Vapor−Liquid Equilibria for the Binary System of 1,1,1-Trifluoroethane (HFC-143a) + Butane (R600) at Various Temperatures

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Isothermal vapor−liquid equilibrium data for the binary mixture of 1,1,1-trifluoroethane (HFC-143a) + butane (R600) were measured at (273.15, 283.15, 293.15, 303.15, 313.15, and 323.15) K, respectively. The experiments were carried out using a continuous circulation-type equilibrium apparatus to measure temperature, pressure, and the compositions of the liquid and vapor phases. The experimental data were correlated with the Peng−Robinson equation of state (PR-EOS) using the van der Waals mixing rule. Calculated results showed good agreement with experimental data. Azeotropic behavior was not found in the temperatures studied here.

Introduction

Hydrofluorocarbons (HFCs) and hydrocarbons (HCs) have been considered as promising alternative refrigerants in place of chlorofluorocarbons (CFCs) since their ozone depletion potentials are very low. HFCs are stable but very expensive, and their global warming potential (GWP) is relatively high. On the other hand, hydrocarbons are flammable but are not expensive, and their GWP is equal to zero. The mixtures of these two compounds may have good potential for alternative refrigerants. Vapor−liquid equilibrium (VLE) data are required as one of the most important types of information to evaluate the performance of refrigeration cycles and to determine their optimal compositions. However, very few experimental data for the binary system of HFC-143a + butane have been reported previously in the literature.[1]

In this work, isothermal VLE data for the binary mixture of HFC-143a + butane at six equally spaced temperatures between (273.15 and 323.15) K were measured using a circulation-type equilibrium apparatus in which both phases were continuously recirculated. The experimental and the literature[1] data were correlated with the Peng−Robinson equation of state (PR-EOS)[2] using the van der Waals mixing rule.[3] In the range of experimental temperatures, the average absolute deviations of pressure and vapor phase compositions between experimental and calculated values were determined, and the relevant parameters were presented. All the calculated values with this model give good agreement with the experimental data. This system exhibits near-azeotropic behavior in the temperatures studied here.

Experimental

Chemicals. HFC-143a was supplied by Hi-tech Co. (China) with a guaranteed mass fraction purity higher than 0.999, and R600 (butane) was supplied by MG Industry (UK) with a guaranteed mass fraction purity higher than 0.995. Furthermore, we also analyzed these two pure components with a gas chromatograph endowed with TCD. The resulted mass fraction purities of HFC-143a and R600 were higher than 0.999 and 0.9985, respectively. They were used without further purification.

Experimental Apparatus. A schematic diagram of the apparatus for measuring the VLE is given in our previous works. Since the vapor−liquid equilibrium apparatus used in this work was the same as that used in our previous work,[4–7] it is only briefly described here. It was a circulation-type in which both liquid and vapor phases were recirculated continuously. The equilibrium cell was a type-316 stainless steel vessel within an inner volume of about 85 cm^3. In its middle part, two Pyrex glass windows of 20 mm thickness were installed before and behind so that the liquid level, mixing and circulating behavior, and critical phenomena could be observed by a back light during operation. A stirrer, rotated at variable speeds by an external magnet, was used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases.

The temperature of the equilibrium cell in the water bath was maintained by a circulator from Jeio Tech, Korea. The temperature in the cell was measured with a platinum-resistance sensor (Pt 100Ω) and a digital temperature indicator model F250MkII precision thermometer from Automatic Systems Laboratories, Ltd., United Kingdom. They were calibrated by the National Measurement Accreditation Service calibration laboratory. The total uncertainty in temperature measurements is estimated to be within 0.01 K, including sensor uncertainty, 0.001 K, temperature resolution, 0.001 K, and measurement uncertainty, 0.001 K. The pressure was measured with a pressure transducer, model XPM60, and a digital pressure calibrator, model PC106, from Beamax, Finland. Pressure calibrations are traceable to National Standards. The calibrator uncertainty was 0.0005 MPa; the sensor uncertainty was 0.0001 MPa; and measurement uncertainty was 0.0001 MPa. Therefore, the total uncertainty of the pressure measurement is estimated to be within 0.001 MPa.

