

# Vapor–Liquid Equilibria of the Binary System HFC134a/HCFC133a

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Eighteen values of the bubble-point and dew-point temperature, pressure, and molar volume for the binary HFC134a/HCFC133a system were measured with a constant-volume method. The saturated points were observed with a transparent sample cell inside a thermostatic bath. The experimental results for the variable compositions cover the temperature range of 300–360 K, corresponding to the pressure range of 0.2909–2.6393 MPa. The experimental uncertainties of temperature and pressure are estimated to be no greater than  $\pm 10$  mK and  $\pm 3.4$  kPa; the maximum and minimum uncertainties of molar volume are 3.63% and 0.043%, respectively. The binary interaction constants  $k_{ij}$  of the Peng–Robinson (PR) equation and the Lee–Kesler–Plöcker (LKP) equation were determined with the experimental data on the basis of the present measurements. The binary interaction constant  $k_{ij}$  of the PR equation is 0.013, and the maximum saturated pressure calculation deviation is 0.71%. When bubble-point and dew-point properties were estimated using the LKP equation, the interaction constants  $k_{ij}$  are 0.9933 and 0.9942, respectively, and the maximum saturated pressure calculation deviations are 0.61% and 0.89%, respectively. Using the PR and LKP equations with the corresponding estimated  $k_{ij}$  values, the deviations of calculating the saturated temperature are  $\pm 0.2$  K and  $\pm 1$  K, respectively. The calculation results of vapor–liquid equilibrium properties based on the PR equation of state are also presented.

## Introduction

The chlorofluorocarbon (CFC) substances do great damage to the ozone layer of the atmosphere, which affects the global ecological balance and human health. HFC134a has been proposed as a working fluid to replace refrigerant CFC12. To purify HFC134a from the binary mixture HFC134a/HCFC133a in the manufacturing process for HFC134a, the vapor–liquid equilibrium properties for this mixture must be known. However, those thermodynamic properties are not always available. This paper reports bubble-point and dew-point measurements of the binary HFC134a (1,1,1,2-tetrafluoroethane)/HFC133a (1-chloro-2,2,2-trifluoroethane) system.

## Experimental Section

**Materials.** HFC134a and HCFC133a were supplied by Institute of Xi'an Modern Chemistry. The purities were 99.9 mass %.

**Apparatus.** The experimental measurements were performed with a set of constant-volume method apparatuses that were used in our previous measurements of  $PVT_x$  properties of R22/R142b,<sup>1</sup> R22/R113,<sup>2</sup> R152a,<sup>3</sup> R22/R152a.<sup>4</sup> The bubble points and dew points are determined by a direct observation method when the temperature is cycled repeatedly. For the bubble point, a bubble with a diameter which is less than 0.1 mm can be observed because of the surface tension of liquids and the refraction of light. The temperature range is only 0.8 mK from the bubble appearance to vanishing. For the dew point, the humid film with a dim lightness has been observed in a range of temperature of 1.2 mK before the film vanished. Before this study, we constructed equipment to make the sample cell hermetic. The apparatus used in this work is shown in Figure 1. The experimental sample cell A is a 1Cr18Ni9Ti stainless

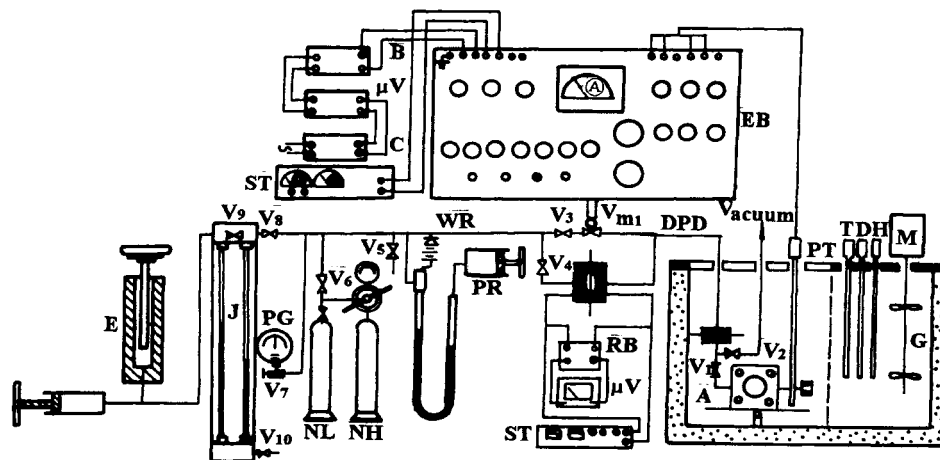
steel cylinder with quartz optical glasses on each side. The sample cell is connected to a diaphragm-type pressure transducer, whose sensor (CN) has been modified to minimize the dead volume. The stainless steel diaphragm separates the sample from the nitrogen gas. The inner volume was calibrated three times by weighing distilled water needed to fill the cell at atmospheric pressure and ambient temperature. The value of volume  $V_A$  is  $24.7036 \pm 0.0037$  cm<sup>3</sup>.

