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Vapor–Liquid Equilibria of CFC Alternative Refrigerant Mixtures: Trifluoromethane (HFC-23) + Difluoromethane (HFC-32), Trifluoromethane (HFC-23) + Pentafluoroethane (HFC-125), and Pentafluoroethane (HFC-125) + 1,1-Difluoroethane (HFC-152a)

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Isothermal vapor–liquid equilibria for three binary mixtures of CFC alternative refrigerants were determined in an equilibrium apparatus in which both phases were continuously recirculated. The pressures and vapor and liquid compositions were measured for the binary systems trifluoromethane (HFC-23) + difluoromethane (HFC-32) and trifluoromethane (HFC-23) + pentafluoroethane (HFC-125) at 283.15 and 293.15 K and pentafluoroethane (HFC-125) + 1,1-difluoroethane (HFC-152a) at 293.15 K. The experimental data were correlated with the Peng–Robinson–Stryjek–Vera equation of state using the Huron–Vidal original mixing rule. Calculated results with this equation showed good agreement with the experimental data.

KEY WORDS: binary mixtures; HFC-23; HFC-32; HFC-125; HFC-152a; Peng–Robinson–Stryjek–Vera equation of state; vapor–liquid equilibria.

1. INTRODUCTION

Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants, or cleaning agents due to their outstanding properties. However, production and use of CFCs are currently being phased out under the international Montreal Protocol agreement because of global

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environmental concerns. HFC mixtures have been considered promising candidates for replacement of CFC compounds since their ozone depletion potentials are low. Vapor–liquid equilibrium data are required as one of the most important types of information in evaluating the performance of refrigeration cycles and in determining the optimal compositions of the working fluids.

In this work, we measured isothermal vapor–liquid equilibria for the binary systems trifluoromethane (HFC-23) + difluoromethane (HFC-32) and trifluoromethane (HFC-23) + pentafluoroethane (HFC-125) at 283.15 and 293.15 K and pentafluoroethane (HFC-125) + 1,1-difluoroethane (HFC-152a) at 293.15 K. The experimental results were correlated with the Peng–Robinson–Stryjek–Vera (PRSV) equation of state combined with the NRTL excess Gibbs free-energy model and the Huron–Vidal original mixing rules [1].

2. EXPERIMENTAL

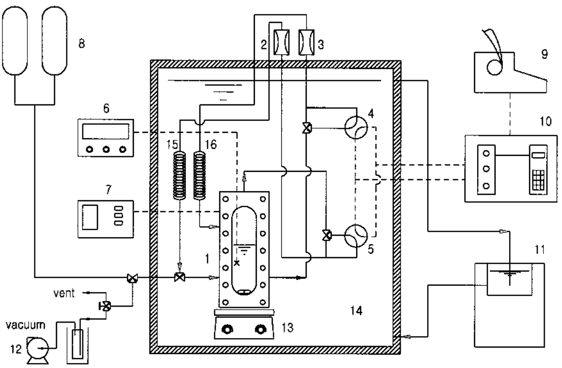
2.1. Chemical/Purity

High-grade chemicals of HFC-23, HFC-32, HFC-125, and HFC-152a having purities higher than 99.8 mass% were supplied by Du Pont. The purities of the chemicals were guaranteed by the manufacturer, and they were used without any further purification.

2.2. Vapor–Liquid Equilibrium Apparatus

Vapor–liquid equilibria were measured in an 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 [2, 3]. The schematic diagram of the apparatus is shown in Fig. 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 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 and a digital temperature indicator model F250MkII precision thermometer from Automatic Systems



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

Fig. 1. Schematic diagram of the experimental apparatus.

Laboratories Ltd., United Kingdom. They were calibrated by a 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. Nos. 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 ±0.005 MPa.

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 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 (TCD) and a Porapak Q column from Alltech Company. The experimental data at the equilibrium state were measured at least three times to ensure repeatability.

