Phase Equilibria of Chlorofluorocarbon Alternative Refrigerant Mixtures. Binary Systems of Trifluoromethane + Isobutane at 283.15 and 293.15 K and 1,1,1-Trifluoroethane + Isobutane at 323.15 and 333.15 K

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Isothermal vapor−liquid equilibrium data of the binary mixtures of trifluoromethane (HFC-23) + isobutane (R600a) and 1,1,1-trifluoroethane (HFC-143a) + isobutane have been measured at 283.15 and 293.15 K and at 323.15 and 333.15 K, respectively. The experiment was carried out with a circulation-type equilibrium apparatus with the measurement of temperature, pressure, and the compositions of the liquid and vapor phases. The experimental data were correlated with the Peng−Robinson equation of state using the Wong and Sandler mixing rules.

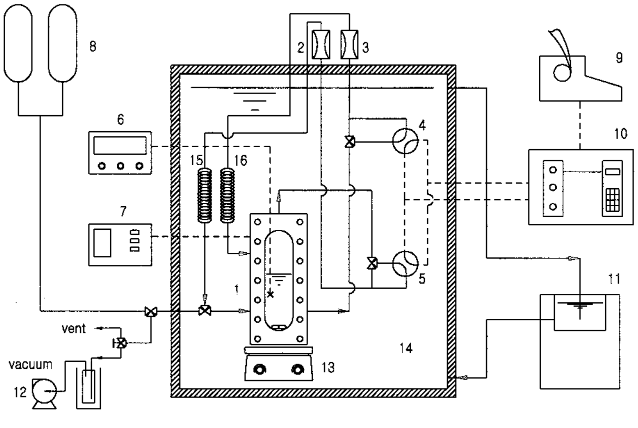
Introduction

Hydrofluorocarbons (HFCs) and hydrocarbons have been considered as promising alternative refrigerants in place of chlorofluorocarbons (CFCs), since their ozone depletion potentials and global warming potentials are low. HFCs are stable but very expensive; on the other hand, hydrocarbons are flammable but very inexpensive. The mixtures of the two compounds may have good potential as alternative refrigerants. Vapor−liquid equilibrium data are required as one of the most important types of information in evaluating the performance of refrigeration cycles and determining their optimal compositions. Azeotropic mixtures have merit, since their behaviors are similar to those of pure compounds. However, no or very few experimental data have been reported previously in the literature. In this work, we measured VLE data for two binary systems of trifluoromethane (HFC-23) + isobutane at 283.15 and 293.15 K and 1,1,1-trifluoroethane (HFC-143a) + isobutane at 323.15 and 333.15 K, respectively. Experimental data were correlated with the Peng−Robinson equation of state (Peng and Robinson, 1976) using the Wong and Sandler mixing rule (Wong and Sandler, 1992).

Experimental Section

Chemicals. High-grade chemicals, having purity greater than 99.9 mass % as shown in Table 1, were used for the measurements of VLE. The purities of the chemicals were guaranteed by the manufacturers, and they were used without any further purification.

Apparatus. Vapor−liquid equilibria were measured in a circulation-type apparatus in which both vapor and liquid phases were continuously recirculated. The experimental apparatus used in this work is the same as that used in previous work (Lee et al., 1999). The schematic diagram of the apparatus used in this work is shown in Figure 1. The equilibrium cell is a 316 stainless steel vessel with an inner volume of about 85 cm^3. In its middle part, a pair of Pyrex glass windows of 20-mm thickness was installed so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed during operation. A stirrer rotated with variable speeds by an external magnet was installed to accelerate the attainment of the equilibrium state and reduce any concentration gradient in both



1. Equilibrium cell
2. Vapor circulation pump
3. Liquid circulation pump
4. Liquid sampling valve
5. Vapor sampling valve
6. Temperature indicator
7. Pressure indicator
8. Sample reservoir
9. Integrator
10. Gas chromatograph
11. Circulator
12. Vacuum pump
13. Magnetic stirrer
14. Constant temperature water bath
15. Vapor phase heat exchanger
16. Liquid phase heat exchanger

Figure 1. Schematic diagram of the experimental apparatus.

