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Phase Equilibria of Chlorofluorocarbon Alternative Refrigerant Mixtures

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Isothermal vapor−liquid equilibrium data were determined for binary systems of difluoromethane/1,1,1,2-tetrafluoroethane (HFC-32/HFC-134a), difluoromethane/pentafluoroethane (HFC-32/HFC-125), difluoromethane/1,1,1-trifluoroethane (HFC-32/HFC-143a), and difluoromethane/1,1-difluoroethane (HFC-32/HFC-152a). The vapor and liquid compositions and pressures were measured in a circulation-type apparatus at 303.15 K and 323.15 K. The experimental data were compared with literature results and correlated with the Canahan−Starling−De Santis equation of state within the uncertainty of ±1.0%.

Introduction

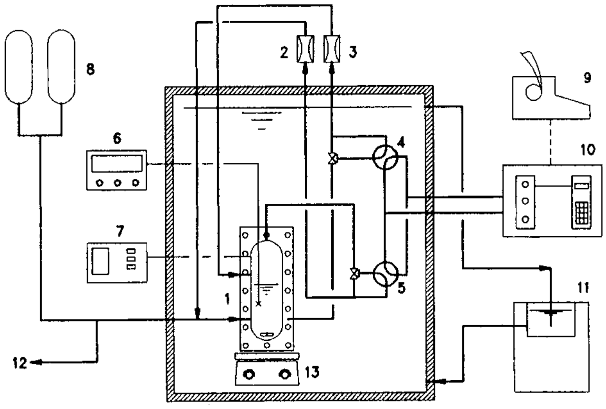
Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants, or cleaning agents due to their outstanding properties. However, production and use of CFCs are currently being phased out under the international Montreal Protocol agreement because of global environmental concerns. HFC mixtures have been considered as promising candidates for replacement of CFC compounds since their ozone depletion potentials are low. The vapor−liquid equilibrium data are required as important basic information in evaluating the performance of refrigeration cycles and determining their optimal compositions.

In this work, vapor−liquid equilibria (VLE) for binary mixtures of difluoromethane/1,1,1,2-tetrafluoroethane (HFC-32/HFC-134a), difluoromethane/pentafluoroethane (HFC-32/HFC-125), difluoromethane/1,1,1-trifluoroethane (HFC-32/HFC-143a), and difluoromethane/1,1-difluoroethane (HFC-32/HFC-152a) were measured at 303.15 K and 323.15 K. The experimental results were correlated with the Canahan−Starling−De Santis equation of state.

Experimental Section

Materials. HFC-32, HFC-125, HFC-134a, HFC-143a, and HFC-152a were supplied by Du Pont. The purities were 99.9 mass %, respectively.

Apparatus. Vapor−liquid equilibria were measured in a circulation-type apparatus in which both vapor and liquid phases were continuously recirculated. The schematic diagram of the experimental system is shown in Figure 1. The stainless steel equilibrium cell with an inner volume of about 85 cm^3 was equipped with dual glass windows in order to make it possible to observe the inside during operation. The temperature of the equilibrium cell in the water bath was maintained constant by a circulator from Jeio Tech with an accuracy of ±0.1 K. The temperature in the cell was measured with a platinum resistance sensor from Automatic Systems Laboratories Ltd., and the uncertainty was estimated to be ±0.1 K. The pressure was measured with a pressure transducer model PC 106, Digital Pressure Gauge, Beamax, and the 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. After the equilibrium was reached, the vapor and liquid samples were taken from the recycling loop and on-line injected into the gas chromatograph of Gow-Mac model 550P. 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 three times in order to ensure accuracy. The performance of the system was tested by comparing the measured data with published results of Chung and Kim (1997), Higashi (1995, 1997), and Nagel and Bier (1995).



1. Equilibrium Cell
2. Liquid circulation pump
3. Vapor circulation pump
4. Liquid sampling valve
5. Vapor sampling valve
6. Temperature indicator
7. Pressure indicator
8. Sample supplying pump
9. Integrator
10. Gas chromatograph
11. Circulator
12. Vaccum pump
13. Magnetic stirrer
14. Constant temperature water bath

Figure 1. Schematic diagram of the experimental apparatus.