The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump (Milton Roy Company) to reach the equilibrium state rapidly in the cell. The composition of the phases was determined by means of a gas chromatograph (Gow-Mac model 550P) con-

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Table 1. Characteristic Properties of the Chemicals (Critical Temperature T_c, Critical Pressure P_c, Acentric Factor ω) from Database REFPROP 6.01[8]

component	chemical formula	molecular weight	T_c/K	P_c/MPa	ω
HFC-143a(1)	$C_2H_3F_3$	84.04	346.04	3.776	0.2611
butane (2)	C_4H_{10}	58.12	425.16	3.796	0.1995

Table 2. Comparison of the Measured Pure Component Vapor Pressures P, with Reference Vapor Pressures P_{REF} from the Database REFPROP 6.01[8]

T/K	P/MPa	P_{REF}/MPa	ΔP^a/MPa	$\lvert\Delta P/P\rvert^b$
		butane		
273.15	0.104	0.103	0.001	
283.15	0.150	0.149	0.001	0.007
293.15	0.208	0.208	0.000	0.000
303.15	0.284	0.284	0.000	0.000
313.15	0.378	0.379	−0.001	0.003
323.15	0.494	0.497	−0.003	0.006
average value				**0.004**
		HFC-143a		
273.15	0.620	0.620	0.000	0.000
283.15	0.837	0.837	0.000	0.000
293.15	1.104	1.106	−0.002	0.002
303.15	1.432	1.435	−0.003	0.002
313.15	1.830	1.832	−0.002	0.001
323.15	2.298	2.308	−0.010	0.004
average value				**0.002**

[a] $\Delta P = P - P_{REF}$. [b] $\lvert\Delta P/P\rvert = \{\lvert P - P_{calcd}\rvert\}/P$.

nected online to the VLE cell. The response of the thermal conductivity detector (TCD) was carefully calibrated using the mixture prepared gravimetrically and the gas chromatographers (GC) with a Porapak Q column from Alltech- Company. Data derived from gas chromatography were treated with a computer program (Autochro-WIN from Young-Lin Instrument Co., Ltd.) The uncertainty for the GC measurement and calibration is estimated to be within 0.001 in area fraction.

Experimental Procedures. Experiments to measure VLE data for the binary system of HFC-143a (1) + butane (2) at various temperatures were performed by the following procedures. At the beginning, the system was evacuated to remove all inert gases. A certain amount of butane was supplied to the cell, and then the temperature of the entire system was held constantly by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A certain amount of HFC-143a was introduced into the cell from a sample reservoir. The mixture in the cell was stirred continuously with the magnetic stirrer for over 1 h. Both the vapor and liquid phases were recirculated by the dual-head circulation pump until an equilibrium state was established. According to our experimental experiences, 1 h or more was sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath as well as the vapor and liquid phases. After equilibration, the pressure in the equilibrium cell was measured, and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by immediately injecting them into the GC, which was connected online to the vapor and liquid sampling valves. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. At least five analyses were performed for each phase, and the average values were considered to correspond to the equilibrium values. Considering the margin of error and the reproducibility of the GC, we generally estimated an overall uncertainty in the measurements of the composition of 0.002 in mole fraction for both the liquid and the vapor phases.

Table 3. Vapor–Liquid Equilibrium Measurements for the HFC-143a (1) + Butane (2) System at (273.15 to 323.15) K

experimental data					
P/MPa	x_1	y_1	P/MPa	x_1	y_1
	T = 273.15 K			T = 283.15 K	
0.104	0.000	0.000	0.150	0.000	0.000
0.206	0.052	0.424	0.225	0.029	0.233
0.296	0.117	0.583	0.360	0.104	0.520
0.378	0.213	0.682	0.501	0.221	0.679
0.445	0.338	0.755	0.574	0.318	0.735
0.476	0.428	0.787	0.626	0.423	0.772
0.512	0.541	0.826	0.681	0.541	0.816
0.537	0.630	0.856	0.714	0.634	0.842
0.561	0.737	0.881	0.747	0.725	0.873
0.580	0.810	0.906	0.770	0.793	0.897
0.591	0.852	0.921	0.795	0.868	0.927
0.604	0.899	0.941	0.811	0.910	0.947
0.618	0.957	0.973	0.828	0.955	0.972
0.620	1.000	1.000	0.837	1.000	1.000
	T = 293.15 K			T = 303.15 K	
0.208	0.000	0.000	0.284	0.000	0.000
0.378	0.059	0.399	0.487	0.060	0.391
0.627	0.202	0.650	0.768	0.189	0.623
0.729	0.304	0.714	0.989	0.364	0.737
0.808	0.407	0.768	1.050	0.429	0.758
0.866	0.505	0.802	1.130	0.525	0.794
0.922	0.611	0.835	1.226	0.658	0.839
0.965	0.701	0.863	1.281	0.738	0.865
0.996	0.764	0.884	1.315	0.789	0.885
1.028	0.830	0.909	1.355	0.850	0.911
1.053	0.880	0.931	1.383	0.895	0.934
1.072	0.923	0.932	1.410	0.941	0.959
1.087	0.954	0.959	1.432	1.000	1.000
1.097	0.981	0.981			
1.104	1.000	1.000			
	T = 313.15 K			T = 323.15 K	
0.378	0.000	0.000	0.494	0.000	0.000
0.611	0.060	0.352	0.690	0.042	0.254
0.758	0.108	0.468	0.854	0.085	0.396
0.993	0.210	0.615	1.320	0.255	0.629
1.195	0.335	0.697	1.503	0.355	0.696
1.355	0.462	0.757	1.697	0.482	0.747
1.448	0.553	0.790	1.783	0.546	0.773
1.537	0.645	0.823	1.868	0.614	0.798
1.616	0.731	0.855	2.014	0.733	0.844
1.672	0.795	0.881	2.079	0.789	0.870
1.717	0.846	0.904	2.164	0.863	0.907
1.745	0.881	0.922	2.202	0.900	0.929
1.786	0.932	0.952	2.243	0.939	0.954
1.830	1.000	1.000	2.298	1.000	1.000

