Vapor−Liquid Equilibria for the Trifluoromethane + 1,1,1,2-Tetrafluoroethane System

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Isothermal vapor−liquid equilibrium data for the binary system of HFC-23 (trifluoromethane, IUPAC) + HFC-134a (1,1,1,2-tetrafluoroethane, IUPAC) were measured at $T = (258.15 \text{ to } 293.15)$ K in a circulation-type equilibrium apparatus. The experimental results were correlated with the Peng−Robinson−Stryjek−Vera (PRSV) equation of state using the Wong-Sandler mixing rule. The overall average deviation of pressure by the PRSV equation of state was 0.734 %, and the average deviation of vapor-phase composition by the PRSV equation of state was 0.0055.

Introduction

As a result of the regulation of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) mixtures are considered to be promising candidates for replacement of CFCs and HCFCs because their ozone depletion potentials are zero.[1−3] Vapor−liquid equilibrium (VLE) data are required as one of the important basic properties in evaluating the performance of refrigeration cycles and determining their optimal compositions. Few experimental data have been reported previously in the literature for the system such of HFC-23 (trifluoromethane, IUPAC) + HFC-134a (1,1,1,2-tetrafluoroethane, IUPAC).[4,5]

In this work, the isothermal VLE for the binary system of HFC-23 + HFC-134a from $T = (258.15 \text{ to } 293.15)$ K were measured in an equilibrium apparatus with a continueous vapor-phase circulation. Experimental data were correlated with the Peng−Robinson−Stryjek−Vera (PRSV)[6] cubic equation of state using the Wong−Sandler (WS)[7] mixing rule.

Experimental Section

Materials. The chemicals of HFC-23 ($w > 0.999$) and HFC-134a ($w > 0.999$) were supplied by Zhejiang Chemical Engineering Research Institute, China, and Honeywell Co. Ltd, USA, respectively. They were used without any further purification.

Apparatus. In this work, we used the same apparatus that was used for the VLE measurement of the HFC-125 (1,1,1,2,2-pentafluoroethane, IUPAC) + HFC-161 (fluoroethane, IUPAC) system.[8] The apparatus includes a thermostat bath, an equilibrium cell, temperature and pressure controllers, and a measurement device.

The temperature of the equilibrium cell in the thermostat bath was maintained by the refrigeration subsystem and heater subsystem. The temperature fluctuation in the bath is less than ± 4 mK in 1 h. The temperature measurement is made with a four-lead 25-Ω platinum resistance thermometer (Yunnan Instrument) with an uncertainty of ± 5 mK (ITS) and a Keithley 2010 data acquisition/switch unit with an uncertainty of less than ± 1 mK. The overall temperature uncertainty for the bath and the temperature measurement system was estimated to be less than ± 10 mK.

The pressure measurement system includes a pressure transducer (Druck PMP4010), a differential pressure null transducer (Xi'an Instrument, 1151DP), an oil-piston type dead-weight pressure gauge (Xi'an Instrument, YS-60), and an atmospheric pressure guage (Ningbo Instrument, DYM-1). A sensitive differential pressure null transducer separates the sample form the N_2-filled system. The accuracy of the differential pressure null transducer is 0.25 % within the range from (0 to 7.5) kPa. Its maximum uncertainty is 0.18 kPa. The oil-piston type dead-weight pressure gauge is less than 0.02 % within the range from (0.1 to 6.0) MPa, and its maximum uncertainty is 1.2 kPa. The accuracy of the pressure transducer is 0.04 %, and its maximum allowable pressure is 3.5 MPa, which was calibrated by the oil-piston type dead-weight pressure gauge before the experiments. The maximum uncertainty of the atmosphere gauge is ± 0.05 kPa. The whole pressure measurement system has an uncertainty of ± 1.6 kPa.

The vapor phase in the equilibrium cell was continuously recirculated by a vapor circulation pump. After equilibrium was reached, the vapor sample was withdrawn from the recycling loop, and the liquid sample was taken from the sample cell to the liquid sample line. Then they were sent and injected on-line into a gas chromatograph (GC) model 112A. Considering the margin of error and the reproducibility of GC, we generally estimated an overall accuracy in the measurements of the composition of ± 0.001 in mole fraction for both liquid and vapor phases.

