Phase Equilibria of CFC Alternative Refrigerant Mixtures. Binary Systems of Trifluoromethane (HFC-23) + 1,1,1,2-Tetrafluoroethane (HFC-134a) and Trifluoromethane (HFC-23) + 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) at 283.15 and 293.15 K

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Isothermal vapor−liquid equilibria for the binary mixtures of trifluoromethane (HFC-23) + 1,1,1,2-tetrafluoroethane (HFC-134a) and trifluoromethane + 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) were measured at 283.15 and 293.15 K. The experiments were carried out with a circulation-type equilibrium apparatus with measurement of the temperature, pressure, and compositions of the liquid and vapor phases. The experimental data were correlated with the Peng−Robinson equation of state using the Wong−Sandler mixing rules. Results calculated with this equation showed good agreement with the experimental data. Azeotropic behavior has not been found in either of these mixtures.

Introduction

Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants, or cleaning agents due to their special properties. However, production and use of CFCs are currently being phased out under the international Montreal Protocol agreement because of global environmental concerns. Hydrofluorocarbon (HFC) mixtures are considered to be promising candidates for replacement of CFC compounds because their ozone depletion potentials are low. Vapor−liquid equilibrium (VLE) data are required to evaluate the performance of refrigeration cycles and to determine their optimal compositions. However, few experimental data have been reported previously in the literature for these systems.[1,2] In this work, we measured VLE data for two binary systems of trifluoromethane (HFC-23) + 1,1,1,2-tetrafluoroethane (HFC-134a) and trifluoromethane + 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) at 283.15 and 293.15 K, respectively. Experimental data were correlated with the Peng−Robinson equation of state[3] (PR EOS) using Wong−Sandler mixing rules.[4]

Experimental Section

Chemicals. High-grade chemicals, having purity >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 with a circulation-type apparatus in which both vapor and liquid phases were continuously recirculated. Descriptions of the experimental apparatus and procedure have been reported in our previous publications[5−10] and are only briefly discussed here. The equilibrium cell is a type-316 stainless steel vessel with an inner volume of ~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 gradients. The temperature of the equilibrium cell in the water bath was maintained constant by a circulator from Jeio Tech with a stability of ±0.01 K. The temperature in the cell was measured with a platinum resistance sensor and digital temperature indicator model F250MkII Precision Thermometer from Automatic Systems Laboratories Ltd. They were calibrated by a NAMAS accredited calibration Laboratory. The uncertainty was estimated to be ±0.01 K. The total uncertainty in temperature measurements is estimated to be 0.05 K, including the precision of the standard thermometer and the fluctua-

Table 1. Suppliers and Purities of the Chemicals

component	supplier	purity/(mass %)
HFC-23	Dupont, USA	>99.9
HFC-134a	Dupont, USA	>99.9
HFC-227ea	Dupont, USA	>99.9

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 6.01[13]
HFC-134a	374.21	4.059	0.3268	REFPROP 6.01[13]
HFC-227ea	374.89	2.929	0.3632	REFPROP 6.01[13]

Table 3. Comparison of the Measured Pure Component Vapor Pressures with the Calculated Values from the Database REFPROP 6.01[13]

		P/MPa			
component	T/K	measd	calcd	ΔP^a/MPa	$\lvert\Delta P/P\rvert^b$/(%)
HFC-23	283.15	3.2800	3.2740	0.0060	0.183
	293.15	4.2029	4.2020	0.0009	0.021
HFC-134a	283.15	0.4158	0.4146	0.0012	0.289
	293.15	0.5736	0.5717	0.0019	0.331
HFC-227ea	283.15	0.2803	0.2797	0.0006	0.214
	293.15	0.3905	0.3891	0.0014	0.358