Table 1. Suppliers and Purities of the Chemicals

component	supplier	purity/(mass %)
HFC-23	Dupont, USA	>99.9
HFC-143a	Dupont, USA	>99.9
isobutane	Jeongil Chemical Co., Korea	>99.9

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phases. The temperature of the equilibrium cell in the water bath was maintained constant by a circulator from Jeio Tech, Korea, with a stability of ±0.01 K. The temperature in the cell was measured with a platinum resistance sensor and a digital temperature indicator model F250MkII precision thermometer from Automatic Systems Laboratories Ltd., U.K. They were calibrated by NAMAS accredited calibration laboratory. Its uncertainty was estimated to be ±0.01 K. The total error in temperature measurements is estimated to be within 0.05 K, including the precision of the standard thermometer and the fluctuation of the temperature controller. The pressure was measured with a pressure transducer, model XPM60, and digital pressure calibrator, model PC 106, from Beamax, Finland. Pressure calibrations are traceable to National Standards (Center for Metrology and Accreditation cert. no. M-95P077, 14.11.1995, M-M 730, 16.11.1995 and M-95P078, 16.11.1995), and their uncertainties were estimated to be within ±0.05 bar. The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump from the Milton Roy company. After equilibrium was reached, the vapor and liquid samples were taken from the recycling loop and on-line injected into a Gow-Mac model 550P gas chromatograph. The gas chromatograph was equipped with a thermal conductivity detector and a Porapak Q column from Alltech company. The experimental data at the equilibrium state were measured at least three times in order to ensure the repeatability.

Experimental Procedure. Experiments for a binary system were performed by the following procedure. The whole system was evacuated with a vacuum pump to remove all the inert gases. A certain amount of isobutane was introduced into the cell, and then the temperature of the entire system was maintained constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A proper amount of HFC-23 (for HFC-23 + isobutane) or HFC-143a (for HFC-143a + isobutane) was supplied to the cell from a charging cylinder. The mixture in the cell was then stirred continuously with the magnetic stirrer for over 1 h. Both vapor and liquid phases were recirculated by the high-pressure pump until the equilibrium state was established. It is believed that 1 h or more is sufficient to obtain thermal equilibrium between the cell fluid and the thermostated bath. After 1 h or more from the beginning, pressure was measured and then vapor and liquid samples were taken 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 gas chromatograph, which was connected on-line to both vapor and liquid sampling valves. The gas chromatograph was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. The composition uncertainty of the liquid and vapor phase compositions was estimated to be within ±0.5 mol %, including the uncertainty of the calibration curve. The performance of the experimental system was tested by comparing the measured data with the published results of Chung and Kim (1997), Higashi (1995), and Nagel and Bier (1995). The selected system was HFC-32 + HFC-134a because the data of the binary systems concerned in this paper (HFC-23 + isobutane and HFC-143a + isobutane) were not available in the literature. As can be seen in Figure 2, the experimental measurements for the HFC-32 + HFC-134a system show good agreement with the published results. At 303.15 K, the pressure deviations ($|\delta P|/P$) from the measurements of Chung and Kim (1997), Higashi (1995), and Nagel and Bier (1995) were found to be 1.41%, 0.49%, and 1.19% for the P, T, x measurements and 0.99%, 0.64%, and 0.90% for P, T, y measurements, respectively. At 323.15 K, the pressure deviation from the measurements of Chung and Kim (1997) was 1.22% for the P, T, x measurements and 1.18% for the P, T, y measurements.