2.3. Experimental Procedures

Experiments for a binary system were performed by the following procedure. The system was first evacuated to remove all inert gases. A certain amount of HFC-32 (or HFC-125, HFC-152a) was introduced into the cell, and then the temperature of the entire system was maintained by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A targeted amount of HFC-23 (for HFC-23 + HFC-32, HFC-23 + HFC-125) or HFC-125 (for HFC-125 + HFC-152a) was supplied to the cell from a charging cylinder. The mixture in the cell was stirred continuously with the magnetic stirrer for over 1 h. Both the vapor and the liquid phases were recirculated by the dual-head circulation pump until an 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 start, 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 gas chromatograph, which was connected on-line to the 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 uncertainty of the liquid and vapor phase compositions was estimated to be within ± 0.25 mol%, including the uncertainty of the calibration curve. The performance of the experimental system was tested by comparing the measured data for HFC-32 + HFC-134a with published results [4–6] in previous studies [2, 3], and the measured data for HFC-125 + HFC-152a were compared with the published results of Nishiumi et al. [7]. Data for HFC-23 + HFC-32 and HFC-23 + HFC-125 mixtures were not available in the literature.

3. CORRELATION

Stryjek and Vera [8] proposed the temperature dependence of the α term in the Peng–Robinson equation of state. The Stryjek–Vera modification of the α term was proposed to account for the temperature dependence of the α term at low temperatures.

In this study, the VLE experimental data were correlated with the PRSV equation of state, which can be expressed as follows:

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

$$b=0.077796\,\frac{RT_c}{P_c} \tag{2}$$

$$a(T)=\left(0.457235\,\frac{R^2T_c^2}{P_c}\right)\alpha(T) \tag{3}$$

$$\alpha(T)=[1+\kappa(1-\sqrt{T_c/T})]^2 \tag{4}$$

Here we use the temperature dependence of the α term proposed by Stryjek and Vera.

$$\kappa=\kappa_0+\kappa_1(1+T_r^{0.5})(0.7-T_r) \tag{5}$$

$$\kappa_0=0.378893+1.4897153\omega-0.17131848\omega^2+0.0196554\omega^3 \tag{6}$$

where k_1 is a specific constant for each pure compound. The k_1 value of the PRSV equation is obtained by fitting pure-component vapor pressure (P^{vap})-versus-temperature data.

The Huron–Vidal original mixing rule [9] was used here 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

$$a=b\left[\sum x_i\left(\frac{a_i}{b_i}\right)+\frac{G_\gamma^{\mathrm{ex}}}{C^*}\right] \tag{7}$$

$$b=\sum_i x_i b_i \tag{8}$$

where $C^*=\ln(\sqrt{2}-1)/\sqrt{2}=-0.62323$ and G^{ex} is an excess Gibbs free-energy.

4. RESULTS AND DISCUSSION

Table I shows a comparison of measured vapor pressures of pure HFC-23, HFC-32, HFC-125, and HFC-152a with those calculated from the database REFPROP 6.01 [10], which is considered to be reliable for the pure compounds considered and consistent with other literature data. The deviations (ΔP) between measured and calculated values from the data of REFPROP 6.01 [10] are within 5 kPa. The experimental data for isothermal vapor–liquid equilibria for the binary systems HFC-23 + HFC-32, HFC-23 + HFC-125, and HFC-125 + HFC-152a are shown in Tables II,

Table I. Comparison of the Measured Pure-Component Vapor Pressures with Calculated Values from the Database REFPROP 6.01 [10]

Component	T (K)	P (MPa) Measured	P (MPa) REFPROP	ΔP (kPa)[a]	$\Delta P/P$ (%)[b]
HFC-23	283.15	3.279	3.275	4	0.0012
	293.15	4.199	4.202	3	0.0007
HFC-32	283.15	1.103	1.107	4	0.0036
	293.15	1.480	1.475	5	0.0034
HFC-125	283.15	0.907	0.908	1	0.0011
	293.15	1.207	1.205	2	0.0017
HFC-152a	293.15	0.514	0.512	2	0.0039

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

Table II. Vapor–Liquid Equilibrium Measurements for the HFC-23 (1) + HFC-32 (2) System

