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Phase Equilibria of CFC Alternative Refrigerant Mixtures: Binary Systems of Isobutane + 1,1,1,2-Tetrafluoroethane, + 1,1-Difluoroethane, and + Difluoromethane

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Isothermal vapor−liquid equilibria were measured in the binary systems 1,1,1,2-tetrafluoroethane + isobutane at 303.2 and 323.2 K, 1,1-difluoroethane + isobutane at 303.2, 313.2, 323.2, and 333.2 K, and difluoromethane + isobutane at 301.8 and 321.8 K in a circulation-type equilibrium apparatus. The experimental data were well correlated with the Peng−Robinson equation of state using the Wong and Sandler mixing rules.

Introduction

Hydrofluorocarbons (HFCs), such as 1,1,1,2-tetrafluoroethane (HFC-134a; $C_2H_2F_4$), 1,1-difluoroethane (HFC-152a; $C_2H_4F_2$), and difluoromethane (HFC-32; CH_2F_2) are promising alternative refrigerants to replace dichlorodifluoromethane (CFC-12; CCl_2F_2) and chlorodifluoromethane (HCFC-22; $CHClF_2$). Isobutane is also one of the well-known hydrocarbon refrigerants, which is widely used in Europe. The ozone depletion potentials (ODPs) of HFC-134a, HFC-152a, HFC-32, and isobutane are zero, since they do not contain chlorine atoms. Their global warming potentials (GWPs) are less than those of CFC-12 and HCFC-22 because they contain more hydrogen atoms and thus have a shorter atmospheric lifetime (Lisal and Vacek, 1996). HFCs are stable but very expensive; on the other hand, hydrocarbons are flammable but very cheap. The mixtures of the two compounds may have a good potential for alternative refrigerants.

Vapor−liquid equilibrium data are required as one of the most important basic properties in evaluating the performance of the refrigeration cycle and determining their optimal compositions. Azeotropic mixtures have merit, since their behavior is similar to that of pure compounds. However, no (or very few) experimental data have been previously reported in the literature.

In this work, we measured the isothermal vapor−liquid equilibria (VLE) for the three binary systems HFC-134a + isobutane at 303.2 and 323.2 K, 1,1-difluoroethane + isobutane at 303.2, 313.2, 323.2, and 333.2 K, and difluoromethane + isobutane at 301.8 and 321.8 K. The experimental data were correlated with the Peng−Robinson equation of state (Peng and Robinson, 1976) using the Wong-Sandler mixing rules (Wong and Sandler, 1992).

Experimental Section

Chemicals. High-grade chemicals having purities greater than 99.8 mass %, 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.

Table 1. Suppliers and Purities of the Chemicals

component	supplier	purity/mass %
HFC-134a	Dupont, USA	>99.9
HFC-152a	Dupont, USA	>99.9
HFC-32	Dupont, USA	>99.8
isobutane	Jeongil Chemical Co., Korea	>99.9

Experimental Apparatus. The experimental equipment used to measure the isothermal VLE in this work is a circulation-type apparatus in which both phases were continuously recirculated. The explanation of the experimental apparatus and the procedure has been reported in our previous publications (Lim and Kim, 1997; Lim et al., 1994, 1996, 1997) and is briefly summarized here. The system consists of four major parts: an equilibrium cell, a duplex circulation pump, vapor and liquid sampling valves, and a temperature-controlled air bath. The stainless steel equilibrium cell (Penberthy-Houdaile Co., USA) was equipped with dual glass windows for visual observation of the phases at equilibrium. The volume of the equilibrium cell was about 80 cm^3. The temperatures in the cell were measured with a K-type thermocouple (OMEGA Co.) and a digital indicator (OMEGA model DP41-TC), which was calibrated by KRISS (Korea Institute of Standards and Science) with an uncertainty of ±0.1 K. The pressure in the cell was measured with a Heise pressure gauge (Model CMM 104637), which was calibrated with a dead weight gauge (NAGANO KEIKI PD12) having an uncertainty of ±0.001 MPa. A dual-head circulation pump (Milton Roy Co., USA) was used to circulate the liquid at one head and the vapor at the other. A temperature control system was equipped to maintain the system temperature constant within ±0.1 K. Two six-port sampling valves (Rheodyne Instruments, Model 7413) were used to collect the circulating vapor- and liquid-phase samples. They were directly connected to a gas chromatograph (HP-5890 series II) equipped with a thermal conductivity detector and column packed with Porapak Q (Alltech Co.). Except for the duplex circulation pump, all the equilibrium apparatus was located in a temperature-controlled air bath.