Correlation. In this work, the experimental VLE data were correlated with the Peng−Robinson equation of state (PR-EOS).[2]

PR-EOS.

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

with

$$a(T) = \left(0.45724\frac{R^2T_c^2}{P_c}\right)\alpha(T) \tag{2}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{3}$$

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

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where the parameter a is a function of temperature; b is constant; k is a constant characteristic of each substance; ω is the acentric

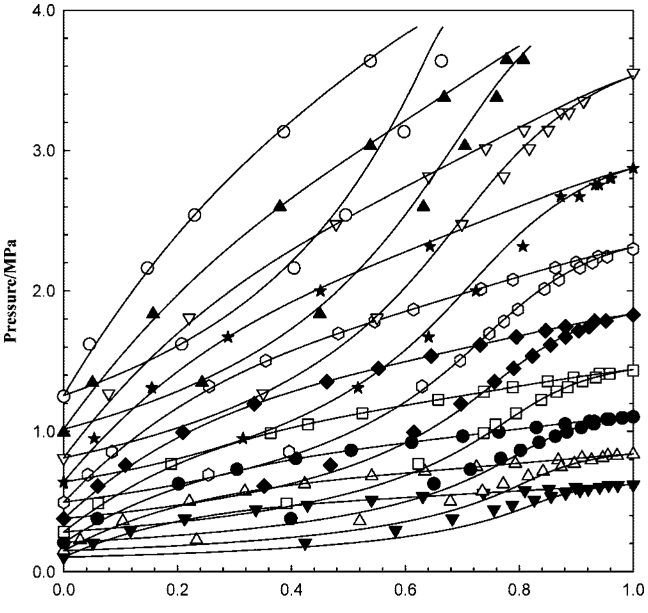

Figure 1. $P-x-y$ diagram for HFC-143a (1) + butane (2). Experimental data at ▼, 273.15 K; △, 283.15 K; ●, 293.15 K; □, 303.15 K; ◆, 313.15 K; ⬡, 323.15 K; ★, 333.15 K;[1] ▽, 343.15 K;[1] ▲, 353.15 K[1]; ○, 363.15 K;[1] and −, calculated with the PR-EOS using the van der Waals mixing rule.

factor; P (MPa) is the pressure; P_c (MPa) is the critical pressure; T (K) is the absolute temperature; T_c (K) is the critical temperature; T_r is the reduced temperature; and v is the molar volume.

The van der Waals mixing rules[3] were used in this work to obtain EOS parameters for a mixture from those of the pure components. These mixing rules for a cubic equation of state can be written as

$$b = \sum_i x_i b_i \qquad a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

with

$$a_{ij} = a_{ji} \tag{7}$$

and

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{8}$$

where, k_{ij} is the adjustable binary interaction parameter.

The critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for both HFC-143a and butane that were used to calculate the parameters for the PR-EOS are provided in Table 1. The parameter of PR-EOS was obtained by minimizing the following objective function.

$$\text{objective function} = \frac{1}{N}\sum_j^N \left[\left(\frac{P_{j,\text{exptl}} - P_{j,\text{calcd}}}{P_{j,\text{exptl}}}\right)^2\right] \tag{9}$$

Results and Discussion

Table 2 shows the comparison of measured vapor pressures of pure HFC-143a and butane with those calculated from the database REFPROP 6.01,[8] which is considered to be reliable for the pure compounds considered and consistent with other literature data. As can be seen in this table, the average values of absolute relative deviations of $P(|\Delta P/P|)$ between measured and calculated values were 0.002 for HFC-143a and 0.004 for butane. The experimental data of isothermal VLE for the binary system of HFC-143a (1) + butane (2) are listed in Table 3. These tables list the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium and

