International Journal of Thermophysics, Vol. 21, No. 4, 2000

Vapor–Liquid Equilibria for the 1,1,1-Trifluoroethane (HFC-143a) + 1,1,1,2-Tetrafluoroethane (HFC-134a) System

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Received December 27, 1999

A vapor–liquid equilibrium apparatus has been developed and used to obtain data for the binary HFC-143a + HFC-134a system. Fifty-four equilibrium data are obtained for the HFC-143a + HFC-134a system over the temperature range from 263.15 to 313.15 K at 10 K intervals. The experimental data were correlated with the Carnahan–Starling–De Santis (CSD) and Peng–Robinson (PR) equations of state. Based upon the present data, the binary interaction parameters for the CSD and PR equations of state were calculated for six isotherms for the HFC-143a + HFC-134a system. The binary interaction parameters for both equations of state were fitted by a linear equation as a function of temperature. The present data were in good agreement with the calculated results from the CSD equation of state, and the deviations were less than 1.0% with the exception of two points.

KEY WORDS: binary interaction parameters; equation of state; HFC-134a; HFC-143a; vapor–liquid equilibrium.

1. INTRODUCTION

Because of the need to substitute for traditional CFCs and HCFCs with new environmentally friendly compounds, pure HFCs and HCs and

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0195-928X/00/0700-0871$18.00/0

mixtures of these fluids are being investigated as alternative refrigerants. For binary or ternary mixtures with other similar compounds or with hydrocarbons, vapor–liquid equilibrium data are particularly important to verify the quality of the methods and to design or retrofit the refrigeration system. This paper reports vapor–liquid equilibrium (VLE) data for the HFC-143a + HFC-134a system.

2. MEASUREMENT OF VAPOR–LIQUID EQUILIBRIUM

Phase equilibrium experimental methods are classified as either static, flow, or circulation, depending upon how the system is equilibrated [1]. In this study, the circulation method is used, and the apparatus for measuring the vapor–liquid equilibrium is shown schematically in Fig. 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 interior 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 more than 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 ITS-90. The

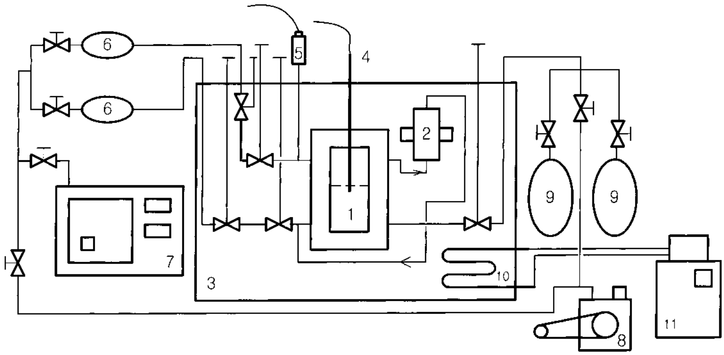

Fig. 1. Schematic diagram of the vapor–liquid equilibrium apparatus.

uncertainty of the temperature measurement is estimated to be within ±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 evacuated cylinders. The space between the two valves for a liquid sample is about 0.05 cm^3. The volume of the cylinders 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 in diameter; mesh range, 80/100). Helium gas was used as a carrier gas, and the flow rate was set to 15 $\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$. The gas chromatograph is calibrated with mixtures of known compositions prepared by a gravimetric method. The calibrating mixtures were prepared at compositions in the full range to be studied. The uncertainty of composition of the liquid and vapor samples was estimated to be within ±0.5 mol%. The experimental data at one condition were measured at least three times in order to ensure reliability.

3. RESULTS AND DISCUSSION

3.1. Sample Purity

The samples of pure HFC-134a and HFC-143a were supplied by Ulsan Chemical Co. and Du Pont Co., respectively. The manufacturers stated that the purity of samples was 99.9 mass%. These samples were used without further purification.