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

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Table 4. Vapor−Liquid Equilibrium Measurements for the HFC-23 (1) + HFC-134a (2) System

x_1	y_1 exptl	y_1 calcd	Δy_1[a]	P/MPa exptl	P/MPa calcd	ΔP^b/MPa
			T/K = 283.15			
0.0000	0.0000	0.0000	0.0000	0.4158	0.4136	0.0022
0.0403	0.1830	0.2027	−0.0197	0.5136	0.5108	0.0028
0.0838	0.3205	0.3519	−0.0314	0.6148	0.6164	−0.0016
0.1195	0.4156	0.4420	−0.0264	0.7022	0.7037	−0.0014
0.2033	0.5722	0.5882	−0.0160	0.9114	0.9108	0.0006
0.3370	0.7184	0.7258	−0.0074	1.2472	1.2492	−0.0020
0.4719	0.8135	0.8107	0.0028	1.6162	1.6035	0.0127
0.6753	0.9009	0.8951	0.0058	2.1280	2.1718	−0.0438
0.8015	0.9438	0.9358	0.0080	2.6170	2.5582	0.0588
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	0.5736	0.5708	0.0029
0.0773	0.2642	0.2892	−0.0250	0.7732	0.7799	−0.0066
0.1239	0.3874	0.4045	−0.0171	0.9130	0.9116	0.0014
0.2648	0.6215	0.6205	0.0010	1.3348	1.3254	0.0094
0.4007	0.7500	0.7391	0.0109	1.7504	1.7517	−0.0013
0.5929	0.8569	0.8438	0.0131	2.4014	2.4039	−0.0025
0.8135	0.9302	0.9267	0.0035	3.2410	3.2554	−0.0144
1.0000	1.0000	1.0000	0.0000	4.2029	4.2103	−0.0074

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

Table 5. Vapor−Liquid Equilibrium Measurements for the HFC-23 + HFC-227ea (2) System

x_1	y_1 exptl	y_1 calcd	Δy_1[a]	P/MPa exptl	P/MPa calcd	ΔP^b/MPa
			T/K = 283.15			
0.0000	0.0000	0.0000	0.0000	0.2803	0.2764	0.0039
0.0315	0.2175	0.2358	−0.0183	0.3637	0.3610	0.0027
0.0760	0.3920	0.4265	−0.0345	0.4718	0.4765	−0.0047
0.1533	0.5879	0.6041	−0.0162	0.6734	0.6725	0.0009
0.2669	0.7287	0.7384	−0.0097	0.9728	0.9637	0.0091
0.4609	0.8486	0.8539	−0.0053	1.4842	1.4974	−0.0132
0.5985	0.8994	0.9016	−0.0022	1.8888	1.9065	−0.0177
0.7216	0.9345	0.9332	0.0013	2.3194	2.2884	0.0310
0.8944	0.9765	0.9715	0.0050	2.8955	2.8616	0.0339
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	0.3905	0.3853	0.0052
0.0522	0.2727	0.2705	0.0022	0.5417	0.5231	0.0186
0.1400	0.4891	0.5188	−0.0297	0.7522	0.7703	−0.0181
0.1910	0.5886	0.6069	−0.0183	0.9102	0.9227	−0.0125
0.2885	0.7172	0.7200	−0.0028	1.2618	1.2321	0.0297
0.5416	0.8576	0.8665	−0.0089	2.1174	2.1362	−0.0188
0.6667	0.9021	0.9063	−0.0042	2.6140	2.6257	−0.0117
0.7832	0.9352	0.9360	−0.0008	3.1265	3.1037	0.0228
0.9034	0.9728	0.9659	0.0069	3.6985	3.6461	0.0524
1.0000	1.0000	1.0000	0.0000	4.2029	4.2103	−0.0074

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

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

system	T/K	NRTL parameters[a]			δP^b/(%)	δy^c
HFC-23/ HFC-134a	283.15	K_{ij} = 0.107	A_{ij} = 0.420	A_{ji} = −0.302	0.719	0.0117
	293.15	K_{ij} = 0.100	A_{ij} = 0.869	A_{ji} = −0.913	0.377	0.0088
HFC-23/ HFC-227ea	283.15	K_{ij} = 0.270	A_{ij} = 3.829	A_{ji} = −2.420	0.885	0.0093
	293.15	K_{ij} = 0.264	A_{ij} = −1.395	A_{ji} = 1.264	1.455	0.0074

