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Precise Measurements of the Vapor-Liquid Equilibria (VLE) of HFC-32/134a Mixtures Using a New Apparatus

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A new apparatus for precise measurements of the vapor-liquid equilibria of mixtures by the circulation method has been developed. This apparatus has two special components: a high-stability temperature control system and a helium pressurization system. The temperature in the liquid bath surrounding the sample cell is kept constant within ±0.5 mK. The helium pressurization system increases the pressure of the sampled mixture when measuring the compositions at low temperatures by gas chromatography. With these components, the uncertainty in measuring the vapor-liquid equilibria has been reduced. Using this apparatus, the vapor-liquid equilibria of HFC-32/134a mixtures were measured in a temperature range of 263.15 to 293.15 K. These results are in good agreement with the calculated results from REFPROP (Ver. 6.01) with a relative pressure difference of about 2%.

KEY WORDS: circulation method; HFC-134a; HFC-32; mixture; refrigerant; vapor-liquid equilibrium.

1. INTRODUCTION

Development of new alternative refrigerants is an important issue for solving the problems due to the ozone depletion and the global warming introduced by CFCs and HCFCs. It is known that the coefficient of performance (COP) for a refrigeration system using a non-azeotropic mixture

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as the working fluid is better than that using a pure refrigerant [1]. The vapor-liquid equilibrium (VLE) data of the mixture is often used for evaluating the COP. Therefore, in order to precisely evaluate the theoretical COP, it is imperative to precisely measure the VLE of mixtures that may be used as new alternative refrigerants.

The previous apparatus [2] for measuring VLE data controlled the temperature of the equilibrium cell by an air-cooling system. Thus, the apparatus could not be operated at temperatures lower than 273 K. In order to evaluate the mixture as a working fluid for refrigeration or heat pump systems, VLE data of the mixture at lower temperature are required. In addition, the uncertainty in the temperature measurement in the VLE apparatus described in previous papers [2–4] was ± 15 to 30 mK, which contributed significantly to the experimental uncertainty.

For precise measurements of VLE, a new apparatus was developed. Details of this apparatus are described in the next section. Using the new apparatus, VLE data for HFC-32 (CH_2F_2) + HFC-134a (CH_3FCF_3) mixtures were measured. In the future, VLE of hydrocarbon + hydrofluorocarbon mixtures will be measured for the development of new refrigerants.

2. APPARATUS

Figure 1 is a schematic of the VLE apparatus developed in this study. This apparatus consists of four components: a liquid thermostat bath (LT) with a vapor-liquid cell (VL), a device for pressurizing a sampled mixture with helium gas (HC-VS-LS), an air thermostat bath (AT) for heating the pressurized mixtures, and a gas chromatograph (GC) for measuring the composition of the mixture. The GC (Shimadzu, GC-8A) is equipped with a Porapak-Q column (2 m long, ID: 3 mm, mesh range: 50/80).

2.1. High-Stability Temperature Control System

Since the previous thermostat bath [2] was cooled by an air-cooling system, it was difficult to operate at temperatures lower than 273 K. In this study, a liquid-cooling system with an antifreeze solution is used. This system operates at temperatures down to 253 K. Figure 2 shows a schematic of the improved liquid thermostat bath (LT in Fig. 1). Its external dimensions are length 800 mm × width 500 mm × height 470 mm, and the thickness of the wall is 80 mm except for the upper wall. An ethylene glycol plus water solution is used as the bath fluid. At the right side of Fig. 2, the cooling and heating system used to control the temperature of the bath is shown. A cooling coil (P) is connected to a liquid circulation thermostat