P (MPa)	x_1	y_1
	$T = 283.15$ K	
1.103	0.000	0.000
1.262	0.081	0.169
1.598	0.252	0.428
1.815	0.368	0.549
2.018	0.471	0.642
2.262	0.584	0.733
2.458	0.676	0.797
2.713	0.788	0.873
2.909	0.859	0.917
3.279	1.000	1.000
	$T = 293.15$ K	
1.480	0.000	0.000
1.582	0.045	0.093
1.867	0.169	0.292
2.238	0.326	0.485
2.463	0.415	0.573
2.738	0.520	0.668
3.056	0.637	0.759
3.337	0.734	0.828
3.550	0.807	0.876
4.199	1.000	1.000

Table III. Vapor–Liquid Equilibrium Measurements for the HFC-23 (1) + HFC-125 (2) System

P (MPa)	x_1	y_1
	$T = 283.15$ K	
0.907	0.000	0.000
0.981	0.045	0.107
1.186	0.149	0.309
1.421	0.263	0.475
1.608	0.360	0.577
1.828	0.461	0.671
2.118	0.581	0.765
2.369	0.681	0.831
2.561	0.753	0.877
2.816	0.842	0.926
3.016	0.911	0.959
3.279	1.000	1.000
	$T = 293.15$ K	
1.207	0.000	0.000
1.410	0.084	0.188
1.690	0.210	0.386
1.962	0.321	0.516
2.203	0.408	0.605
2.471	0.507	0.688
2.800	0.622	0.775
3.199	0.748	0.859
3.610	0.866	0.925
3.918	0.941	0.968
4.199	1.000	1.000

Table IV. Vapor–Liquid Equilibrium Measurements for the HFC-125 (1) + HFC-152a (2) System

P (MPa)	x_1	y_1
	$T = 293.15$ K	
0.514	0.000	0.000
0.597	0.127	0.218
0.633	0.201	0.315
0.710	0.327	0.485
0.824	0.505	0.662
0.929	0.654	0.784
1.084	0.851	0.917
1.207	1.000	1.000

Table V. Characteristic Properties of the Pure Components[a]

Component	Chemical formula	MW	T_c (K)	P_c (MPa)	ω
HFC-23	CHF_3	70.01	299.07	4.836	0.2634
HFC-32	CH_2F_2	52.02	351.26	5.782	0.2768
HFC-125	C_2HF_5	120.03	339.33	3.629	0.3035
HFC-152a	CHF_2CH_3	66.05	386.41	4.517	0.2752

[a] Data source: REFPROP 6.01 [10].

III, and IV, respectively. Each table lists the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium.

The vapor–liquid equilibrium data of these binary mixtures (HFC-23 + HFC-32, HFC-23 + HFC-125, and HFC-125 + HFC-152a) were correlated with the PRSV equation of state combined with the NRTL excess free-energy models and the Huron–Vidal original mixing rule. The critical properties (T_c, P_c) and acentric factors (ω) of the pure components (HFC-23, HFC-32, HFC-125 and HFC-152a) used to calculate the parameters for the PRSV equation of state are given in Table V. The optimal values of parameter k_1 of each pure component in the range of experimental temperatures are listed in Table VI.

Figures 2, 3, and 4 compare the experimental measurements with calculated values for the systems HFC-23 + HFC-32, HFC-23 + HFC-125 at 283.15 and 293.15 K and HFC-125 + HFC-152a at 293.15 K, respectively. As can be seen in Fig. 4, experimental measurements for the HFC-125 + HFC-152a system at 293.15 K showed good agreement with results published previously. The pressure deviations ($\Delta P/P$) of the measurements from the data of Nishiumi et al. [7] were found to be 0.63% for the P, T, x measurements and 0.69% for the P, T, y measurements. All binary parameters of the NRTL excess free-energy model in the PRSV equation of state and the average absolute deviations of pressure [AAD% (P)] and

Table VI. Optimal k_1 Values of Pure Components in the PRSV Equation of State

Component	Temperature range (K)	k_1	Data source
HFC-23	283.15–293.15	−0.2321	REFPROP 6.01 [10]
HFC-32		−0.1258	
HFC-125		−0.0816	
HFC-152a		−0.1896	

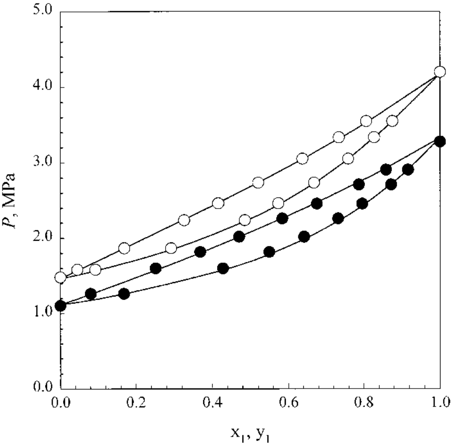


Fig. 2. *P–x–y* diagram for the HFC-23 (1) + HFC-32 (2) system: (●) experimental data at 283.15 K; (○) experimental data at 293.15 K; (——) calculated.