[a] The unit of A_{ij} and A_{ji} is kJ·mol^{-1}. [b] $\delta P = 1/N\sum|(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}| \times 100$. [c] $\delta y = 1/N\sum|y_{\text{exptl}} - y_{\text{calcd}}|$.

tion of the temperature controller. The pressure was measured with a pressure transducer, model XPM60 and digital pressure calibrator model PC 106 from Beamax. Pressure calibrations are traceable to National Standards (Finland, Center for Metrology and Accreditation certifications M-95P077, 14.11.1995; M-M 730, 16.11.1995; and M-95P078, 16.11.1995), and their uncertainty was estimated to be ±0.05 bar. The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump from Milton Roy Co. When equilibrium was reached, the circulation pump was stopped and the pressure was measured. Then, the vapor and liquid samples were withdrawn from the recycling loop and injected on-line 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 Co. The experimental data at the equilibrium state were measured at least five times to ensure the repeatability. The composition uncertainty of the liquid and vapor phase composition is estimated to be within ±0.2 mol %, including a margin of error and the reproducibility of GC.

Experimental Procedure. Experiments for a binary system were performed by the following procedure. The whole system was evacuated by a vacuum pump to remove the inert gases. A target amount of HFC-134a (or HFC-227ea) 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. Then, the proper amount of HFC-23 was supplied to the cell from a charging cylinder. The mixture in the cell was stirred continuously by a magnetic stirrer for >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. The compositions of the samples were measured by immediately injecting them into the gas chromatograph, which is connected on-line to both the vapor and liquid sampling valves. The gas chromatograph was calibrated with pure components of known purity and with standard mixtures of known composition that were prepared gravimetrically.

Results and Correlation

Isothermal vapor−liquid equilibria were measured for the binary systems of HFC-23 + HFC134a and HFC-23 + HFC-227ea at 283.15 and 293.15 K. The VLE data were correlated with the PR EOS.[3] The PR EOS is expressed as

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

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 pressure, P_C/MPa is the

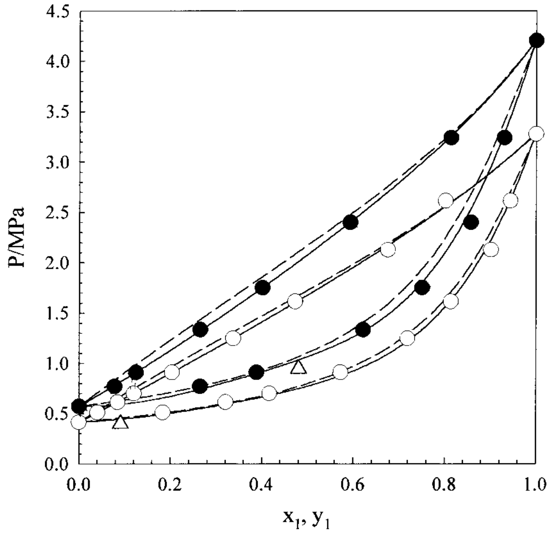

Figure 1. $P-x-y$ diagram for the HFC-23 (1) + HFC-134a (2) system at 283.15 and 293.15 K: ○, experimental at 283.15 K; ●, experimental at 293.15 K; △, liquid phase composition at 273.15 K, Sand et al.[1]; —, calculated with the P−R EOS using Wong−Sandler mixing rules; − −, correlated by REFPROP.[13]

