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Vapor−Liquid Equilibria for the Difluoromethane (HFC-32) + 1,1,1-Trifluoroethane (HFC-143a) System

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Isothermal vapor−liquid equilibrium data of the binary system of difluoromethane (HFC-32) + 1,1,1-trifluoroethane (HFC-143a) were obtained in the temperature range from 263.15 K to 313.15 K. Temperature, pressure, and compositions of the liquid and vapor phases were measured with a circulation type apparatus. The experimental data were correlated with the Canahan−Starling−De Santis, Peng−Robinson, and Redlich−Kwong−Soave equations of state.

Introduction

As a result of the regulation of CFCs and HCFCs, pure HFCs and HCs and mixtures of these fluids are being investigated as alternative refrigerants. Thermophysical properties are essential to the evaluation of these refrigerants.

In this study, isothermal vapor−liquid equilibrium data of the binary system of difluoromethane (HFC-32) + 1,1,1-trifluoroethane (HFC-143a) were obtained in the temperature range from 263.15 K to 313.15 K and correlated with the Canahan−Starling−De Santis (CSD), Peng−Robinson (PR), and Redlich−Kwong−Soave (RKS) equations of state.

Experimental Section

Chemicals. The samples of pure HFC-32 and HFC-143a were supplied by Ulsan Chemical Co. and Du Pont Co., respectively. The manufacturers stated that the purity of the samples was 99.9 mass %. These samples were used without further purification.

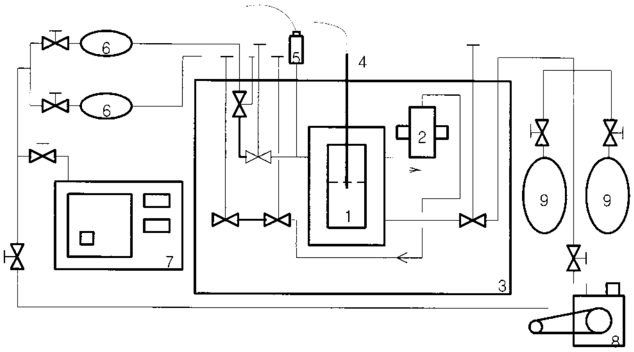

Figure 1. Schematic diagram of the vapor−liquid equilibrium apparatus: 1, equilibrium cell; 2, magnetic pump; 3, isothermal bath; 4, RTD; 5, pressure transducer; 6, sample cylinder; 7, gas chromatograph; 8, vacuum pump; 9, refrigerant vessel.

Apparatus. Phase equilibrium experimental methods are classified as either static, flow, or circulation, depending upon how the mixture is equilibrated. In this study, the circulation method is used, and the apparatus for measuring the vapor−liquid equilibrium is shown schematically in Figure 1. The apparatus consists of an equilibrium unit, a sampling and analysis unit, and a supply unit. The most important unit is the equilibrium unit that consists of an equilibrium cell, a magnetic pump, and the isothermal bath. The equilibrium cell is made of type 316 stainless steel with an inner volume of about 128 cm^3. It is equipped with dual glass windows in order to observe the inside during operation. The magnetic pump circulates the vapor phase to ensure proper mixing and to reach equilibrium quickly. The equilibrium cell and the magnetic pump are immersed in the isothermal bath filled with silicon oil. The temperature of the isothermal bath was maintained at its set point by a circulator. The cell temperature was maintained within ±0.02 K for >1 h. The cell temperature was measured with a 100 Ω platinum resistance sensor and a precision thermometer (YOKOGAWA, 7563) with a precision of 0.01 K. The thermometer was calibrated on the ITS-90. The uncertainty of the temperature measurement is estimated to be ±0.1 K. The pressure is measured with a pressure transducer (Druck, PDCR 922) with a precision of 0.1 kPa. The uncertainty of the pressure measurement is estimated to be ±2 kPa. After equilibrium was reached, vapor and liquid samples were trapped in a space between two valves and introduced into preevacuated cylinders. The space between two valves for a liquid sample is about 0.1 cm^3. The volume of the cylinder is sufficient for the liquid sample to completely evaporate. The compositions of the vapor and liquid samples are analyzed with a gas chromatograph (Hewlett-Packard, 5890II) equipped with a thermal conductivity detector. The column is a Porapak-Q column (1.83 m long; 3.18 mm diameter; mesh range, 80/100). Helium gas was used as a carrier gas, and the flow rate was set to 15 cm^3·min^{-1}. The gas chromatograph is calibrated with mixtures of know composition prepared by a gravimetric method. The calibration mixtures were prepared with compositions in the full range to be studied. The uncertainty of the composition of the liquid and vapor samples was estimated to be ±0.3 mol %. The experimental data at one condition were obtained at least three times in order to ensure accuracy.