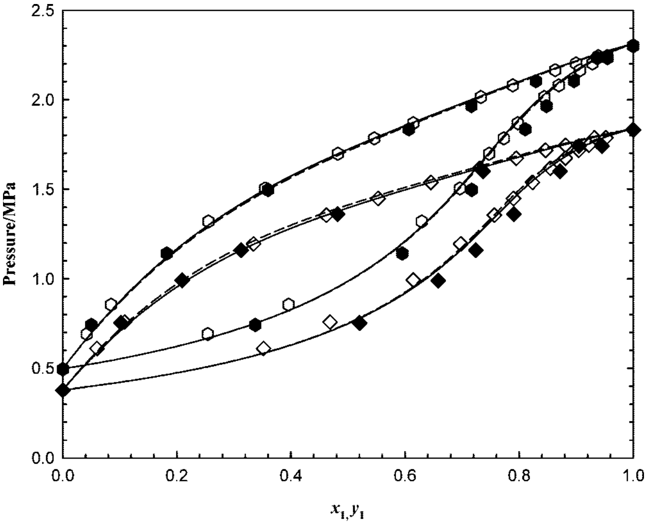

Figure 2. Comparison between the present VLE data (white) with Im et al.'s work[1] (black) [1] for HFC-143a (1) + butane (2) at ◇, 313.15 K; and ⬡, 323.15 K. The calculated data with the PR-EOS using the van der Waals mixing rule for −, our data and for ----, Im et al.'s data [1].

Table 4. Optimal Values of the Binary Parameter k_{12} and Average Relative Deviations of P and Absolute Average Deviation of y

	PR-EOS		
T/K	$^a k_{12}$	^{b}ARD-P^c	AAD-y
273.15	0.1237	0.013	0.021
283.15	0.1224	0.011	0.020
293.15	0.1226	0.007	0.009
303.15	0.1271	0.006	0.004
313.15	0.1275	0.006	0.004
323.15	0.1269	0.004	0.002
333.15[1]	0.1295	0.002	0.013
343.15[1]	0.1276	0.003	0.009
353.15[1]	0.1291	0.008	0.017
363.15[1]	0.1351	0.006	0.021
average values	**0.1272**	**0.007**	**0.012**

[a] k_{12} is the binary interaction parameter. [b] ARD-P = $1/N\ \sum(P_{\text{exptl}} - P_{\text{calcd}})/P$. [c] AAD-$y$ = $1/N\ \sum|y_{\text{exptl}} - y_{\text{calcd}}|$.

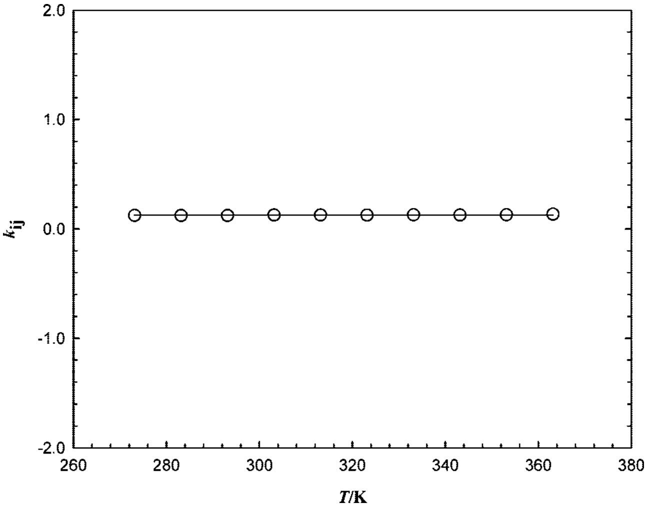

Figure 3. Parameter k_{ij} obtained by using the PR-EOS with the van der Waals mixing rule. The equation of the fitting line is $k_{ij} = 0.1272$.