3.2. Vapor Pressures of Pure Refrigerants

Before starting the VLE measurements on mixtures, the vapor pressures of pure refrigerants HFC-134a and HFC-143a were measured. Six data on the vapor pressures for HFC-134a and six data for HFC-143a were obtained at six temperatures, 263.15, 273.15, 283.15, 293.15, 303.15, and 313.15 K. The measured vapor pressure were compared with those given in REFPROP 6.01 [2], the JARef book [3], and the ASHRAE handbook [4]. The deviation plot of the vapor pressures is shown in Fig. 2. The relative deviations of the vapor pressures of HFC-134a from REFPROP 6.01, the JARef book, and the ASHRAE handbook are within ±0.25, ±0.45, and ±0.21%, respectively. The relative deviations for HFC-143a from REFPROP 6.01, the

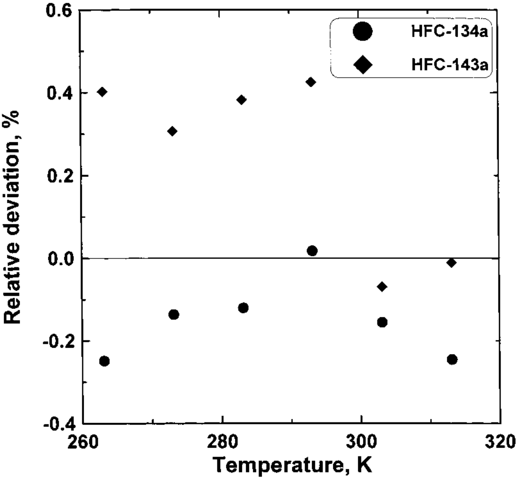

Fig. 2. Relative deviations between the measured vapor pressures and the values calculated from REFPROP 6.01 [2] for the HFC-134a + HFC-143a system.

JARef book, and Giuliani et al. [5] are within ±0.43, ±0.55, and ±0.55%, respectively.

3.3. Vapor–Liquid Equilibrium

The vapor–liquid equilibrium data for the HFC-143a + HFC-134a system measured over the temperature range from 263.15 to 313.15 K at 10 K intervals are presented in Fig. 3 and in Table I. These data are compared with Peng–Robinson (PR) [6] and Carnahan–Starling–De Santis (CSD) [7, 8] equations of state and the published results of Kubota and Matsumoto [9]. At 303.15 K, the absolute average deviation of pressure is 1.41% and the maximum deviation is 3.13%. These results are also shown in Fig. 3.

3.4. Equations of State

The experimental results were correlated with the PR and CSD equations of state using the van der Waals mixing rules. The PR [6] equation of state is as follows:

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

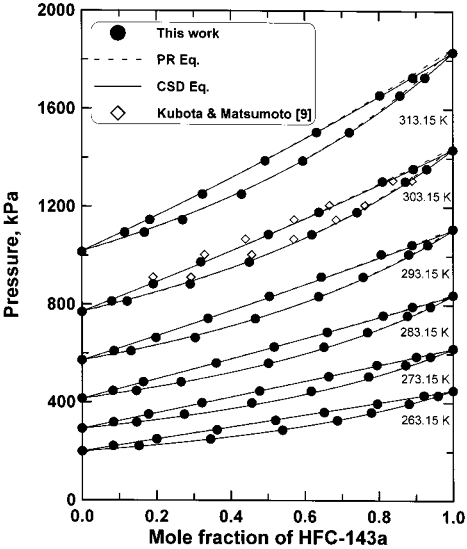

Fig. 3. Vapor–liquid equilibrium data for the HFC-143a + HFC-134a system compared with the calculated results from the CSD and PR equations of state.