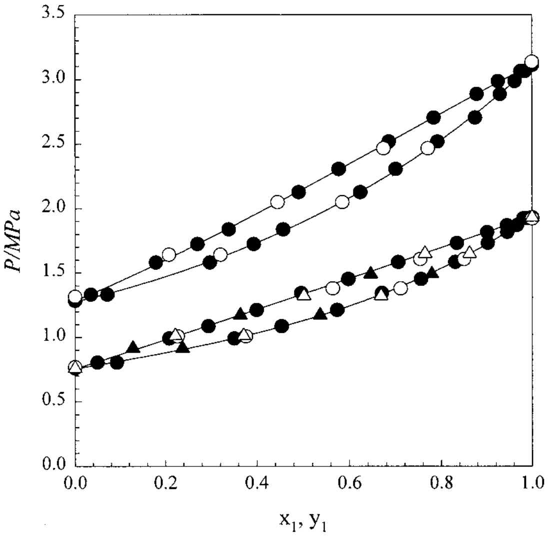

Figure 2. $P-x-y$ diagram of the HFC-32 (1) + HFC-134a (2) system at 303.15 and 323.15 K: (●) present work; (○) Chung and Kim; (▲) Higashi; (△) Nagel and Bier.

Results and Correlation

Isothermal vapor−liquid equilibria were measured for the binary systems of HFC-23 + isobutane at 283.15 and 293.15 K and HFC-143a + isobutane at 323.15 and 333.15 K. The VLE data were correlated with the Peng−Robinson equation of state (Peng and Robinson, 1976). The Peng−Robinson equation of state is expressed as follows:

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

with

$$a(T) = (0.457232R^2T_c^{\ 2}/P_c)\alpha(T) \tag{2}$$

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

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

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

and where the parameter a is a function of temperature, b is constant, κ is a constant characteristic of each substance, ω is the acentric 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 molar volume. The Wong−Sandler mixing rule (Wong and Sandler, 1992) was used in this work to obtain equation of state parameters for a mixture from those of the pure components. This mixing rule for a cubic equation of state can be written as

Table 2. Characteristic Properties of the Chemicals

component	T_c/K	P_c/MPa	ω	source
HFC-23	299.07	4.836	0.2634	REFPROP(v. 6.01, 1998)
HFC-143a	346.04	3.776	0.2611	REFPROP(v. 6.01, 1998)
isobutane	407.85	3.640	0.1853	REFPROP(v. 6.01, 1998)

Table 3. Comparison of the Measured Pure Components' Vapor Pressures with the Calculated Values from the Database REFPROP 6.01 (1998)

		P/MPa			
component	*T*/K	exp	cal	ΔP^a/MPa	$\Delta P/P^b$/(%)
isobutane	283.15	0.2240	0.220	0.0040	1.786
	293.15	0.3050	0.301	0.0040	1.311
	323.15	0.6833	0.684	0.0007	0.102
	333.15	0.8704	0.868	0.0024	0.276
HFC-23	283.15	3.2800	3.275	0.0050	0.152
	293.15	4.2029	4.202	0.0009	0.021
HFC-143a	323.15	2.3038	2.308	0.0042	0.182
	333.15	2.8690	2.874	0.0050	0.174

[a] $\Delta P = |P_{\text{exp}} - P_{\text{cal}}|$. [b] $\Delta P/P = |(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}| \times 100$.

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

with

$$(b - a/RT)_{ij} = \frac{1}{2}[(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \tag{7}$$

and

$$\frac{a_{\text{m}}}{b_{\text{m}}} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^{\text{E}}}{C} \tag{8}$$

and where C is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the Peng−Robinson equation (1976) used in this work. Also, A_∞^{E} is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy model (Wong et al., 1992); in this study we use the NRTL model (Renon and Prausnitz, 1968) given by

$$\frac{A_\infty^{\text{E}}}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{9}$$

with

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \quad \text{and} \quad \tau_{ij} = A_{ij}/(RT) \tag{10}$$

where G_{ij} is the local composition factor for the NRTL model, τ_{ij} is the NRTL model binary interaction parameter, $A_{ij} = (g_{ij} - g_{jj})$, g_{ij} is an interaction energy parameter of $i-j$, α_{ij} is a nonrandomness parameter, and R is the universal gas constant (8.314 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The critical properties (T_c, P_c) and acentric factors (ω) of HFC-23, HFC-143a, and isobutane used to calculate the parameters for the Peng−Robinson equation of state are given in Table 2. We have set the nonrandomness parameter,α_{ij}, equal to 0.3 for all the binary mixtures studied here. The Marquardt algorithm (1973) was applied to obtain the parameters with the following objective function:

Table 4. Vapor−Liquid Equilibrium Measurements for the HFC-23 (1) + Isobutane (2) System

	y_1			*P*/MPa		
x_1	exp	cal	$\Delta y_1{}^a$	exp	cal	ΔP^b/MPa
			T/K = 283.15			
0.0000	0.0000	0.0000	0.0000	0.2240	0.2197	0.0043
0.0139	0.3168	0.3227	−0.0059	0.3295	0.3310	−0.0015
0.0435	0.5918	0.5840	0.0078	0.5530	0.5542	−0.0012
0.1000	0.7440	0.7430	0.0010	0.9380	0.9316	0.0064
0.2284	0.8475	0.8403	0.0072	1.5700	1.5824	−0.0124
0.3083	0.8722	0.8626	0.0096	1.8690	1.8698	−0.0008
0.3710	0.8835	0.8739	0.0096	2.0762	2.0476	0.0286
0.6123	0.9093	0.9005	0.0088	2.5060	2.5052	0.0008
0.8340	0.9384	0.9328	0.0056	2.8090	2.8887	−0.0797
0.9691	0.9828	0.9819	0.0009	3.2060	3.2111	−0.0051
1.0000	1.0000	1.0000	0.0000	3.2800	3.2907	−0.0107
			T/K = 293.15			
0.0000	0.0000	0.0000	0.0000	0.3050	0.3009	0.0041
0.0328	0.4638	0.4719	−0.0081	0.5932	0.5950	−0.0018
0.0634	0.6048	0.6186	−0.0138	0.8432	0.8448	−0.0016
0.0951	0.6849	0.6956	−0.0107	1.0792	1.0807	−0.0015
0.1043	0.7054	0.7112	−0.0058	1.1616	1.1452	0.0164
0.1306	0.7354	0.7460	−0.0106	1.3100	1.3200	−0.0100
0.1480	0.7572	0.7634	−0.0062	1.4264	1.4286	−0.0022
0.1625	0.7713	0.7755	−0.0042	1.5128	1.5149	−0.0021
0.1960	0.7978	0.7976	0.0002	1.7064	1.7012	0.0052
0.2592	0.8337	0.8254	0.0083	2.0078	2.0085	−0.0007
0.3074	0.8506	0.8398	0.0108	2.2100	2.2103	−0.0003
0.4015	0.8702	0.8595	0.0107	2.5383	2.5413	−0.0030
0.5238	0.8887	0.8772	0.0115	2.8715	2.8838	−0.0123
0.6445	0.9016	0.8920	0.0096	3.1535	3.1677	−0.0142
0.7508	0.9231	0.9070	0.0161	3.4440	3.4127	0.0313
0.8549	0.9408	0.9298	0.0110	3.7295	3.6929	0.0366
0.9331	0.9658	0.9594	0.0064	3.9898	3.9545	0.0353
1.0000	1.0000	1.0000	0.0000	4.2029	4.2103	−0.0074

[a] $\Delta y_1 = y_{\text{exp}} - y_{\text{cal}}$. [b] $\Delta P = P_{\text{exp}} - P_{\text{cal}}$.