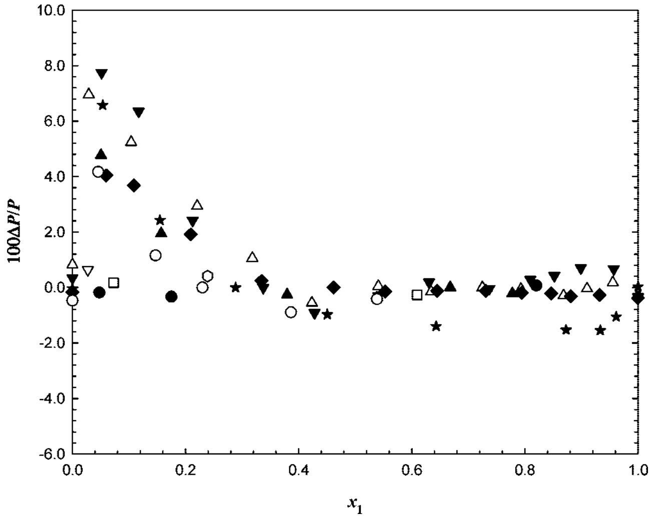

Figure 4. Deviation of pressure for the system HFC-143a (1) + butane (2) from the PR-EOS using the van der Waals mixing rule at ▼, 273.15 K; △, 283.15 K; ●, 293.15 K; □, 303.15 K; ◆, 313.15 K; ⬡, 323.15 K; ★, 333.15 K;[1] ▽, 343.15 K;[1] ▲, 353.15 K;[1] and ○, 363.15 K.[1]

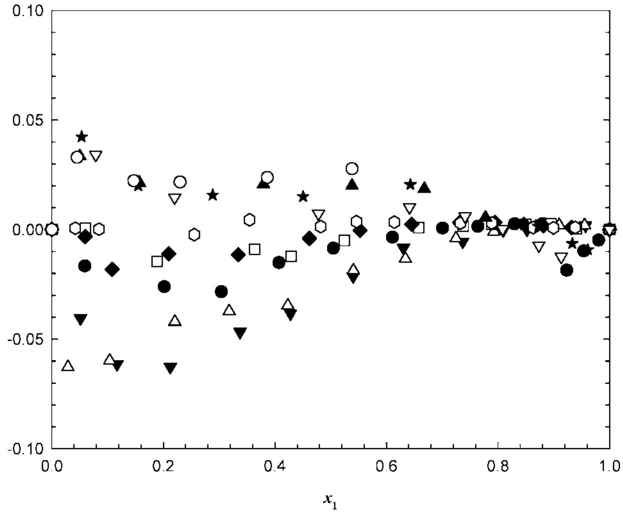

Figure 5. Deviation of vapor composition for the system HFC-143a (1) + butane (2) from the PR-EOS using the van der Waals mixing rule at ▼, 273.15 K; △, 283.15 K; ●, 293.15 K; □, 303.15 K; ◆, 313.15 K; ⬡, 323.15 K; ★, 333.15 K;[1] ▽, 343.15 K;[1] ▲, 353.15 K;[1] and ○, 363.15 K.[1]

the deviations between measured and calculated pressures (ΔP) and vapor compositions (Δy), point by point.

Figure 1 shows the comparison of measured and calculated values with the PR-EOS using the simple mixing rule (van der Waals mixing rule) for the binary system of HFC-143a (1) + butane (2) at various temperatures including the data from ref 1. Figure 2 shows the comparison between the present VLE data with Im et al.'s work[1] for HFC-143a (1) + butane (2) at (313.15 and 323.15) K. Both data were calculated with the PR-EOS using the van der Waals mixing rule. As can be seen in this figure, both experimental data agreed well with calculated data; however, our data showed a little bit better results.

The interaction parameters of the binary mixtures for each isotherm, the binary parameters k_{ij}, and the average relative deviations of pressure (ARD-P) and average absolute deviation of vapor-phase composition (AAD-y) between measured and calculated values are reported in Table 4. The binary parameter, k_{ij}, has been shown in Figure 3. These parameters showed almost the same values with various temperatures. This means that the binary interaction parameters were temperature independent, and the average value was 0.1272 as given in Table 4 and Figure 3. The average values of ARD-P and AAD-y for all ten temperatures were 0.007 and 0.012 for the PR-EOS. The results of error estimations with the PR-EOS for P and y were shown in Figures 4 and 5, respectively. As can be seen in these figures and relatively low ARD-P and AAD-y, a simple mixing rule such as the van der Waals mixing rule is sufficient in calculating this binary system of HFC-143a + butane. In theses temperatures, azeotropic behavior has not been found, but a composition range between 0.9 and 1.0 shows near-azeotropic behavior.

Conclusions

VLE data for binary systems of HFC-143ea (1) + butane (2) were measured at six equally spaced temperatures between (273.15 and 323.15) K using a circulation-type equilibrium apparatus. The experimental data including literature data[1] were correlated with the PR-EOS using the van der Waals mixing rules. Calculated results with these equations have given satisfactory results in comparison with the experimental data. This system shows near azeotropic behavior in the composition rage of 0.9 to 1.0 for the full temperature range studied here. These results indicate that the Peng−Robinson equation of state with the van der Waals mixing rules can be used to estimate pressures and compositions for the mixture of HFC-143a + butane in the temperature range studied here.

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