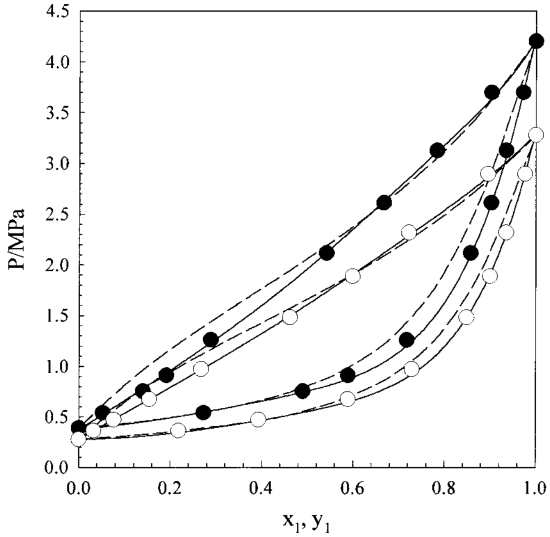

Figure 2. $P-x-y$ diagram for the HFC-23 (1) + HFC-227ea (2) system at 283.15 and 293.15 K: ○, experimental at 283.15 K; ●, experimental at 293.15K; —, calculated with the P−R EOS using Wong−Sandler mixing rules; − −, correlated by REFPROP.[13]

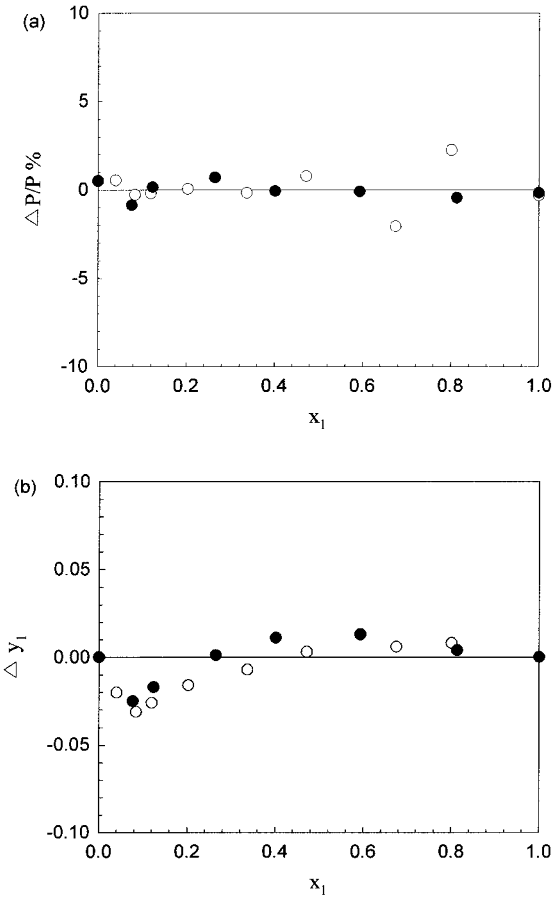

Figure 3. Deviation of the HFC-23 (1) + HFC-134a (2) binary system: (a) $\Delta P/P\%$ versus x_1; (b) Δy_1 versus x_1; ○, experimental at 283.15 K; ●, experimental at 293.15 K;

critical pressure, T/K is absolute temperature, T_C/K is the critical temperature, T_r is the reduced temperature, and v/cm^3·mol^{-1} is molar volume. The Wong−Sandler mixing rules[4] were 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

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{(1 - A^E_\infty/CRT - \sum_i x_i a_i/RTb_i)} \tag{6}$$

with

$$(b - a/RT)_{ij} = {}^1/_2[(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \tag{7}$$

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A^E_\infty}{C} \tag{8}$$

and where C is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR equation[1] 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;[11] in this study we use the NRTL model[12] given by

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

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 the $i-j$), α_{ij} is a nonrandomness parameter, and R is the universal gas constant (8.314 J·K^{-1}·mol^{-1}). The critical properties (T_C and P_C) and acentric factors (ω) of HFC-23, HFC-134a, and HFC-227ea used to calculate the parameters for the PR EOS are given in Table 2. We have set the nonrandomness parameter, α_{ij}, equal to 0.3 for all of the binary mixtures studied here. The parameters of these equations were obtained by minimizing the following