Results and Discussion

Isothermal vapor−liquid equilibrium data were measured for the binary system of HFC23 + HFC134a from $T = (258.15 \text{ to } 293.15)$ K, which are shown in Table 2 and Figure 2. Throughout the paper, x and y indicate the liquid and vapor mole fractions, respectively, while p stands for the pressure in MPa. The VLE data were correlated with the PRSV [6] equation of state. The PRSV equation of state is expressed as follows:

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

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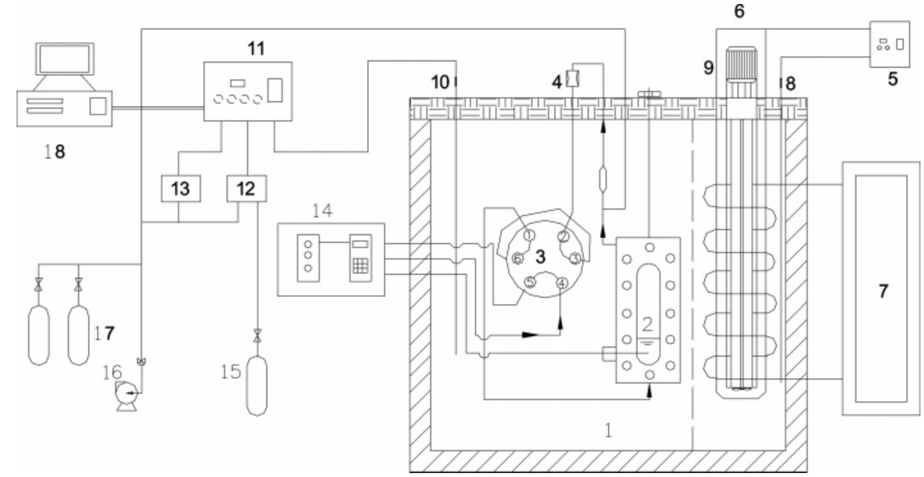

Figure 1. Experimental apparatus for the VLE measurement: 1, thermostat bath; 2, equilibrium cell; 3, six-way valve; 4, vapor circulation pump; 5, temperature controller; 6, heater; 7, refrigeration system; 8, platinum resistance thermometer; 9, motor blender; 10, high-accuracy platinum resistance thermometer; 11, Keithley 2010 data acquisition/switch unit; 12, differential pressure null transducer; 13, pressure transmitter; 14, gas chromatograph; 15, high-pressure nitrogen container; 16, vacuum pump; 17, sample reservoir; 18, computer.

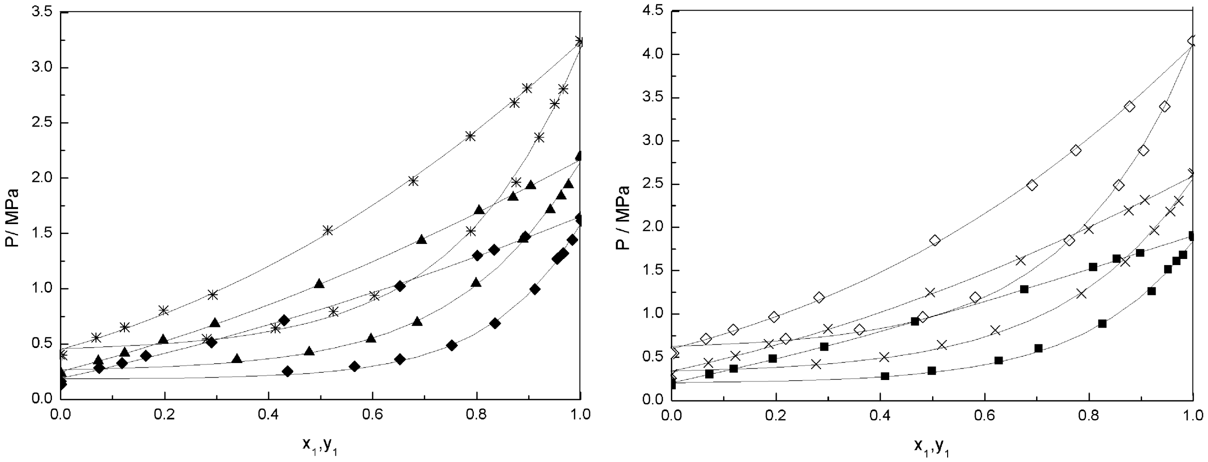

Figure 2. *p*−*x*−*y* diagram for the HFC-23 (1) + HFC-134a (2) system; ◆, 258.15 K; ■, 263.15 K; ▲, 268.15 K; ×, 275.15 K; ∗, 283.15 K; ◇, 293.15 K; −, PRSV equation of state.

Table 1. Critical Properties and Acentric Factor Used in This Paper[9]

	T_c/K	P_c/MPa	*w*
HFC-23	299.07	4.836	0.2634
HFC-134a	374.21	4.059	0.3268

with

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

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

$$\alpha(T) = [1 + k(1 - T_r^{\ 1/2})]^2 \tag{4}$$

$$k = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{5}$$

and where the parameter *a* is a function of temperature, *b* is constant, *k* is a constant characteristic of each substance, *ω* is the acentric factor. *p* is pressure, *T* is the critical pressure, *T* is the absolute temperature, T_c is the critical temperature, T_r is the reduced temperature (T/T_c), and *υ* is mole volume. The value of critical temperature T_c, critical pressure p_c, and acentric factor *ω* for HFC-23 and HFC-134a in eqs 1 to 5 are given in Table 1.

