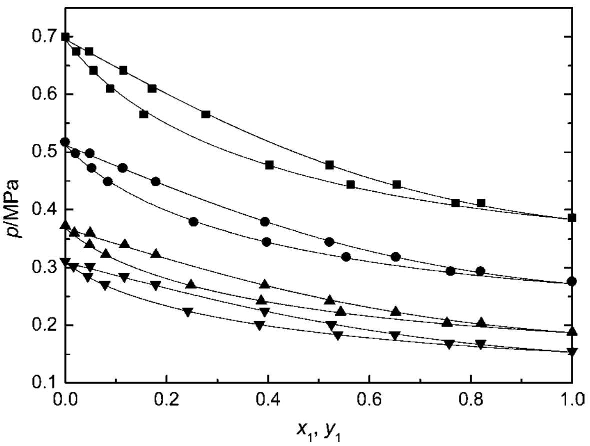

Figure 1. VLE data for the R134 (1) + R161 (2) system at four temperatures: ▼, 263.15 K; ▲, 268.15 K; ●, 278.15 K; ■, 288.15 K; −, calculated using the PR-HV-NRTL model.

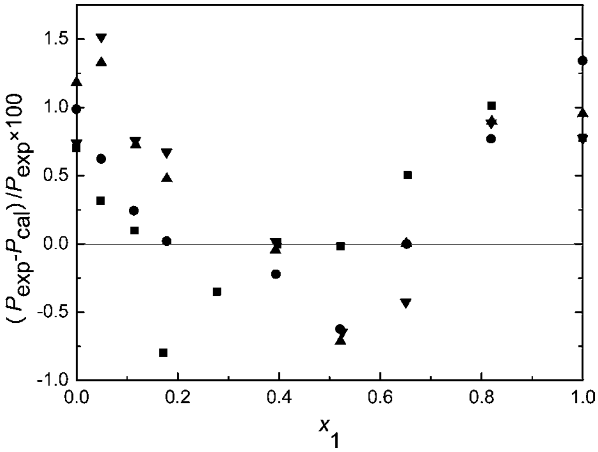

Figure 2. Deviations of the pressure between the experimental data and the calculated data: ▼, 263.15 K; ▲, 268.15 K; ●, 278.15 K; ■, 288.15 K.

The adjustable parameters A_{ij} and A_{ji} in the NRTL model were correlated from the experimental data by means of minimizing the following objective function (F) using the gradient method

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

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.

All of the experimental and calculated data are shown in Table 4 and plotted in Figure 1. The symbol p_{exp} refers to the pressures of the systems; $x_{1\text{exp}}$ and $y_{1\text{exp}}$ represent the mole fractions of the liquid and vapor phases for R134, respectively; $y_{1\text{cal}}$ refers to the mole fraction of the vapor phase obtained from the calculation; $\Delta\ p$ and $\Delta\ y$ represent the deviations between the experimental data and the calculated value. As shown in Figure 1, the correlated results agree well with the experimental data at each temperature. The relative deviations of the pressures and the deviations of vapor-phase mole fraction are shown in Figures 2 and 3, respectively. The average absolute deviations (AAD) of the vapor-phase mole fraction and the average absolute relative deviations (AARD) of pressure are presented in Table 5. The values of the adjustable parameters A_{ij} and A_{ji} in the NRTL model are also shown in Table 5. In this temperature range, no azeotropic behavior was found.

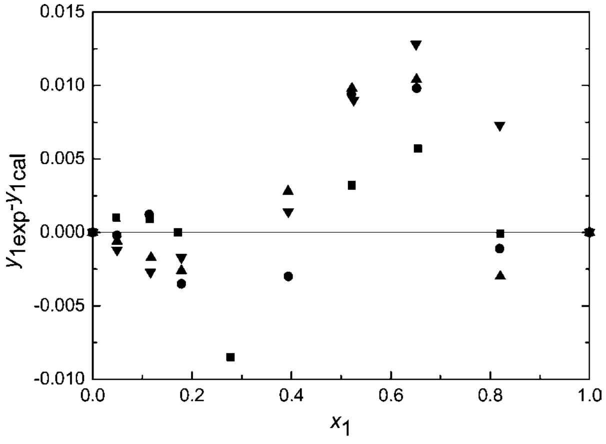

Figure 3. Deviations of the mole fraction of the vapor phase between the experimental data and the calculated data: ▼, 263.15 K; ▲, 268.15 K; ●, 278.15 K; ■, 288.15 K.

Table 5. Binary Parameters and Deviations for the R134 + R161 System

T/K	263.15	268.15	278.15	288.15
A_{ij}/K	−183.138	−187.766	−188.604	−188.939
A_{ji}/K	76.070	79.552	79.579	75.842
AARD p^a	0.75	0.69	0.55	0.50
AAD y^b	0.0040	0.0034	0.0031	0.0022

[a] AARD $p = (100/N)\ \sum_{i=1}^{N}\ ((|P_{\text{exp}} - P_{\text{cal}}|)/P_{\text{exp}})$. [b] AAD $y = \sum_{i=1}^{N}\ (|y_{i\text{exp}} - y_{i\text{cal}}|/N)$.