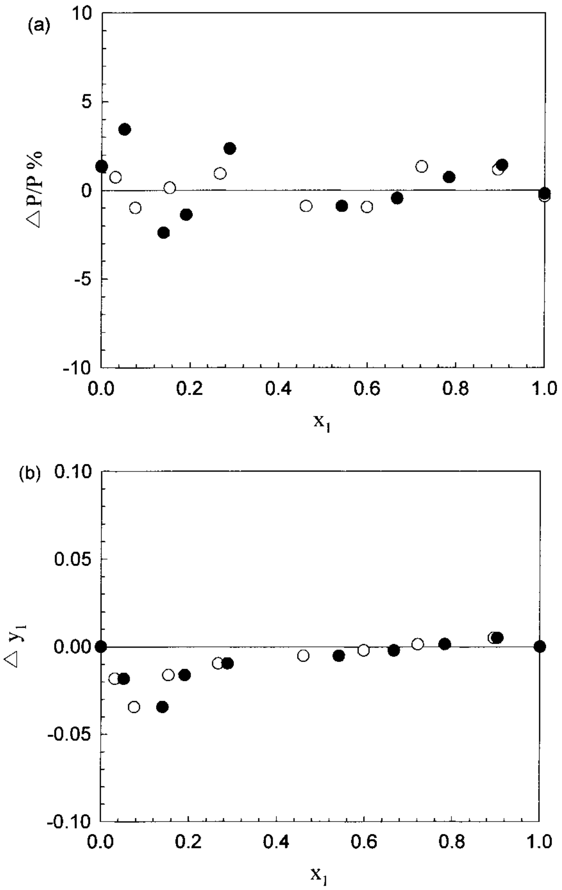

Figure 4. Deviation of the HFC-23 (1) + HFC-227ea (2) binary system: (a) $\Delta P/P\%$ versus x_1; (b) Δy_1 versus x_1; ○, experimental at 283.15 K; ●, experimental at 293.15 K.

objective function:

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

Table 3 is a comparison of measured vapor pressures of pure HFC-23, HFC-134a, and HFC-227ea with those calculated from the database REFPROP 6.01,[13] which is considered to be reliable for the pure compounds considered and consistent with other literature data. The average deviations ($|\delta P|/P$) between measured and calculated values from the data of REFPROP 6.01[13] are 0.102% for HFC-23, 0.310% for HFC-134a, and 0.286% for HFC-227ea. The experimental vapor pressure data for the pure components and isothermal vapor liquid equilibria for the HFC-23 + HFC-134a and HFC-23 + HFC-227ea mixtures are shown in Tables 4 and 5. Each table lists the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium and the deviations between measured and calculated pressures (ΔP) 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 (δP) and vapor phase composition (δy) between measured and calculated values. The overall deviations of pressure by the PR EOS were 0.52% for HFC-23 + HFC-134a and 1.17% for HFC-23 + HFC-227ea, those by PEFPROP[13] were 3.81% for HFC-23 + HFC-134a and 8.31% for HFC-23 + HFC-227ea, and average deviations of vapor phase compositions by the PR EOS are 0.0102 for the HFC-23 + HFC-134a system and 0.0083 for the HFC-23 + HFC-227ea system. Figures 1 and 2 show comparisons of measured and calculated values using the PR EOS and REFPROP[13] for HFC-23 + HFC-134a and HFC-23 + HFC-227ea at 283.15 and 293.15 K. Figures 3 and 4 show the comparison of the relative pressure and vapor phase mole fraction of HFC-23 between the measured data and the calculated values. From these figures and the low average deviations, we conclude that the values calculated with the PR EOS and the Wong−Sandler mixing rules give comparatively good agreement with experimental data. Both isothermal systems exhibit no azeotropes.

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