Results and Correlation

Vapor−liquid equilibrium data for the binary system of HFC-32 + HFC-143a were obtained over the temperature range from 263.15 to 313.15 K at 10 K intervals. The vapor pressures of the pure components HFC-32 and HFC-143a were also measured. These data are presented in Table 1 and in Figure 2. The measured vapor pressures were

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Table 1. Vapor−Liquid Equilibrium Data for the HFC-32 + HFC-143a System

	mole fraction of HFC-32			mole fraction of HFC-32	
P/kPa	liquid	vapor	P/kPa	liquid	vapor
T = 263.15 K					
450.1	0.0000	0.0000	565.1	0.5664	0.6112
475.4	0.0996	0.1384	577.7	0.6564	0.6984
497.0	0.1842	0.2448	589.6	0.7908	0.8076
524.1	0.2938	0.3663	585.0	0.8846	0.8890
545.5	0.4189	0.4798	580.4	1.0000	1.0000
T = 273.15 K					
621.8	0.0000	0.0000	782.9	0.5653	0.6125
656.3	0.0954	0.1414	797.7	0.6571	0.7020
686.1	0.1804	0.2538	816.4	0.7905	0.8069
721.8	0.2849	0.3514	814.0	0.8845	0.8901
753.8	0.4162	0.4822	811.8	1.0000	1.0000
T = 283.15K					
839.9	0.0000	0.0000	1056.7	0.5664	0.6119
884.3	0.0928	0.1366	1077.6	0.6537	0.7062
925.2	0.1797	0.2461	1102.6	0.7918	0.8080
970.8	0.2894	0.3524	1103.9	0.8835	0.8918
1015.1	0.4197	0.4810	1106.4	1.0000	1.0000
T = 293.15K					
1110.7	0.0000	0.0000	1406.6	0.6001	0.6456
1187.6	0.1096	0.1653	1424.5	0.6582	0.6959
1236.7	0.1986	0.2706	1458.6	0.7891	0.8074
1295.1	0.3136	0.3942	1467.1	0.8858	0.8939
1350.0	0.4474	0.5084	1473.9	1.0000	1.0000
T = 303.15K					
1434.0	0.0000	0.0000	1820.3	0.6011	0.6463
1532.9	0.1165	0.1563	1847.1	0.6590	0.6922
1587.2	0.1844	0.2494	1899.4	0.7927	0.8087
1662.8	0.3003	0.3694	1911.9	0.8839	0.8912
1742.2	0.4382	0.4977	1926.9	1.0000	1.0000
T = 313.15 K					
1831.8	0.0000	0.0000	2328.7	0.5926	0.6343
1946.5	0.1099	0.1470	2364.8	0.6535	0.6881
2021.1	0.1847	0.2361	2429.7	0.7884	0.8043
2115.3	0.3008	0.3586	2457.0	0.8827	0.8901
2221.5	0.4385	0.4908	2481.0	1.0000	1.0000

Table 2. Critical Properties and Acentric Factor of Pure Components

	HFC-32	HFC-143a
critical temperature, T_c/K	351.255[a]	345.86[c]
critical pressure, P_c/kPa	5782[b]	3769.7[d]
acentric factor	0.2768[b]	0.2611[b]

[a] Kuwabara et al. (1995). [b] REFPROP 6.01 (McLinden et al., 1998). [c] Aoyama et al. (1996). [d] Giuliani et al. (1995).