To have good representation of the VLE, we chose the WS[7] mixing rules:

$$b = \frac{\sum_i \sum_j x_i x_j (b - (a/RT))_{ij}}{1 - ((\sum_i (x_i(a_i/b_i))/RT) + (A_\infty^E/CRT))} \tag{6}$$

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{7}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)\right](1 - k_{ij}) \tag{8}$$

where k_{ij} is a binary interaction parameter and *C* is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the PRSV equation of state used in this work. A_∞^E is an excess Helmholtz free energy model at infinite pressure that can be equated to a low-pressure

Table 2. Vapor−Liquid Equilibrium Measurements for the HFC-23 (1) + HFC-134a (2) System

p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1	p/MPa	x_1	y_1
T = 258.15 K			T = 263.15 K			T = 268.15 K			T = 275.15 K			T = 283.15 K			T = 293.15 K		
0.2833	0.0741	0.3452	0.3017	0.0731	0.4090	0.3561	0.0712	0.3399	0.4449	0.0692	0.2782	0.5647	0.0691	0.2772	0.7359	0.0621	0.2194
0.3275	0.1179	0.5637	0.3639	0.1196	0.4981	0.4248	0.1223	0.4790	0.5253	0.1208	0.4086	0.6610	0.1239	0.4100	0.8423	0.1148	0.3608
0.3928	0.1640	0.6513	0.4827	0.1941	0.6263	0.5413	0.1957	0.5980	0.6644	0.1851	0.5193	0.8114	0.1994	0.5213	0.9880	0.1929	0.4829
0.5154	0.2901	0.7510	0.6192	0.2932	0.7028	0.6925	0.2954	0.6866	0.8380	0.2985	0.6211	0.9539	0.2939	0.6000	1.2127	0.2792	0.5830
0.7150	0.4296	0.8338	0.9074	0.4669	0.8251	1.0439	0.4957	0.7998	1.2588	0.4942	0.7864	1.5374	0.5147	0.7854	1.8734	0.5012	0.7635
1.0245	0.6524	0.9109	1.2818	0.6766	0.9201	1.4435	0.6928	0.8900	1.6261	0.6682	0.8705	1.9803	0.6793	0.8725	2.5125	0.6874	0.8581
1.2993	0.8016	0.9540	1.5360	0.8084	0.9510	1.7103	0.8039	0.9428	1.9880	0.7982	0.9264	2.3874	0.7892	0.9164	2.9154	0.7711	0.9055
1.3517	0.8333	0.9653	1.6319	0.8533	0.9674	1.8341	0.8688	0.9636	2.2068	0.8752	0.9567	2.6912	0.8736	0.9467	3.4219	0.8741	0.9465
1.4713	0.8938	0.9830	1.7014	0.8985	0.9793	1.9365	0.9028	0.9778	2.3284	0.9053	0.9733	2.8232	0.8979	0.9633			

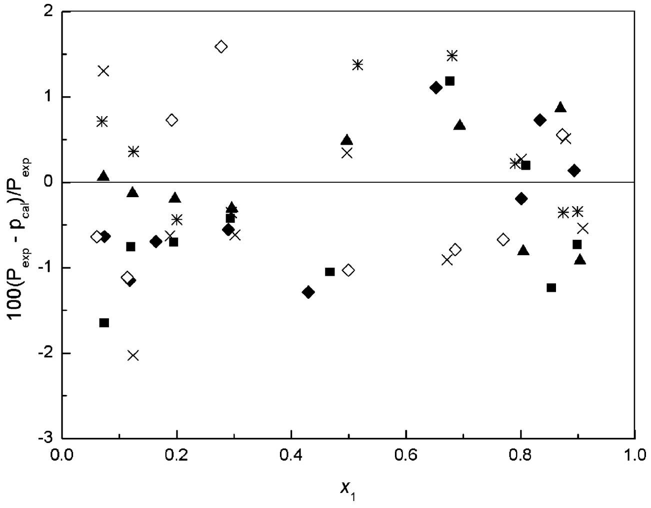

Figure 3. Deviation of saturated pressure for the HFC-23 + HFC-134a system; ◆, 258.15 K; ■, 263.15 K; ▲, 268.15 K; ×, 275.15 K; ∗, 283.15 K; ◇, 293.15 K.