The sample is collected to the sampling cell by liquid-nitrogen condensation. Its mass is measured by chemical balances TG-31, whose measurement range is 0–1000 g, with a sensitivity of 0.5 mg.

The temperature measurement system includes a 25  $\Omega$  platinum resistance thermometer calibrated on the ITS-90 and a thermometer bridge (QJ-69). The temperature of the sample is measured by the temperature of the medium silicone oil in a high-temperature thermostatic bath (25–180 °C), with the thermometer bridge and the platinum resistance thermometer mounted in the vicinity of the sample cell. The temperature of the oil bath is controlled to within  $\pm 1$  mK by a temperature-controlling system. In this study, considering the accuracy of the thermometer, bridge, and thermostatic bath, the uncertainty of the temperature measurements is estimated to be  $\pm 10$  mK.

The pressure measurement system includes a dead-weight pressure gauge, a mercury differential pressure gauge, and a differential pressure detector. The pressure is determined by means of the pressure of the nitrogen gas, which is balanced with the sample pressure. Regarding the temperature deformations of the diaphragm, the pressure difference of the transducer caused by temperature deformations was calibrated. Considering all possible errors, the uncertainty for pressure measurements is estimated to be no greater than  $\pm 3.4$  kPa.

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**Figure 1.** Schematic diagram of the experimental apparatus: A, sample cell; CN, sensor connected to nitrogen; DPD, differential pressure detector; E, dead-weight pressure gauge; EB, thermometer bridge; ECD, galvanometer; FD, diaphragm-type pressure transducer; G, stirrer; H, heater; J, mercury differential pressure gauge; NH, high-pressure nitrogen gauge cylinder; NL, low-pressure nitrogen gauge cylinder; PG, bourdon pressure gauge; PR, differential pressure regulating device; PS, stabilizer; PT, platinum resistance thermometer; RB, measuring resistance; RV, pressure reducer; TB, thermostated bath; WR, alarm; V1–V10, valves; M, solenoid motor.

**Table 1.** Vapor-Pressure Data of HCFC22

<i>T</i> /K	$p_{\text{exp}}$ /MPa	$p_{\text{cal}}$ /MPa	dev/% <sup>a</sup>
310.54	1.4395	1.4383	0.083
315.64	1.6273	1.6288	-0.092
320.19	1.8120	1.8140	-0.110
325.24	2.0384	2.0372	0.059
330.83	2.3052	2.3073	-0.091
335.43	2.5507	2.5488	0.075
340.61	2.8404	2.8429	-0.088
345.71	3.1543	3.1568	-0.079

$$^a \text{dev} = 100(p_{\text{exp}} - p_{\text{cal}})/p_{\text{cal}}$$

The molar volume of the sample in the cell is determined by the ratio of the inner volume of the cell and the quantity of the sample charged into the cell. The uncertainty of the molar volume is estimated as 0.043–3.63% in the molar volume range from 90.55 cm<sup>3</sup>·mol<sup>-1</sup> to 4682.51 cm<sup>3</sup>·mol<sup>-1</sup>.

To verify the reliability of the experimental apparatus mentioned above, vapor-pressure measurements of HCFC22 (purity 99.95%) were performed with this apparatus. Eight experimental data were obtained at temperatures from 310.4 K to 345.71 K. Compared with Wagner's vapor-pressure equation,<sup>5</sup> the average deviation is 0.085% and the maximum deviation is 0.11%. The results of the comparison are given in Table 1.

Wagner's vapor-pressure equation is given by

$$\ln p_r = \frac{n_1 \vartheta + n_2 \vartheta^{1.5} + n_3 \vartheta^2 + n_4 \vartheta^{4.5}}{T_r} \quad (1)$$

where  $T_r = T/T_c$ ,  $\vartheta = 1 - T_r$ , and for HCFC22,  $n_1 = -7.149\,993\,69$ ,  $n_2 = 2.222\,153\,754$ ,  $n_3 = -1.923\,902\,01$ ,  $n_4 = -3.259\,731\,82$ ,  $T_c = 369.28$  K, and  $p_c = 4.9885$  MPa.

## Results and Discussion

Nine bubble-point data were obtained in the temperature range from 300 K to 350 K, in the pressure range from 0.2909 MPa to 2.3931 MPa, in the molar volume range from 90.55 cm<sup>3</sup>·mol<sup>-1</sup> to 107.56 cm<sup>3</sup>·mol<sup>-1</sup>, and in the composition range from 10 mol % to 90 mol % HFC134a. Nine dew-point data were obtained in the temperature range from 318 K to 358 K, in the pressure range from 0.5011 MPa to 2.3931 MPa, in the molar volume range from 90.55 cm<sup>3</sup>·mol<sup>-1</sup> to 107.56 cm<sup>3</sup>·mol<sup>-1</sup>, and in the composition

**Table 2.** Bubble-Point Data of the HFC134a/HCFC133a System

<i>T</i> /K	$p_{\text{exp}}$ /MPa	$x^a$ /mole fraction	$v^b$ /cm <sup>3</sup> ·mol <sup>-1</sup>
300.02	0.2909	0.1146	90.55
305.14	0.3993	0.2173	91.13
314.75	0.5907	0.3065	92.88
320.43	0.7863	0.4265	94.07
326.71	0.9998	0.5074	95.69
332.84	1.3064	0.6381	97.65
338.54	1.6375	0.7495	100.11
343.25	1.9451	0.8324	102.77
349.92	2.3931	0.9106	107.56

<sup>a</sup> The liquid composition of HFC134a. <sup>b</sup> The liquid molar volume.