compared with those given in REFPROP 6.01 (McLinden et al., 1998), the JARef book (Sato et al., 1994), and the ASHRAE handbook (1997). The relative deviations of the vapor pressure of HFC-32 from REFPROP 6.01, the JARef book, and the ASHRAE handbook are within ±0.38%, ±0.45%, and ±0.38%, respectively. The relative deviations for HFC-143a from REFPROP 6.01, the JARef book, and Giuliani et al. (1995) are within ±0.64%, ±0.50%, and ±0.30%, respectively. In Figure 2, the experimental results were compared with the published results of Fujiwara et al. (1992) and Lee et al. (1999). At 273.15 K, the absolute average deviation of pressure from Fujiwara et al. (1992) is 1.22% and the maximum deviation is 2.59%. At 303.15 K, the absolute average deviation of pressure from Lee et al. (1999) is 1.18% and the maximum deviation is 3.73%. The vapor pressures of the pure refrigerants in Lee et al. were higher than results in the open literature by 1.24%. Therefore, in Figure 2, the present pressures at 303.15 K are lower than results from Lee et al.

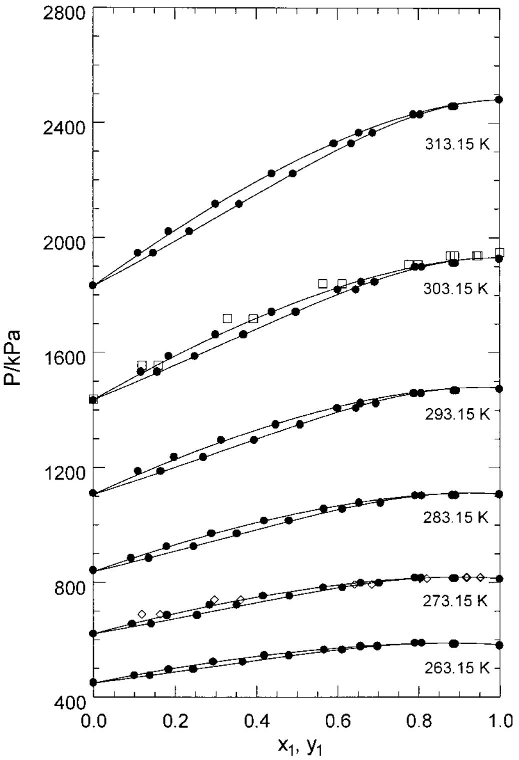

Figure 2. Vapor−liquid equilibrium data for the HFC-32 + HFC-143a system compared with the calculated results from the Canahan−Starling−De Santis equation of state: (●) this work; (◇) Fujiwara et al.; (□) Lee et al.; (−) CSD.

Table 3. Coefficients of the CSD EOS Used for Data Correlation (Huber et al., 1996)

	HFC-32	HFC-143a
a_0/kPa·L^2·mol^{-2}	1662.2699	2763.9092
a_1/K^{-1}	$-2.197\,522\,7 \times 10^{-3}$	$-2.509\,055\,9 \times 10^{-3}$
a_2/K^{-2}	$-8.889\,027 \times 10^{-6}$	$-1.797\,107\,7 \times 10^{-6}$
b_0/L·mol^{-1}	0.077 987 924	0.133 152 59
b_1/L·mol^{-1}·K^{-1}	$-0.752\,381\,02 \times 10^{-4}$	$-1.589\,537\,9 \times 10^{-4}$
b_2/L·mol^{-1}·K^{-2}	$-0.530\,107\,1 \times 10^{-7}$	$-0.583\,310\,54 \times 10^{-7}$

The experimental results were correlated with the Canahan−Starling−De Santis (De Santis 1976), Peng−Robinson (Peng and Robinson, 1976), and Redlich−Kwong−Soave (Soave, 1972) equations of state using the van der Waals mixing rules. The mixing rules are as follows:

$$a = \sum\sum x_i y_j a_{ij} \tag{1}$$

$$b = \sum\sum x_i y_j b_{ij} \tag{2}$$

$$b_{12} = (b_{11}^{1/3} + b_{22}^{1/3})^3/8 \tag{3}$$

$$a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2} \tag{4}$$

where k_{12} is the binary interaction parameter. The critical properties and acentric factors are given in Table 2. The coefficients of the CSD equation of state were cited from REFPROP 5.0 (Huber et al., 1996). They are listed in Table 3.