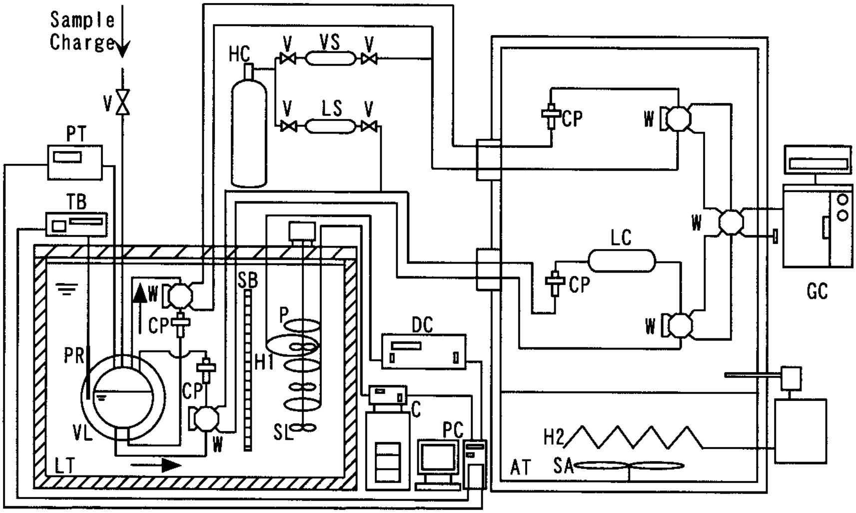

Fig. 1. Schematic of the vapor-liquid equilibrium apparatus. LT: liquid thermostat bath, VL: vapor-liquid cell, PR: 100 Ω standard platinum resistance thermometer, CP: circulation pump, W: six-way switching valve, SB: shield board, P: cooling coil, SL, SA: stirrer, H1, H2: heater, TB: thermometer bridge, PT: pressure transducer, C: liquid circulation thermostat bath, DC: DC power supply, PC: personal computer, HC: helium cylinder, LS: helium supercharge cylinder for liquid sample, VS: helium supercharge cylinder for vapor sample, LC: cylinder for liquid sample, AT: air thermostat bath, GC: gas chromatograph, V: valve.

bath (C in Fig. 1; Julabo, FP40-HD), in which a temperature-controlled alcohol solution circulates. The temperature of this alcohol solution is kept lower than the target temperature to cool the LT. An annular heating wire (H1) is connected to a dc power source (DC in Fig. 1; HEWLETT-PACKARD, HP6655A), and the output of this source is controlled by a computer-based PID algorithm (PC in Fig. 1) so that the output of a temperature sensor (PR; Netsushin, NSR-300) in VL is equal to the target temperature. The stirrer (SL) is placed inside the cooling coil. A shield board (SB) is installed between VL and H1 so that the heated and cooled antifreeze solution does not contact directly with VL.

The inner volume of VL is about 163 cm^3, and it is located in the center of the thermostat bath. Reinforced glasses are used at both ends of the cell so that the condition in the cell can be observed through these glasses from the window of the thermostat bath. Two holes for sample charge and pressure measurement are located on the upper wall of the cell. The equilibrium pressure is measured by a calibrated pressure transducer (PT; Paroscientific, 2900AT). The standard uncertainty of the pressure measurement is estimated to be 0.01% of pressure reading plus 0.01% of