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

x_1	y_1	P/MPa
	T/K = 303.2	
0.0000	0.0000	0.408
0.0387	0.1959	0.483
0.0852	0.3206	0.559
0.1657	0.4441	0.654
0.2531	0.5205	0.732
0.3965	0.6039	0.807
0.4864	0.6462	0.844
0.5637	0.6704	0.862
0.5990	0.6823	0.872
0.6897	0.7192	0.876
0.7727	0.7562	0.881
0.8657	0.8156	0.863
0.9086	0.8530	0.846
0.9370	0.8937	0.828
0.9724	0.9476	0.798
1.0000	1.0000	0.763
	T/K = 323.2	
0.0000	0.0000	0.665
0.0342	0.1473	0.770
0.0779	0.2660	0.882
0.1452	0.3711	1.007
0.2317	0.4704	1.148
0.3557	0.5610	1.271
0.4595	0.6102	1.342
0.5308	0.6469	1.384
0.5746	0.6659	1.404
0.6674	0.7054	1.421
0.7589	0.7592	1.433
0.8649	0.8316	1.413
0.9085	0.8715	1.393
0.9449	0.9141	1.360
0.9760	0.9604	1.328
1.0000	1.0000	1.284

Table 3. Vapor−Liquid Equilibrium Measurements for the HFC-152a (1) + Isobutane (2) System

x_1	y_1	P/MPa
	T/K = 303.2	
0.0000	0.0000	0.408
0.0693	0.2204	0.482
0.2626	0.4965	0.629
0.5011	0.6484	0.721
0.6671	0.7262	0.757
0.7594	0.7752	0.767
0.8612	0.8410	0.759
0.8910	0.8674	0.758
0.9450	0.9216	0.730
1.0000	1.0000	0.686
	T/K = 313.2	
0.0000	0.0000	5.300
0.3459	0.5609	8.598
0.6133	0.7069	9.690
0.7981	0.8038	9.950
0.8313	0.8254	9.912
0.8657	0.8497	9.904
0.9339	0.9113	9.632
0.9762	0.9630	9.334
1.0000	1.0000	9.058
	T/K = 323.2	
0.0000	0.0000	0.687
0.1731	0.3838	0.927
0.3636	0.5688	1.120
0.6945	0.7492	1.257
0.8006	0.8103	1.273
0.8266	0.8255	1.272
0.8294	0.8275	1.270
0.8988	0.8821	1.258
0.9531	0.9375	1.220
0.9932	0.9907	1.179
1.0000	1.0000	1.177
	T/K = 333.2	
0.0000	0.0000	0.872
0.1767	0.3684	1.190
0.3711	0.5649	1.402
0.6646	0.7320	1.568
0.7449	0.7778	1.597
0.8155	0.8228	1.606
0.8589	0.8546	1.607
0.9149	0.9020	1.590
0.9585	0.9474	1.550
1.0000	1.0000	1.500

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 air bath. After the desired temperature was attained, the pressure of the pure component was measured. A proper amount of HFC-134a (for HFC-134a + isobutane), HFC-152a (for HFC-152a + isobutane), or HFC-32 (for HFC-32 + isobutane) was supplied to the cell from a charging cylinder. Both vapor and liquid phases were allowed to circulate for about 1 h to ensure equilibrium. When the equilibrium was attained, pressure was measured and then vapor and liquid samples were taken from the recycling lines by the vapor and liquid sampling valves (loop volumes: 5μL for vapor, 1μL for liquid). The compositions of the samples were measured by immediately injecting them into the gas chromatograph which is connected on-line to both vapor and liquid sampling valves. We measured the equilibrium concentration at least three times in a row to obtain reliable average values. Deviations of the equilibrium concentration were <±0.001 (mole fraction basis) for both phases.

Results and Discussion

The experimental data for isothermal vapor−liquid equilibria (VLE) for the binary systems HFC-134a (1) + isobutane (2), HFC-152a (1) + isobutane (2), and HFC-32 (1) + isobutane (2) are shown in Tables 2, 3, and 4, respectively. Each table lists the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium. 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:

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

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

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

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

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

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 is pressure, P_c is the critical pressure, T is the absolute temperature, T_c is the critical temperature, T_r is the reduced temperature, and v is the molar volume.