The binary interaction parameter k_{12} was determined by minimizing the following objective function,

$$\mathrm{Obj} = \sum_{i=1}^{N}\left(\frac{P_{\mathrm{cal},i} - P_{\mathrm{exp},i}}{P_{\mathrm{exp},i}}\right)^2 \tag{5}$$

Table 4. Binary Interaction Parameters for the HFC-32 + HFC-143a System and Deviations of Pressure and Vapor Mole Fraction of HFC-32 from Three Equations of State

T/K	k_{12}	$\delta(\Delta P/P)^a$/%	δy^b
	Canahan−Starling−De Santis		
263.15	0.0064	0.294	0.0063
273.15	0.0072	0.258	0.0065
283.15	0.0072	0.231	0.0071
293.15	0.0079	0.456	0.0071
303.15	0.0070	0.296	0.0046
313.15	0.0081	0.159	0.0026
average		0.282	0.0057
	Peng−Robinson		
263.15	0.0169	0.304	0.0074
273.15	0.0169	0.301	0.0063
283.15	0.0161	0.319	0.0069
293.15	0.0162	0.563	0.0068
303.15	0.0148	0.565	0.0050
313.15	0.0159	0.481	0.0030
average		0.422	0.0059
	Redlich−Kwong−Soave		
263.15	0.0135	0.584	0.0043
273.15	0.0121	0.643	0.0056
283.15	0.0102	0.710	0.0068
293.15	0.0100	0.787	0.0089
303.15	0.0083	0.892	0.0079
313.15	0.0102	0.821	0.0053
average		0.731	0.0065

[a] $\delta(\Delta P/P) = (100/N)\Sigma(|P_{\mathrm{exp},i} - P_{\mathrm{cal},i}|/P_{\mathrm{exp},i})_i$. [b] $\delta_y = (1/N)\Sigma(|y_{\mathrm{exp},i} - y_{\mathrm{cal},i}|)_i$.

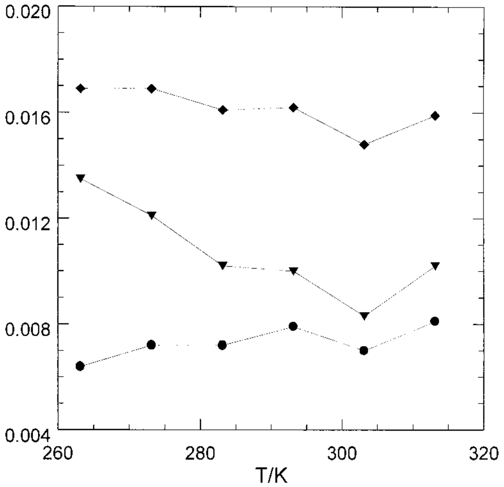

Figure 3. Binary interaction parameters in the Canahan−Starling−De Santis, Peng−Robinsion, and Redlich−Kwong−Soave equations of state for the HFC-32 + HFC-143a system at several temperatures: (●) CSD; (◆) PR; (▼) RKS.

where N is the number of experimental points. For six temperatures, that is, 263.15, 273.15, 283.15, 293.15, 303.15, and 313.15 K, the binary interaction parameters were determined and are presented in Table 4 and in Figure 3. In Figure 3, it is evident that the binary interaction parameter for the CSD equation of state increases slightly as the temperature increases. On the other hand, the binary interaction parameters for both the PR and RKS equations of state decrease as the temperature increases. The binary interaction parameter for the RKS equation of state has a larger temperature dependence than those for the CSD and PR equations of state.