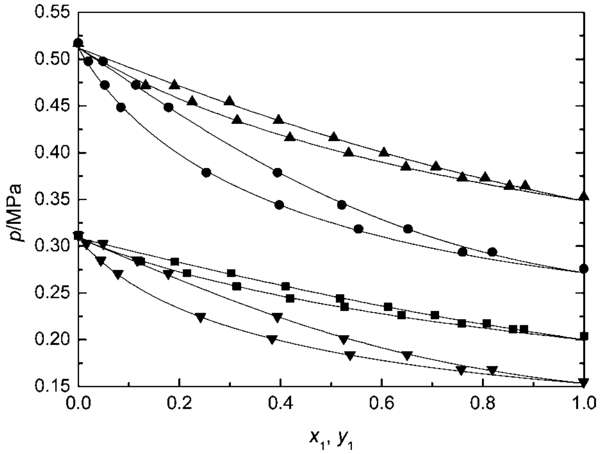

Figure 4. VLE data for R134 + R161 and R134a + R161 systems at (263.15 and 278.15) K: ▼, the R134 + R161 system at 263.15 K; ■, the R134a + R161 system at 263.15 K; ●, the R134 + R161 system at 278.15 K; ▲, the R134a + R161 system at 278.15 K; −, calculated using the PR-HV-NRTL model.

The VLE data of the R134a + R161 system have been measured in our previous work.[6] The phase diagram of the R134a + R161 and R134 + R161 systems at (263.15 and 278.15) K are plotted in Figure 4. It shows that the dew points are much closer to the bubble points in the R134a + R161 system than that in the R134 + R161 system. A detailed comparison of performance in the refrigeration cycle for these two systems needs more physical property data.

Conclusions

In this work, isothermal VLE data of the R134 + R161 system were measured at the temperatures ranging from (263.15 to 288.15) K using a recirculation method. All of the experimental data were correlated by the PR EoS using the HV mixing rule involving the NRTL activity coefficient model. The correlated results show good agreement with the experimental data. The maximum AARD of pressure is 0.75 %, and the maximum AAD of vapor-phase mole fraction is 0.0040. No azeotropic behavior was found in the measured temperature points.

Supporting Information Available:

Experimental data summary and table of experimental data and correlated data for the binary system of R134 (1) + R161 (2). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Zhang, Y.; Gong, M. Q.; Zhu, H. B.; Wu, J. F. Vapor-liquid equilibrium measurements for the ethane + hexafluoroethane system over a temperature range from (199.64 to 242.93) K. *J. Chem. Eng. Data* **2005**, *50*, 2074–2076.

(2) Zhang, Y.; Gong, M. Q.; Zhu, H. B.; Wu, J. F. Vapor-liquid equilibrium data for the ethane + trifluoromethane system at temperatures from (188.31 to 243.76) K. *J. Chem. Eng. Data* **2006**, *51*, 1411–1414.

(3) Zhang, Y.; Gong, M. Q.; Zhu, H. B.; Wu, J. F. Vapor-liquid equilibrium measurements and correlations for an azeotropic system of ethane + hexafluoroethane. *Fluid Phase Equilib.* **2006**, *240*, 73–78.

(4) Zhu, H. B.; Gong, M. Q.; Zhang, Y.; Wu, J. F. Isothermal vapor-liquid equilibrium data for tetrafluoromethane + ethane over a temperature range from (179.68 to 210.03) K. *J. Chem. Eng. Data* **2006**, *51*, 1201–1204.

(5) Zhu, H. B.; Gong, M. Q.; Zhang, Y.; Wu, J. F. Vapor-liquid equilibrium data of the methane + tetrafluoromethane system at temperatures from (159.61 to 178.93) K. *J. Chem. Eng. Data* **2007**, *52*, 463–467.

(6) Dong, X. Q.; Gong, M. Q.; Zhang, Y.; Wu, J. F. Vapor-liquid equilibria of the fluoroethane (R161) + 1,1,1,2-tetrafluoroethane (R134a) system at various temperatures from (253.15 to 292.92) K. *J. Chem. Eng. Data* **2008**, *53*, 2193–2196.

(7) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(8) Huron, M. J.; Vidal, J. New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilib.* **1979**, *3*, 255–271.

(9) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(10) Xuan, Y. M.; Chen, G. M. Experimental study on HFC-161 mixture as an alternative refrigerant to R502. *Int. J. Refrig.* **2005**, *28*, 436–441.

(11) Calm, J. M. In *Property, safety, and environmental data for alternative refrigerants*. Proceedings of the Earth Technologies Forum, Washington, DC, 1998.

(12) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(13) Cui, X. L.; Chen, G. M.; Han, X. H.; Wang, Q. Experimental vapor pressure data and a vapor pressure equation for fluoroethane (HFC-161). *Fluid Phase Equilib.* **2006**, *245*, 155–157.

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