where

$$a(T) = a_c \alpha(T) \tag{2}$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \tag{3}$$

$$\alpha(T) = \left[1 + (0.37464 + 1.5226\omega - 0.26992\omega^2) \left(1 - \left(\frac{T}{T_c} \right)^{1/2} \right) \right]^2 \tag{4}$$

$$b = 0.0778 \frac{RT_c}{P_c} \tag{5}$$

The CSD [7, 8] equation of state is as follows:

$$P = \frac{RT}{v} \left[\frac{1 + y + y^2 - y^3}{(1 - y)^3} \right] - \frac{a}{v(v + b)} \tag{6}$$

where

$$y = \frac{b}{4v} \tag{7}$$

Table I. Vapor–Liquid Equilibrium Data for the HFC-143a + HFC-134a System

	Mole fraction of HFC-143a			Mole fraction of HFC-143a	
P (kPa)	Liquid	Vapor	P (kPa)	Liquid	Vapor
$T = 263.15$ K					
200.1	0.0000	0.0000	360.0	0.6520	0.7796
221.9	0.0834	0.1522	395.9	0.7957	0.8811
249.8	0.1999	0.3449	429.3	0.9214	0.9592
287.4	0.3629	0.5396	450.1	1.0000	1.0000
327.0	0.5208	0.6878			
$T = 273.15$ K					
292.4	0.0000	0.0000	506.8	0.6642	0.7720
318.2	0.0844	0.1462	554.2	0.7946	0.8721
350.5	0.1781	0.2745	589.2	0.9007	0.9385
397.1	0.3219	0.4566	621.8	1.0000	1.0000
446.1	0.4779	0.6171			
$T = 283.15$ K					
414.4	0.0000	0.0000	688.6	0.6606	0.7694
445.7	0.0830	0.1459	755.8	0.8116	0.8768
482.1	0.1644	0.2654	792.4	0.8904	0.9385
560.3	0.3602	0.5018	839.9	1.0000	1.0000
627.6	0.5171	0.6516			
$T = 293.15$ K					
571.8	0.0000	0.0000	913.8	0.6444	0.7575
609.1	0.0857	0.1311	1007.4	0.8067	0.8804
664.2	0.1982	0.3036	1046.1	0.8896	0.9319
742.4	0.3384	0.4663	1110.7	1.0000	1.0000
833.9	0.5041	0.6377			
$T = 303.15$ K					
769.0	0.0000	0.0000	1178.8	0.6387	0.7414
811.8	0.0801	0.1211	1304.4	0.8100	0.8718
882.9	0.1911	0.2908	1356.6	0.8932	0.9292
973.9	0.3194	0.4504	1434.0	1.0000	1.0000
1086.9	0.5018	0.6195			
$T = 313.15$ K					
1014.5	0.0000	0.0000	1504.9	0.6320	0.7208
1094.6	0.1149	0.1677	1655.5	0.8028	0.8569
1145.9	0.1823	0.2703	1728.9	0.8922	0.9244
1250.9	0.3242	0.4289	1831.8	1.0000	1.0000
1388.4	0.4932	0.5951			

Table II. Critical Properties and Acentric Factor of Pure Components

	HFC-134a	HFC-143a
Critical temperature, T_c (K)	374.21[a]	345.86[b]
Critical pressure, P_c (kPa)	4059.0[a]	3769.7[c]
Acentric factor, ϖ	0.3268[a]	0.2611[a]

[a] REFPROP 6.01 [2].
[b] Aoyama et al. [11].
[c] Giuliani et al. [5].

with the following expressions for the temperature-dependent a and b parameters

$$a = a_0 \exp(a_1 T + a_2 T^2) \tag{8}$$

$$b = b_0 + b_1 T + b_2 T^2 \tag{9}$$

P is the pressure in kPa, v is the molar volume in $\mathrm{L \cdot mol^{-1}}$, T is the temperature in K, and $R = 8.314\,45$ is the universal gas constant in $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. Consequently, the a and b parameters in Eqs. (1) and (6) are expressed in $\mathrm{kPa \cdot L^2 \cdot mol^{-2}}$ and $\mathrm{L \cdot mol^{-1}}$, respectively. The subscript c in Eqs. (3)–(5) denotes a critical point property.