Wong−Sandler mixing rules (Wong and Sandler, 1992; Wong et al., 1992) were used in this work to obtain equation of state parameters for a mixture from those of

Table 4. Vapor−Liquid Equilibrium Measurements for the HFC-32 (1) + Isobutane (2) System

x_1	y_1	P/MPa
	T/K = 301.8	
0.0000	0.0000	0.392
0.0328	0.2899	0.579
0.0485	0.3736	0.669
0.0923	0.5164	0.866
0.1229	0.5693	0.994
0.1979	0.6579	1.242
0.2409	0.6862	1.350
0.3680	0.7421	1.575
0.4730	0.7773	1.697
0.5888	0.8017	1.790
0.6889	0.8305	1.859
0.7739	0.8515	1.903
0.8232	0.8667	1.920
0.8675	0.8848	1.932
0.9050	0.9065	1.937
0.9134	0.9081	1.938
0.9347	0.9287	1.933
0.9623	0.9526	1.918
0.9885	0.9849	1.901
1.0000	1.0000	1.895
	T/K = 321.8	
0.0000	0.0000	0.652
0.0229	0.2129	0.873
0.0425	0.2956	0.992
0.0807	0.4173	1.226
0.1127	0.4834	1.403
0.1822	0.5852	1.759
0.2191	0.6182	1.906
0.3654	0.7006	2.344
0.4322	0.7323	2.498
0.5978	0.7839	2.779
0.6606	0.8046	2.869
0.7632	0.8410	2.974
0.8189	0.8619	3.022
0.8585	0.8835	3.056
0.9002	0.9095	3.066
0.9093	0.9159	3.075
0.9342	0.9344	3.077
0.9614	0.9582	3.073
0.9880	0.9867	3.033
1.0000	1.0000	3.022

Table 5. Characteristic Properties of the Chemicals

component	T_c/K	P_c/MPa	ω	data source
HFC-134a	374.3	4.07	0.327	Lee and Chao (1991)
HFC-152a	386.6	4.50	0.256	TRC Tables (1996)
HFC-32	351.6	5.83	0.271	TRC Tables (1996)
isobutane	408.2	3.65	0.183	Reid et al. (1987)

Table 6. Values of Binary Parameters and AAD (%) of *P* and *y*

system	NRTL parameters[a]	AAD[b]/%
HFC-134a + isobutane	$k_{ij} = 0.0795$	0.433 (T = 303.2 K)
	$A_{ji} = 2.0962$	3.336 (T = 323.2 K)
	$A_{ij} = 4.6510$	
HFC-152a + isobutane	$k_{ij} = -0.1949$	0.527 (T = 303.2 K)
	$A_{ji} = 2.2661$	0.708 (T = 313.2 K)
	$A_{ij} = 6.1714$	1.140 (T = 323.2 K)
		1.294 (T = 333.2 K)
HFC-32 + isobutane	$k_{ij} = 0.3277$	0.271 (T = 301.8 K)
	$A_{ji} = 2.3603$	2.712 (T = 321.8 K)
	$A_{ij} = 4.4531$	

[a] Binary parameters for all systems were obtained at 303.2 K (or 301.8 K for HFC-32 + isobutane), and the unit of A_{ij} and A_{ji} is kJ·mol^{-1}. [b] AAD = $(1/N)\sum_i^N[|(P_{i,\mathrm{exptl}} - P_{i,\mathrm{calcd}})/P_{i,\mathrm{exptl}}|] \times 100$.

the pure components. These mixing rules for a cubic equation of state can be written as

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

where

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

and

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

where C is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the Peng−Robinson equation 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) to give

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

where

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

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 $i-j$ interaction, α_{ij} is the nonrandomness parameter, and R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}).