Table 5. Vapor−Liquid Equilibrium Measurements for the HFC-143a (1) + Isobutane (2) System

	y_1			*P*/MPa		
x_1	exp	cal	$\Delta y_1{}^a$	exp	cal	ΔP^b/MPa
			T/K = 323.15			
0.0000	0.0000	0.0000	0.0000	0.6833	0.6833	0.0000
0.0473	0.2015	0.2149	−0.0134	0.8672	0.8712	−0.0040
0.0717	0.2766	0.2872	−0.0106	0.9550	0.9567	−0.0017
0.1099	0.3615	0.3721	−0.0106	1.0796	1.0775	0.0021
0.1831	0.4795	0.4808	−0.0013	1.2792	1.2736	0.0056
0.3919	0.6493	0.6451	0.0042	1.6750	1.6730	0.0020
0.5869	0.7548	0.7437	0.0111	1.9344	1.9359	−0.0015
0.6716	0.7946	0.7852	0.0094	2.0306	2.0334	−0.0028
0.7746	0.8497	0.8401	0.0096	2.1402	2.1423	−0.0021
0.8471	0.8919	0.8843	0.0076	2.2016	2.2121	−0.0105
			T/K = 333.15			
1.0000	1.0000	1.0000	0.0000	2.3038	2.3280	−0.0242
0.0000	0.0000	0.0000	0.0000	0.8704	0.8685	0.0019
0.1144	0.3473	0.3551	−0.0078	1.3390	1.3395	−0.0005
0.3239	0.5827	0.5896	−0.0069	1.9040	1.9020	0.0020
0.4558	0.6729	0.6759	−0.0030	2.1788	2.1714	0.0074
0.6332	0.7656	0.7668	−0.0012	2.4536	2.4593	−0.0057
0.7658	0.8410	0.8344	0.0066	2.6322	2.6383	−0.0061
0.8644	0.9032	0.8943	0.0089	2.7545	2.7589	−0.0044
0.9351	0.9511	0.9458	0.0053	2.8240	2.8365	−0.0125
1.0000	1.0000	1.0000	0.0000	2.8690	2.8973	−0.0283

[a] $\Delta y_1 = y_{\text{exp}} - y_{\text{cal}}$. [b] $\Delta P = P_{\text{exp}} - P_{\text{cal}}$.

Table 3 is a comparison of the measured vapor pressures of pure isobutane, HFC-23, and HFC-143a with those calculated from the database REFPROP 6.01, which is considered to be reliable for the pure compounds considered and consistent with other literature data. The average deviation ($|\delta P|/P$) between measured and calculated values from the data of REFPROP 6.01 is 0.869% for isobutane, 0.086% for HFC-23, and 0.178% for HFC-143a.

Table 6. Values of Binary Parameters and Average Deviations of P and y

		NRTL parameters				
system	T/K	k_{ij}	A_{ij}[a]	A_{ji}[a]	δP^{b}/(%)	δy^{c}
HFC-23 + isobutane	283.15	0.3389	1.323	3.727	0.801	0.0051
	293.15	0.3911	1.899	2.006	0.487	0.0080
HFC-143a + isobutane	323.15	0.2533	3.167	−0.3398	0.294	0.0071
	333.15	0.3650	6.380	−2.9268	0.306	0.0044

[a] The units of A_{ij} and A_{ji} are kJ·mol^{-1}. [b] $\delta P = (1/N)\Sigma|(P_{\mathrm{exp}} - P_{\mathrm{cal}})/P_{\mathrm{exp}}| \times 100$. [c] $\delta y = (1/N)\Sigma|y_{\mathrm{exp}} - y_{\mathrm{cal}}|$.