The same form of mixing rules was used for both equations of state,

$$a = \sum \sum \xi_i \xi_j a_{ij} \tag{10}$$

$$b = \sum \sum \xi_i \xi_j b_{ij} \tag{11}$$

where ξ_i is the mole fraction of the ith component and

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

$$b_{12} = \frac{(b_{11}^{1/3} + b_{22}^{1/3})^3}{8} \tag{13}$$

where k_{12} is the binary interaction parameter. The critical properties and acentric factors are given in Table II. The a and b of the CSD equation of state were cited from REFPROP 5.0 [10]. They are listed in Table III.

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

$$obj = \sum_{i=1}^{N} \left(\frac{P_{\mathrm{cal},\,i} - P_{\mathrm{exp},\,i}}{P_{\mathrm{exp},\,i}} \right) \tag{14}$$

Table III. Coefficients of the CSD Equation of State Used for Data Correlation [10]

Coefficients	HFC-134a	HFC-143a
a_0 (kPa · L^2 · mol^{-2})	3582.171 4	2763.909 2
a_1 (K^{-1})	$-2.811\,136\,2 \times 10^{-3}$	$-2.509\,055\,9 \times 10^{-3}$
a_2 (K^{-2})	$-1.446\,788\,8 \times 10^{-6}$	$-1.797\,107\,7 \times 10^{-6}$
b_0 (L · mol^{-1})	0.141 750 31	0.133 152 59
b_1 (L · mol^{-1} · K^{-1})	$-1.627\,631 \times 10^{-4}$	$-1.589\,537\,9 \times 10^{-4}$
b_2 (L · mol^{-1} · K^{-2})	$-0.628\,932\,64 \times 10^{-7}$	$-0.583\,310\,54 \times 10^{-7}$

where N is the number of experimental points, *obj* is the objective function, and the subscripts cal and exp denote calculated and experimental results, respectively.

For six temperatures, that is, 263.15, 273,15, 283.15, 293.15, 303.15, and 313.15 K, the optimized binary interaction parameters were determined and are presented in Fig. 4. In Fig. 4, it is evident that the binary interaction parameters for both the PR and the CSD equations of state decrease as the temperature increases. The binary interaction parameters for both equations of state were fitted by a linear equation as a function of temperature, respectively. These equations are as follows:

$$\text{PR Eq.:} \qquad k_{12} = -0.0001066T + 0.02879 \tag{15}$$

$$\text{CSD Eq.:} \qquad k_{12} = -0.00009057T + 0.02438 \tag{16}$$

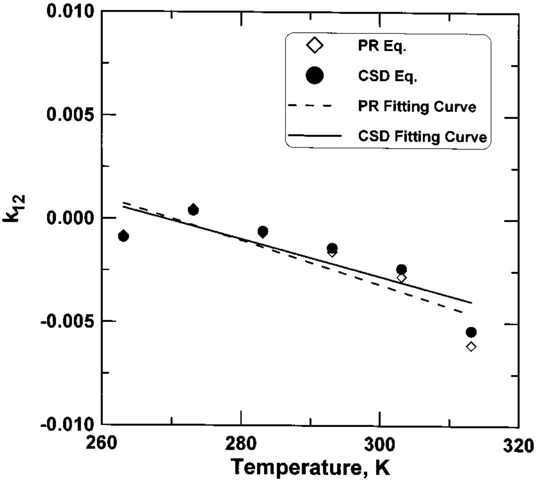

Fig. 4. Binary interaction parameters of PR and CSD equations of state for the HFC-143a + HFC-134a system.

Table IV. Comparison of the Absolute Average Deviations Between the Measured Pressures and the Calculated Values for the HFC-143a + HFC-134a System

	Deviation (%)	
T (K)	Using the optimized interaction parameters	Using the calculated interaction parameters from the linear equations [Eq. (15) or (16)]
	Peng–Robinson equation of state	
263.15	0.29	0.42
273.15	0.29	0.24
283.15	0.18	0.18
293.15	0.51	0.49
303.15	0.37	0.40
313.15	0.29	0.45
Average	0.33	0.36
	Carnahan–Starling–De Santis equation of state	
263.15	0.263	0.338
273.15	0.264	0.273
283.15	0.228	0.260
293.15	0.570	0.577
303.15	0.321	0.352
313.15	0.216	0.262
Average	0.31	0.34

where T is absolute temperature. In Table IV, the absolute average deviation between the measured pressures and the calculated results are given using the optimized interaction parameters at each temperature and the calculated values from Eqs. (15) or (16). As shown in Table IV, the absolute average deviation of pressure for the two cases was generally less than 0.15% for the temperature range investigated.