The relative deviations between the measured pressures and vapor phase mole fraction of HFC-32 and the calculated results from equations of state are given in Table 4. In Table 4, the average deviation between the measured pressures and the calculated results from the CSD equation of state is about 0.29% and that from the PR equation of state is about 0.45%. The average deviation from the RKS equation of state is about 0.70%. As a result, the CSD equation of state correlates the experimental data better than the PR and RKS equations of state.

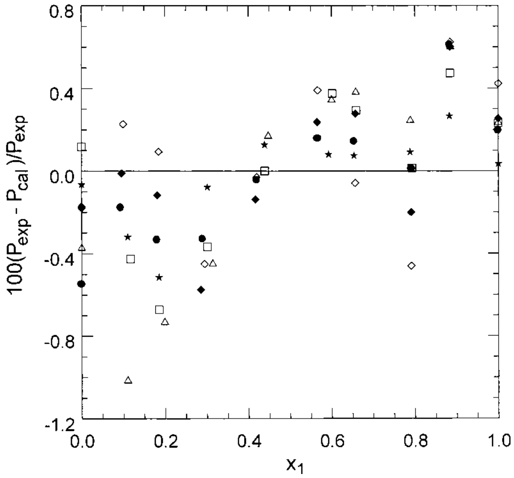

Figure 4. Deviations of bubble point pressures for the HFC-32 + HFC-143a system between the measured data and the calculated results from the Canahan−Starling−De Santis equation of state: (◇) 263.15 K; (◆) 273.15 K; (●) 283.15 K; (△) 293.15 K; (□) 303.15 K; (★) 313.15 K; percent deviation = $100(P_{\mathrm{exp}} - P_{\mathrm{cal}})/P_{\mathrm{exp}}$.

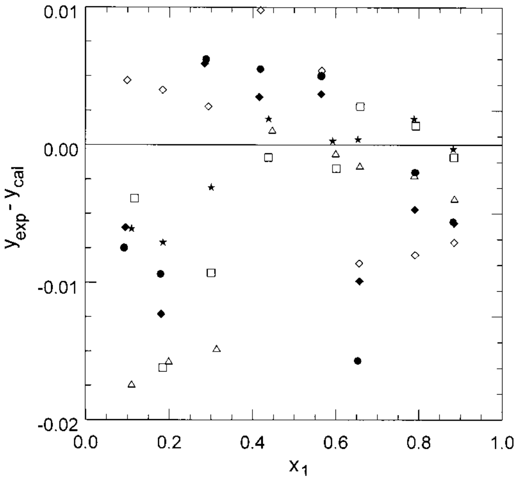

Figure 5. Deviations of vapor-phase mole fractions of HFC-32 for the HFC-32 + HFC-143a system between the measured data and the calculated results from the Canahan−Starling−De Santis equation of state: (◇) 263.15 K; (◆) 273.15 K; (●) 283.15 K; (△) 293.15 K; (□) 303.15 K; (★) 313.15 K; deviation = $y_{\mathrm{exp}} - y_{\mathrm{cal}}$.

Figures 4 and 5 show comparisons between the measured data and the calculated results from the CSD equation of state of the relative pressure and vapor phase mole fraction of HFC-32. In Figure 4, the present data were in good agreement with the calculated results from the CSD equation of state, and the deviations were <0.8% with the exception of one point.

Conclusions

Isothermal vapor−liquid equilibrium data of the binary system of HFC-32 + HFC-143a were obtained at sixty conditions over the temperature range from 263.15 K to 313.15 K at 10 K intervals. The experimental data were correlated with the Canahan−Starling−De Santis, Peng−Robinson, and Redlich−Kwong−Soave equations of state. The Canahan−Starling−De Santis equation of state correlates the experimental data better than the Peng–Robinson and Redlich–Kwong–Soave equations of state.

Nomenclature

a, a_0, a_1, a_2, coefficients of the equation of state
b, b_0, b_1, b_2, coefficients of the equation of state
k_{12}, interaction parameter
Obj, objective function
N, number of data points
P, pressure
T, temperature
x, liquid-phase mole fraction
y, vapor-phase mole fraction

Subscripts

1, composition 1
2, composition 2
c, critical point
cal, calculation
exp, experiment
i, composition i
j, composition j

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