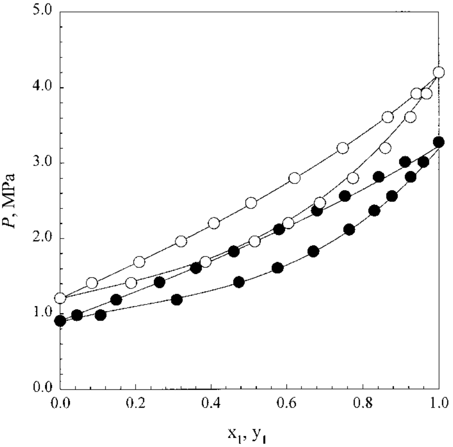


Fig. 3. *P–x–y* diagram for the HFC-23 (1) + HFC-125 (2) system: (●) experimental data at 283.15 K; (○) experimental data at 293.15 K; (——) calculated.

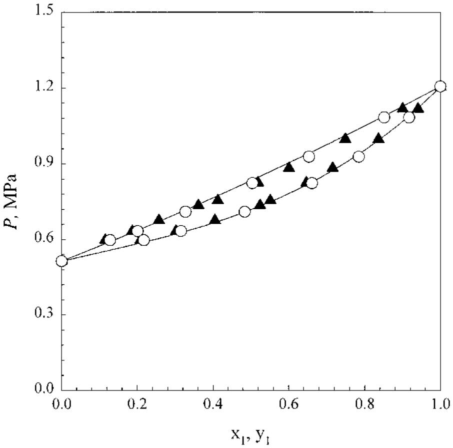


Fig. 4. *P–x–y* diagram for the HFC-125 (1) + HFC-152a (2) system: (○) experimental data at 293.15 K; (▲) Nishiumi et al. [7]; (——) calculated.

vapor phase composition [$\delta(y)$] between measured and calculated values are listed in Table VII. From these figures and the low average deviations of pressure and vapor phase compositions in Table VII, we conclude that our experimental data show good agreement with the calculated values using the PRSV equation of state and Huron–Vidal original mixing rule. Azeotropic behavior has not been found in any of these mixtures.

Table VII. NRTL Parameters and Average Deviations of P and y

System	T (K)	NRTL parameters[a]	AAD(P) (%)[b]	$\delta(y)$[c]
HFC-23(1) + HFC-32(2)	283.15	$A_{12} = -106.74$, $A_{21} = 57.77$	0.809	0.0066
	293.15	$A_{12} = -33.06$, $A_{21} = 52.43$	0.489	0.0047
HFC-23(1) + HFC-125(2)	283.15	$A_{12} = -14.80$, $A_{21} = 50.64$	0.952	0.0065
	293.15	$A_{12} = -39.03$, $A_{21} = 55.72$	0.282	0.0113
HFC-125(1) + HFC-152a(2)	293.15	$A_{12} = -26.512$, $A_{21} = -9.965$	0.598	0.0058

[a] The unit of A_{12} and A_{21} is $\text{cal} \cdot \text{mol}^{-1}$.
[b] $\text{AAD}(P) = (1/N) \sum |(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}| \times 100$.
[c] $\delta(y) = (1/N) \sum |y_{\text{exp}} - y_{\text{cal}}|$.

5. CONCLUSIONS

We measured vapor–liquid equilibria for binary systems of HFC-23 + HFC-32, HFC-23 + HFC-125, and HFC-125 + HFC-152a. The PRSV equation of state with the Huron–Vidal original mixing rule has given satisfactory results in comparison with experimental data. An azeotropic composition was not found in any case.

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