Figure 5 shows the deviations of bubble point pressures for the HFC-143a + HFC-134a system between the measured data and the calculated results from the CSD equation of state using the calculated interaction parameters from the linear equation. In Fig. 5, the present data were in good agreement with the calculated results from the CSD equation of state, and the deviations were less than 1.0% with the exception of two points.

4. SUMMARY

Isothermal vapor–liquid equilibrium data for the binary system of HFC-143a + HFC-134a have been measured, and 54 data points along six

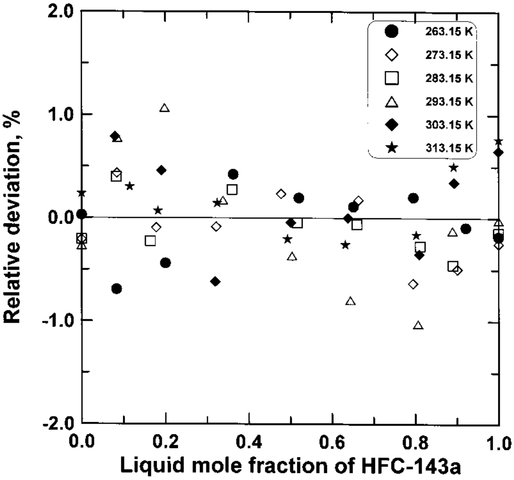

Fig. 5. Relative deviation of bubble point pressures for the HFC-143a + HFC-134a system between the measured data and the calculated results from the CSD equation of state.

isotherms in the temperature range between 263.15 and 313.15 K were obtained, including vapor pressure data for pure components. The experimental data were correlated with the CSD and PR equations of state. The binary interaction parameters for the CSD and PR equations of state were calculated for six isotherms for the HFC-143a + HFC-134a system. The binary interaction parameters for both equations of state were fitted by a linear equation as a function of temperature. The present data were in good agreement with the calculated results from the CSD equation of state, and the deviations were less than 1.0 % with the exception of two points.

REFERENCES

1. W. R. Adams, Ph.D. thesis (Cornell University, Ithaca, NY, 1986).
2. M. McLinden, S. Klein, E. Lemmon, and A. Peskin, *NIST Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures* (REFPROP 6.01) (National Institute of Standards and Technology, Boulder, CO, 1998).
3. H. Sato, Y. Higashi, M. Okada, Y. Takaishi, N. Kagawa, and M. Fukushima, *HFCs and HCFCs* (JARef 1.0) (Japanese Association of Refrigeration, Tokyo, Japan, 1994).
4. *ASHRAE Handbook*, *Fundamentals*, SI ed. (ASHRAE, Atlanta, GA, 1997).
5. G. Giuliani, S. Kumar, P. Zazzini, and F. Polonara, *J. Chem. Eng. Data* **40**:903 (1995).
6. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.* **15**:59 (1976).
7. R. De Santis, F. Gironi, and L. Marrelli, *Ind. Eng. Chem. Fundam.* **15**:183 (1976).

8. G. Morrison and M. O. McLinden, NBS Tech. Note 1226 (U.S. Government Printing Office, Washington, DC, 1986).
9. H. Kubota and T. Matsumoto, *J. Chem. Eng. Japan* **26**:320 (1993).
10. M. Huber, J. Gallagher, M. McLinden, and G. Morrison, *NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixture (REFPROP 5.0)* (National Institute of Standards and Technology, Boulder, CO, 1996).
11. H. Aoyama, G. Kishizawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **41**:1046 (1996).