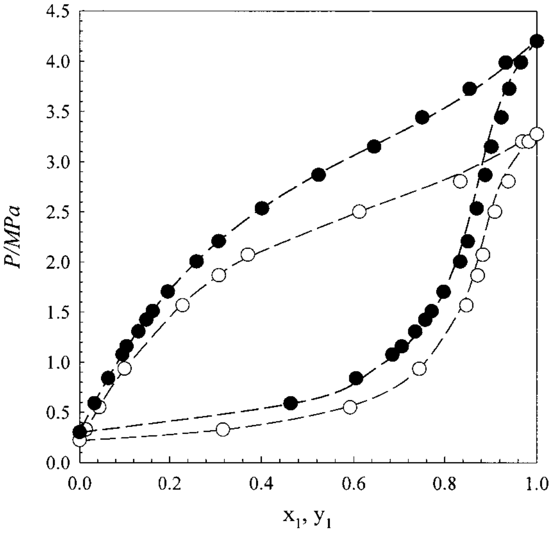

Figure 3. $P-x-y$ diagram for the HFC-23 (1) + isobutane (2) system at 283.15 and 293.15 K: (○) experimental at 283.15 K; (●) experimental at 293.15 K; (- - -) calculated with the Peng−Robinson equation of state using Wong−Sandler mixing rules.

$$\text{objective function} = \frac{1}{N}\sum_{j}^{n}\left[\left(\frac{P_{j,\mathrm{exp}} - P_{j,\mathrm{cal}}}{P_{j,\mathrm{exp}}}\right) \times 100\right]^{2} \quad (11)$$

The experimental vapor pressure data for the pure components and the isothermal vapor−liquid equilibria for the HFC-23 + isobutane and HFC-143a + isobutane mixtures are shown in Tables 4 and 5. Each table lists the measured mole fractions of the liquid and vapor phases, the pressures, and the temperatures at equilibrium and the deviations between measured and calculated pressures ($\Delta P/P$) and vapor compositions (Δy), point by point. Table 6 lists the interaction parameters of binary mixtures for each isotherm, the binary parameters of the NRTL model with Wong−Sandler mixing rules, and the average deviations of pressure ($\delta P/P$) and vapor phase composition (δy) between measured and calculated values. As can be seen in Table 6, the average deviations of pressures are 0.644% for the HFC-23 + isobutane system and 0.30% for the HFC-143a + isobutane system and those of the vapor phase compositions are 0.0066 for the HFC-23 + isobutane system and 0.0058 for the HFC-143a + isobutane system. Figures 3 and 4 show the comparison of measured values with values calculated with a Peng−Robinson equation of state for HFC-23 + isobutane at 283.15 and 293.15 K and for HFC-143a + isobutane at 323.15 and 333.15 K. From these figures and the low average deviations of pressure (<0.65%) and vapor phase compositions (<0.0066) in Table 6, we conclude that the values calculated with the Peng−Robinson equation of state and Wong−Sandler mixing rules give comparatively good agreement with experimental data. Both isothermal systems exhibit no azeotropes.

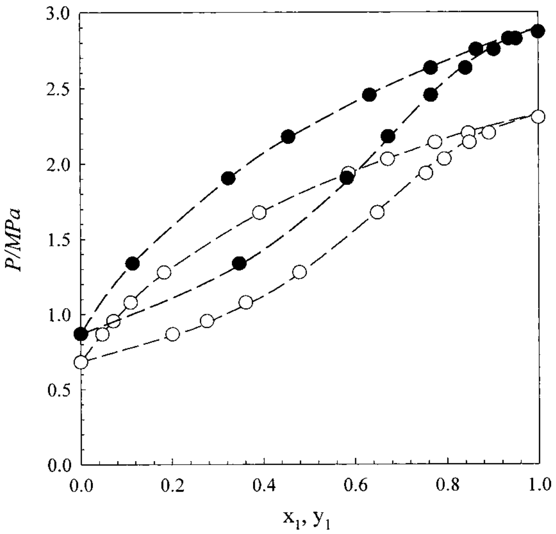

Figure 4. $P-x-y$ diagram for the HFC-143a (1) + isobutane (2) system at 323.15 and 333.15 K: (○) experimental at 323.15 K; (●) experimental at 333.15K; (- - -) calculated with the Peng−Robinson equation of state using Wong−Sandler mixing rules.

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