Results and Discussion

Vapor−liquid equilibria were measured for the binary systems of HFC-32/HFC-134a, HFC-32/HFC-125, HFC-32/HFC-143a, and HFC-32/HFC-152a at 303.15 K and 323.15

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Table 1. Vapor−Liquid Equilibrium Measurements for the HFC-32 (1)/HFC-134a (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
		T=303.15 K			
0.0000	0.0000	7.83	0.7062	0.8304	15.85
0.0493	0.0927	8.06	0.9011	0.9455	18.17
0.2939	0.4544	10.87	1.0000	1.0000	19.32
0.4968	0.6708	13.45			
		T = 323.15 K			
0.0000	0.0000	13.07	0.7837	0.8743	27.04
0.1790	0.2974	15.81	0.9255	0.9624	29.86
0.3390	0.4575	18.39	1.0000	1.0000	31.11
0.5774	0.7007	23.07			

Table 2. Vapor−Liquid Equilibrium Measurements for the HFC-32 (1)/HFC-125 (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
		T = 303.15 K			
0.0000	0.0000	15.73	0.8857	0.8934	19.34
0.2128	0.2530	16.74	0.9522	0.9526	19.44
0.3075	0.3557	17.23	0.9731	0.9737	19.43
0.6331	0.6707	18.65	1.0000	1.0000	19.50
0.7923	0.8127	19.16			
		T = 323.15 K			
0.0000	0.0000	25.20	0.7499	0.7727	30.88
0.3303	0.3684	28.16	0.8758	0.8860	31.28
0.4678	0.5076	29.18	0.9678	0.9691	31.34
0.6267	0.6591	30.24	1.0000	1.0000	31.40

K. Experimental measurements are summarized in Tables 1−4. Each table shows the mole fractions of the liquid and vapor phases and pressures in equilibrium at given temperature conditions.

The experimental VLE data were correlated with the Canahan−Starling−De Santis (CSD) equation of state using the approach of Morrison and McLinden (1986). The coefficients a_0, a_1, a_2 in eq 3 and b_0, b_1, b_2 in eq 4 were cited from REFPROP 5.0 (1996).

$$\frac{Pv}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \frac{a(T)}{RT(v + b(T))} \qquad (1)$$

$$y = b/4v \qquad (?)$$

$$a = a_0\, exp(a_1 T + a_2 T^2) \qquad (3)$$

$$b = b_0 + b_1 T + b_2 T^2 \qquad (?)$$

In this investigation, the following mixing rules were used for the equation of state.

$$a = \sum\sum x_i x_j a_{ij} \qquad (5)$$

$$b = \sum\sum x_i x_j b_{ij} \qquad (6)$$

$$b_{12} = (b1/3_1 + b1/3_2)^3/8 \qquad (7)$$

$$a_{12} = (1 - f_{12})(a_{11} a_{22})^{1/2} \qquad (8)$$

The interaction parameter, f_{12}, was obtained by minimizing the following objective function.

$$Obj = \Gamma(T,x_1,f_{12}) = \sum_i \left(\frac{P_{\mathrm{calc},i} - P_{\mathrm{expt},i}}{P_{\mathrm{expt},i}}\right)^2 \qquad (9)$$

Figures 2−5 compare the experimental measurements with the calculated values for the systems of HFC-32/HFC-134a, HFC-32/HFC-125, HFC-32/HFC-143a, and HFC-32/HFC-152a, respectively. As can be seen in Figure 2, the experimental measurements for HFC-32/HFC-134a system show good agreement with the results published previously. At 303.15 K, the pressure deviations ($\delta P/P$) of the measurements from the data 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, and x measurements and 0.99%, 0.64%, and 0.90% for P, T, and y measurements, respectively. At 323.15 K, the pressure deviation from the data of Chung and Kim (1997) was 1.22% for the P, T, and x measurements and 1.18% for the P, T, and y measurements, respectively. Experimental results for the HFC-32/HFC-125 system were also in a good agreement with the data of Higashi (1997), as shown in Figure 3. All of the interaction parameters and the average absolute deviations of P between measured and calculated values are shown in Table 5. Our expermental data show good agreement