**Table 3.** Dew-Point Data of the HFC134a/HCFC133a System

<i>T</i> /K	$p_{\text{exp}}$ /MPa	$y^a$ /mole fraction	$v^b$ /cm <sup>3</sup> ·mol <sup>-1</sup>
318.78	0.5011	0.2298	4682.51
320.74	0.5404	0.2645	4327.22
324.62	0.6435	0.3319	3618.77
330.81	0.8183	0.4120	2820.60
335.69	1.0383	0.5263	2180.43
340.75	1.3115	0.6277	1679.68
347.28	1.7331	0.7358	1210.33
354.18	2.2451	0.8207	871.17
357.20	2.6393	0.8981	688.81

<sup>a</sup> The vapor composition of HFC134a. <sup>b</sup> The vapor molar volume.

range from 20 mol % to 90 mol % HFC134a. Experimental measurements are summarized in Tables 2 and 3.

The Peng–Robinson (PR)<sup>6</sup> equation has an acceptable accuracy to calculate the vapor–liquid equilibrium. Based on the experimental data mentioned above, the binary parameter  $k_{12}$  of the PR equation was determined. The critical temperature, critical pressure, and acentric factor of HFC134a and HCFC133a needed in the PR equation are listed in Table 4. In the process of seeking the optimum  $k_{12}$ , the following objective function was used:

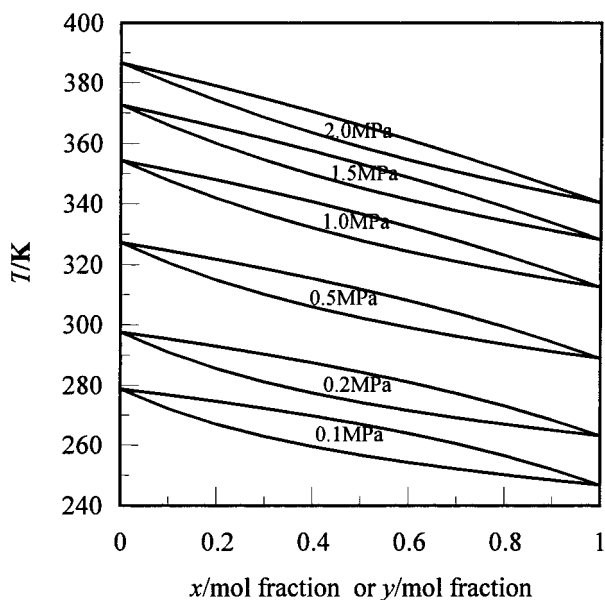
$$\frac{1}{n} \sum_{i=1}^n [(p_{\text{cal},i} - p_{\text{exp},i})/p_{\text{exp},i}]^2 \quad (2)$$

Calculations with  $k_{12} = 0.013$  give a maximum pressure deviation of 0.71%. The PR equation with optimum  $k_{12}$

**Table 4. Constants of HFC134a and HCFC133a Needed by the PR Equation**

substance	$p_c$ /MPa	$T_c$ /K	$\omega^a$	source
HFC134a	4.067	374.25	0.3256	ASHRAE <sup>7</sup>
HCFC133a	4.0116	425.01	0.3027	Liu et al. <sup>8</sup>

<sup>a</sup> Acentric factor.

**Figure 2.** Bubble- and dew-point curves of HFC134a/HCFC133a.

reproduces the bubble-point and the dew-point temperatures; almost all of the results are within  $\pm 0.2$  K.

Figure 2 shows the bubble-point and dew-point curves of this binary system at the different pressures calculated with the PR equation.

The binary interaction constants of the Lee–Kesler–Plöcker (LKP)<sup>9</sup> equation were also determined, but its calculations for the bubble points and dew points are different. For the bubble-point calculation, the binary parameter  $K'_{12}$  of the LKP equation is 0.9933, and for the dew-point calculation,  $K''_{12}$  is 0.9942; the maximum pres-

sure calculation deviations are +0.61% and -0.89%, respectively. The objective function was also used with eq 2 in the process of seeking the optimum  $K'_{12}$  and  $K''_{12}$ .

## Conclusions

In the present study, 18 vapor–liquid equilibrium property data for the binary HFC134a/HCFC133a system have been measured. By means of those experimental data, the PR equation's binary interaction constant parameter was determined, and the bubble-point and dew-point curves of this binary system at the six different pressures, 0.1, 0.2, 0.5, 1.0, 1.5, and 2.0 MPa, have been presented. The LKP equation's binary parameters have also been discussed.

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