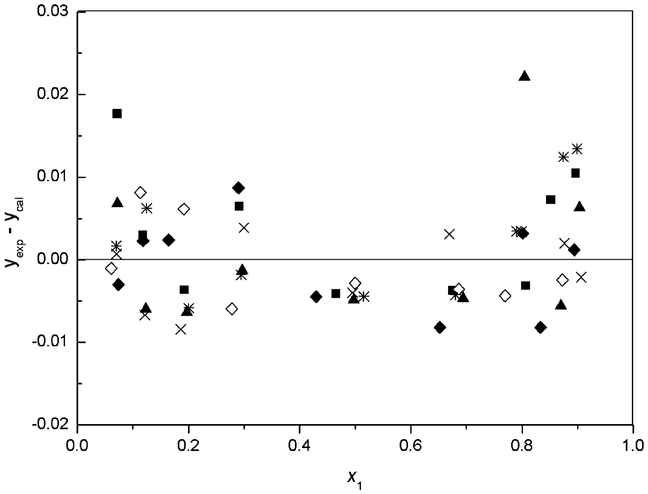

Figure 4. Deviation of the vapor-phase mole fraction of HFC-23 for the HFC-23 + HFC-134a system; ◆, 258.15 K; ■, 263.15 K; ▲, 268.15 K; ×w, 275.15 K; ∗, 283.15 K; ◇, 293.15 K.

Table 3. Values of Binary Parameters and Average Deviations of *p* and *y*

T/K	τ_{12}[a]	τ_{21}[a]	k_{12}	δp/%[b]	δy[c]
258.15	−1.6572	3.2771	0.0513	0.721	0.0050
263.15	−1.8674	4.1065	0.0510	0.885	0.0066
268.15	−1.9573	4.2319	0.0503	0.491	0.0071
275.15	−2.1116	5.0644	0.0493	0.791	0.0036
283.15	−2.0834	4.9485	0.0499	0.631	0.0060
293.15	−2.1372	4.7734	0.0505	0.887	0.0048

[a] The unit of τ_{12} and τ_{21} is J·mol^{-1}, [b] $\delta p = (1/N)\Sigma(|p_{\text{exp}} - p_{\text{cal}}|/p_{\text{exp}}) \times 100$. [c] $\delta y = (1/N)\Sigma|y_{\text{exp}} - y_{\text{cal}}|$.

excess Gibbs free energy model.[10] In this study we use the NRTL [11]model given by

$$\frac{A_{\infty}^{\text{E}}}{RT} = \sum_i x_i \sum_j \frac{x_j \exp(-\alpha_{ji}(\tau_{ji}/RT))}{\sum_k x_k \exp(-\alpha_{ki}(\tau_{ki}/RT))} \tau_{ji} \tag{9}$$

where $\tau_{ii} = 0$ and $\alpha_{ii} = 0$. $\alpha_{ij} = \alpha_{ji}$ and τ_{ij} and τ_{ji} are adjustable parameters. As it is recommended[11] to use $\alpha_{ij} = 0.3$ for system like the current one, only τ_{ij} and τ_{ji} are adjusted directly to VLE data. The adjustment is performed through a simplex algorithm using the objective function:

$$\text{OBF} = \sum_{i=1}^{N} [(y_{\text{e1}} - y_{\text{c1}})^2 + (y_{\text{e2}} - y_{\text{c2}})^2] \tag{10}$$

where N is the number of experimental points, y_{e} is the experimental vapor-phase fractions, and y_{c} is the calculated vapor-phase fractions. With objective function given in eq 10, we determine binary interaction parameters that allow calculating vapor compositions in very good agreement with experimental ones.

Table 3 lists the interaction parameters of binary mixtures for each isotherm, the binary parameters of the NRTL model with the WS mixing rules, and the average relative deviations of pressures (δp) and vapor-phase mole fraction (δy) between measured and calculated values. From the data of binary interaction parameter k_{ij}, it is evident that the binary interaction parameter for the PRSV equation of state changes slightly as the temperature increases. The overall deviations of pressure and vapor phase composition by the PRSV equation of state were 0.734 % and 0.0055, respectively. Figure 3 and Figure 4 show the comparisons of relative pressure and vapor-phase mole fraction between the measured data and the calculated results from the PRSV equation of state. From these figures and the low average deviations, we conclude that the values calculated with the PRSV equation of state and the WS mixing rules give comparatively good agreement with experimental data.

Conclusions

The VLE data for binary systems of HFC-23 + HFC-134a were measured from T = (258.15 to 293.15) K. The model of PRSV equation of state with the WS mixing rule was used to correlate the experimental data. The overall deviation of the pressure by the PRSV equation of state was 0.734 %, and the average deviation of vapor-phase composition by the PRSV equation of state was 0.0055. The predicted results show a good agreement with the experimental data.

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