Table 3. Vapor−Liquid Equilibrium Measurements for the HFC-32 (1)/HFC-143a (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
		T = 303.15 K			
0.0000	0.0000	14.38	0.7755	0.7990	19.08
0.1188	0.1585	15.56	0.8783	0.8888	19.29
0.3292	0.3926	17.19	0.9430	0.9468	19.38
0.5640	0.6115	18.41	1.0000	1.0000	19.50
		T = 323.15 K			
0.0000	0.0000	23.30	0.7475	0.7771	30.06
0.1034	0.1280	24.10	0.8409	0.8592	30.69
0.2607	0.3086	25.78	0.9592	0.9631	31.23
0.5102	0.5613	20.60	1.0000	1.0000	31.50
0.6081	0.6528	29.05			

Table 4. Vapor−Liquid Equilibrium Measurements for the HFC-32 (1)/HFC-152a (2) System

x_1	y_1	P/bar	x_1	y_1	P/bar
		T = 303.15 K			
0.0000	0.0000	6.77	0.7562	0.8648	16.39
0.1326	0.2570	8.52	0.8549	0.9203	17.65
0.4686	0.6485	12.97	0.9226	0.9535	18.40
0.5856	0.7478	14.43	1.0000	1.0000	19.18
0.7060	0.8292	15.73			
		T = 323.15 K			
0.0000	0.0000	11.46	0.6987	0.8278	26.31
0.1022	0.2251	14.16	0.8248	0.9042	28.53
0.2592	0.4634	17.75	0.9272	0.9594	30.14
0.3661	0.5754	20.11	1.0000	1.0000	30.91
0.5330	0.7187	23.31			

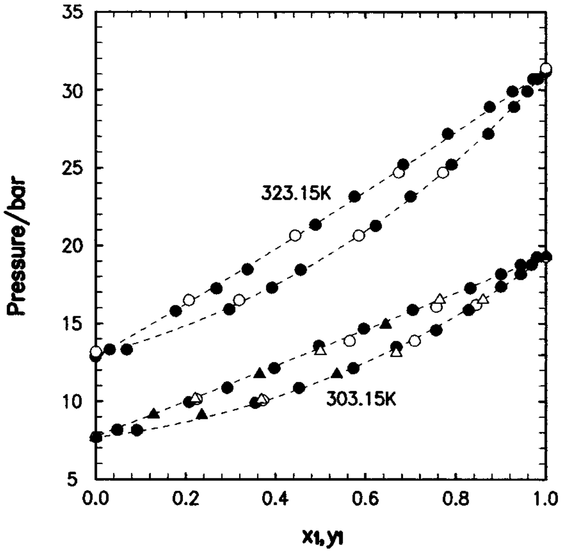

Figure 2. $P-x-y$ diagram of the HFC-32 (1)/HFC-134a (2) system at 303.15 K and 323.15 K: (●) present work; (○) Chung and Kim (1997); (▲) Higashi (1995); (△) Nagel and Bier (1995); (···) calculated.

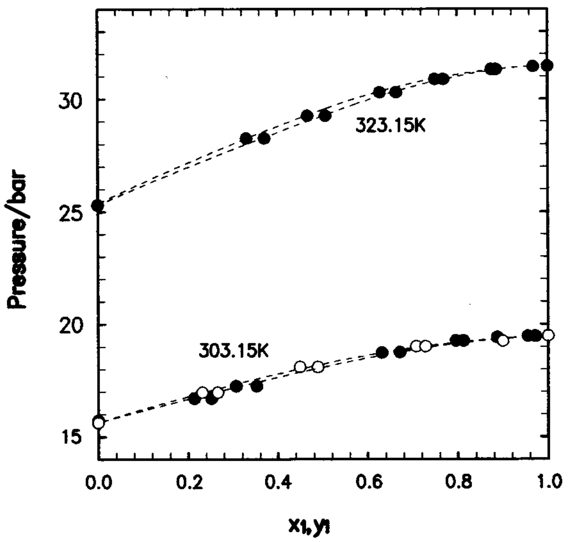

Figure 3. $P-x-y$ diagram of the HFC-32 (1)/HFC-125 (2) system at 303.15 K and 323.15 K: (●) present work; (○) Chung and Kim (1997); (···) calculated.