The critical properties (T_c, P_c) and acentric factors (ω) of HFC-134a, HFC-152a, HFC-32, and isobutane used to calculate the parameters for the Peng−Robinson equation of state are given in Table 5. 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:

$$\mathrm{obj} = \sum_j \left[\left(\frac{P_{j,\mathrm{exptl}} - P_{j,\mathrm{calcd}}}{P_{j,\mathrm{exptl}}}\right) \times 100\right]^2 \tag{11}$$

In these calculations the VLE at 323.2 K (for HFC-134a + isobutane) and 313.2, 323.2, and 333.2 K (for HFC-152a + isobutane) were predicted using the model parameters obtained at 303.2 K. The VLE at 321.8 K (for HFC-32 + isobutane) were predicted using the model parameters obtained at 301.8 K. Because the temperature ranges of the binary systems studied here were relatively short, k_{ij}, A_{ij}, and A_{ji} were fixed with the values obtained at 303.2 K (or 301.8 K for HFC-32 + isobutane). All the binary parameters of both systems and the average absolute deviations (AADs) between measured and calculated values are listed in Table 6.

Figures 1, 2, and 3 show the comparison of measured and calculated values for HFC-134a (1) + isobutane (2) at

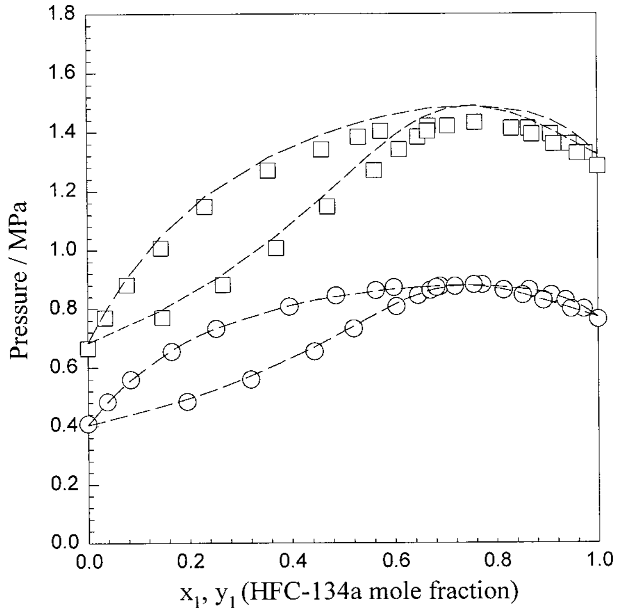

Figure 1. *P-x−y* diagram for the HFC-134a (1) + isobutane (2) system at 303.2 and 323.2 K: (○) experimental at 303.2 K; (□) experimental at 323.2 K; (- - -) calculated at 303.2 and 323.2 K.

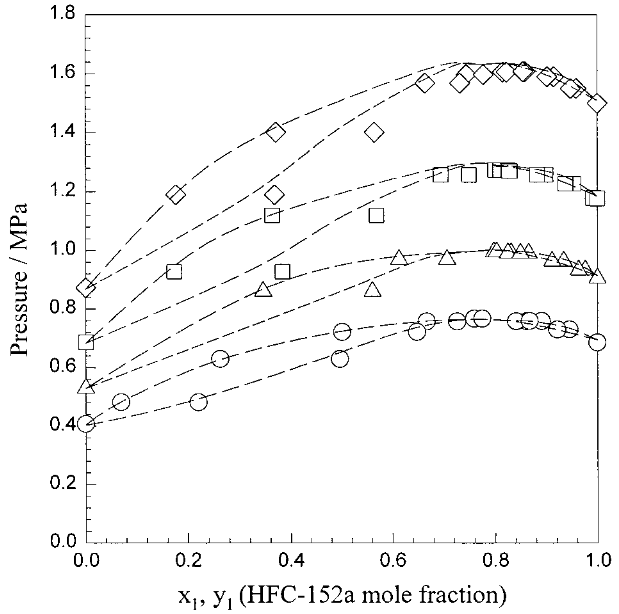

Figure 2. *P-x−y* diagram for the HFC-152a (1) + isobutane (2) system at 303.2, 313.2, 323.2, and 333.2 K: (○) experimental at 303.2 K; (△) experimental at 313.2 K; (□) experimental at 323.2 K; (◇) experimental at 333.2 K; (- - -) calculated at 303.2, 313.2, 323.2, and 333.2 K.