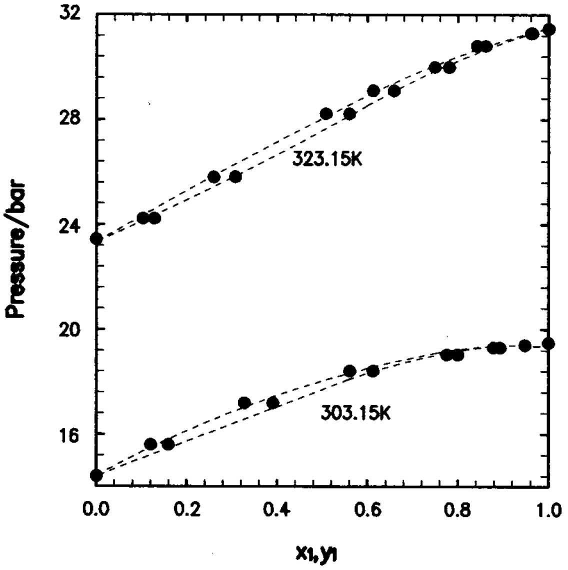

Figure 4. $P-x-y$ diagram of the HFC-32 (1)/HFC-143a (2) system at 303.15 K and 323.15 K: (●) present work; (···) calculated.

with the calculated values using the CSD euqation, and the deviations are less than 1%. Azeotropic behavior has not been found in any of these mixtures.

Conclusions

We measured vapor−liquid equilibria for binary systems of HFC-32/HFC-125, HFC-32/HFC-134a, HFC-32/HFC-143a, and HFC-32/HFC-152a. The CSD equation of state has given satisfactory results in comparison with the experimental data. An azeotropic composition was not found in any case.

Nomenclature

a: attraction parameter of the CSD equation of state

a_0, a_1, a_2: coefficients for the temperature dependence of a

b: molecular volume of the CSD equation of state

b_0,b_1,b_2: coefficients for the temperature dependence of b

f_{12}: interaction parameter

v: molar volume

P: pressure

T: temperature

R: gas constant

x: liquid-phase mole fraction

y: vapor-phase mole fraction

cal: calculated value

expt: experimental value

i, j: component i, j

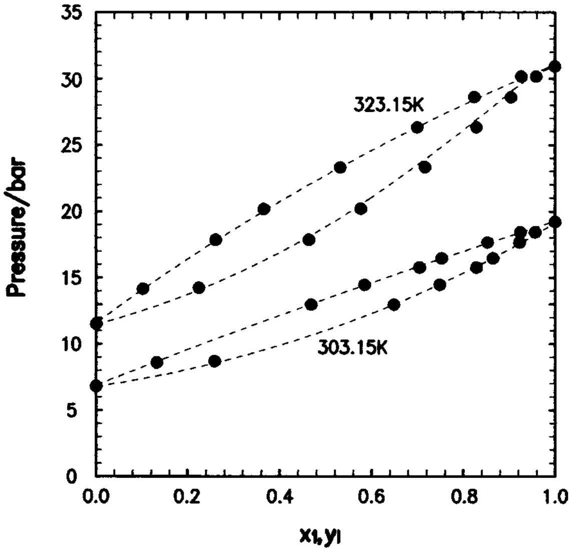

Figure 5. $P-x-y$ diagram of the HFC-32 (1)/HFC-152a (2) system at 303.15 K and 323.15 K: (●) present work; (···) calculated.

Table 5. Interaction Parameters, f_{12}, and AAD[a] (%) of P

	T/K	f_{12}	AAD (%)
HFC-32/HFC-125	303.15	−0.0082	0.49
	323.15	−0.0025	0.07
HFC-32/HFC-134a	303.15	−0.0073	0.97
	323.15	−0.0158	0.94
HFC-32/HFC-143a	303.15	0.0162	0.55
	323.15	0.0014	0.24
HFC-32/HFC-152a	303.15	0.0133	0.57
	323.15	0.0341	0.67

[a] Average absolute deviations (AAD) (%) = $(1/N)\sum_i|P_{\mathrm{expt},i} - P_{\mathrm{calc},i}|/P_{\mathrm{calc},i} \times 100$.

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