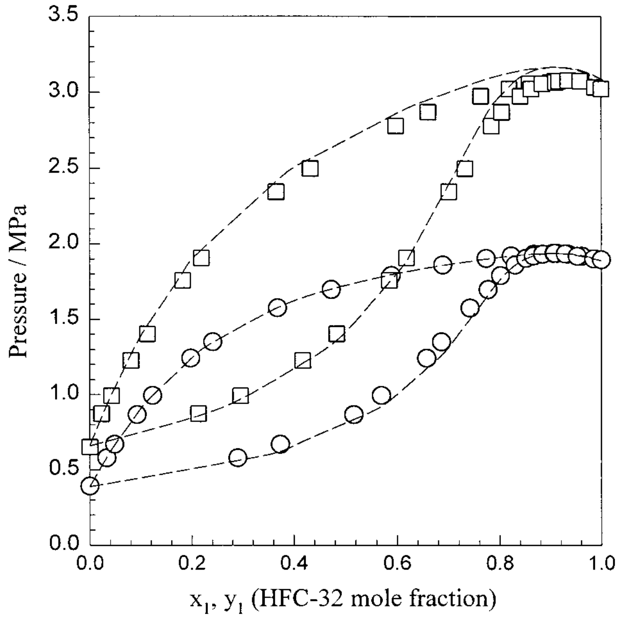

Figure 3. *P-x−y* diagram for the HFC-32 (1) + isobutane (2) system at 301.8 K and 321.8 K: (○) experimental at 301.8 K; (□) experimental at 321.8 K; (- - -) calculated at 301.8 and 321.8 K.

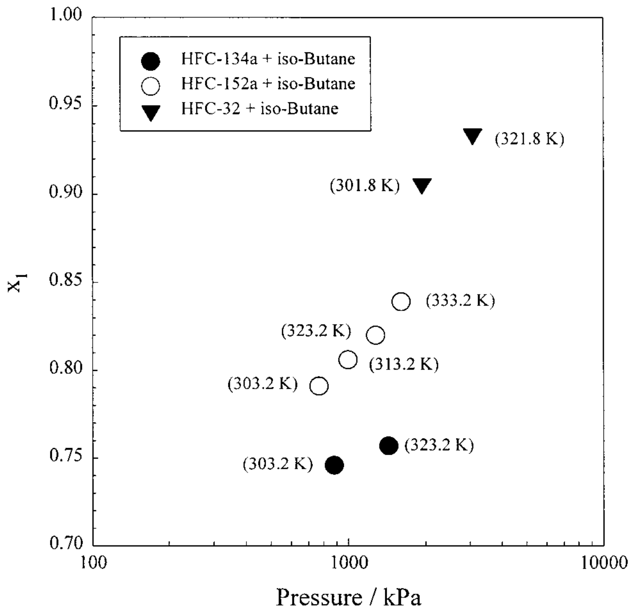

Figure 4. Variation of the azeotropic composition with pressure for the HFC-134a (1) + isobutane (2) system, the HFC-152a (1) + isobutane (2) system, and the HFC-32 + isobutane system.

303.2 and 323.2 K, HFC-152a (1) + isobutane (2) at 303.2, 313.2, 323.2, and 333.2 K, and HFC-32 (1) + isobutane (2) at 301.8 and 321.8 K. As shown in these figures and by the low AAD, the calculated values give good agreement with the experimental data. As given in Table 6, the AAD values of higher temperature than 303.2 K for all systems were slightly larger than those at 303.2 K (or 301.8 K for HFC-32 + isobutane). The calculated data, however, appear to have good agreement with experimental values at each temperature, as seen in Figures 1, 2, and 3. From these results, the NRTL binary parameters obtained in this work can be used for the prediction of VLE in the range of temperatures studied. In all systems, there exist azeotropes; the azeotropic data (temperature, composition, and pressure) of HFC-134a + isobutane, HFC-152a + isobutane, and HFC-32 + isobutane systems are shown in Table 7. Figure 4 represents the variation of the azeotropic composition with pressure at the conditions studied in this work.

Table 7. Azeotropic Data of HFC-134a + Isobutane, HFC-152a + Isobutane, and HFC-32 + Isobutane Systems

system	*T*/K	x_1	*P*/MPa
HFC-134a + isobutane	303.2	0.746	0.882
	323.2	0.757	1.435
HFC-152a + isobutane	303.2	0.791	0.769
	313.2	0.806	0.998
	323.2	0.820	1.278
	333.2	0.839	1.609
HFC-32 + isobutane	301.8	0.906	1.939
	321.8	0.934	3.078

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