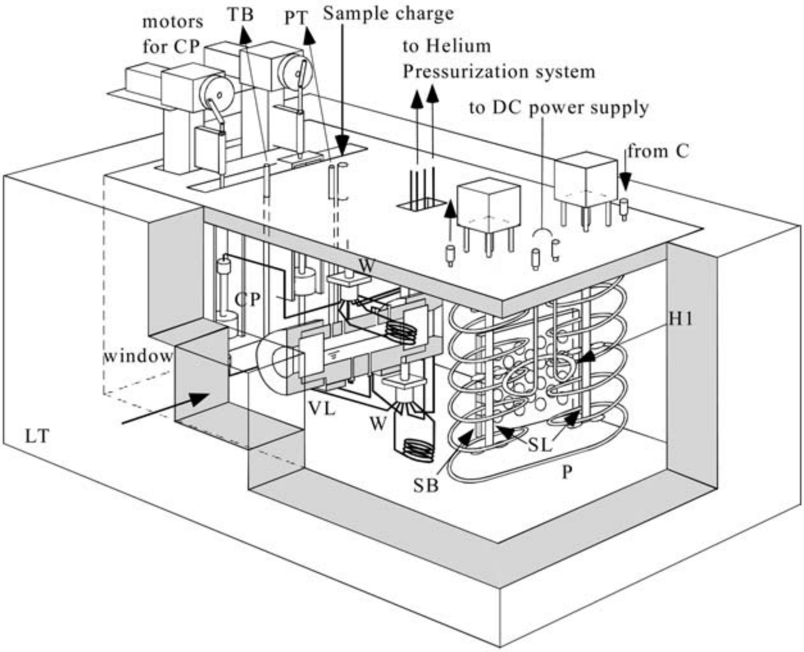

Fig. 2. Schematic of the liquid thermostat bath with a vapor-liquid cell. LT: liquid thermostat bath, VL: vapor-liquid cell, CP: circulation pump, W: six-way switching valve, TB: thermometer bridge, PT: pressure transducer, SB: shield board, SL: stirrer, P: cooling coil, H1: heater.

the full scale. The full scale of this pressure transducer is 6.2 MPa. The temperature sensor (PR) is installed in the side wall of the cell. This temperature sensor is made of a 100 Ω platinum resistance (JPt100) wire, and the temperature is measured by means of reading the resistance of the sensor using an ac bridge circuit (TB; Automatic Systems Laboratories, F-17A) based on ITS-90. The standard uncertainty of the temperature measurement is estimated to be 3 mK considering the effects of self-heating, temperature drift, and the uncertainty in measuring the resistance ratio with the ac bridge. When the temperature is kept constant with fluctuations of less than 0.5 mK over 15 min, this condition is regarded as thermal equilibrium.

The six-way switching valves (W) for sampling the mixture of each phase are placed above and below the cell; the upper valve for the vapor phase and the lower valve for the liquid phase. To achieve complete sample mixing, each phase is independently extracted by a circulating pump (CP) driven by a motor (rotation period is about 10 s) as shown in Fig. 2.

Through a sample loop connected with the six-way switching valve, the extracted mixture is returned into the cell. When the composition of the mixture is to be measured, the six-way switching valves of both phases are simultaneously turned so that the mixture sampled in the sample loop is carried to the helium pressurization system for increasing the pressure.

2.2. Helium Pressurization System

Because the quantity of the sampled mixture of each phase for the composition measurement is so small when it is sampled only once, the pressure of the sampled mixture is very low. Therefore, it is difficult to send the sampled mixture to the gas chromatograph. In order to increase the pressure of the sampled mixture, the quantity of the sampled mixture may be increased by means of sampling several times. However, the withdrawal of many samples changes the equilibrium condition, and increases the uncertainty in measuring the equilibrium pressure, equilibrium temperature, and composition. In order to overcome the difficulty, the sampled mixture is pressurized using helium gas (HC in Fig. 1); because helium is a carrier gas of the gas chromatograph, it does not affect the composition measurement. With the helium pressurization system, a small amount of the sampled mixture is sufficient to determine the composition. In this apparatus, the sampled mixture is pressurized to about 0.2 MPa.

3. RESULTS

Using the apparatus, vapor-liquid equilibria of HFC-32/134a mixtures were measured at four temperatures (263.15, 273.15, 283.15, and 293.15 K). Figure 3 shows these results. Table I lists the measured data.

The purities of HFC-32 and HFC-134a (Asahi Glass Co., Ltd.) are 99.98 and 99.99% in mass fractions, respectively. The standard uncertainty in measuring the liquid and vapor phase compositions is estimated to be 0.2% in mole fraction. This uncertainty was confirmed by measuring a composition of a synthesized mixture that was prepared by blending the pure components with gravimetric weighing. In Fig. 3, the isotherms calculated from REFPROP (Ver. 6.01) [8] are also shown. Both results are in good agreement at all temperatures.

Figure 4 shows the relative deviations of the measured bubble-point pressure P_{exp} from P_{REF} calculated from REFPROP as a function of the measured bubble-point pressure P_{exp}. In this figure, the relative deviations of the results from other studies are also indicated. The relative deviations of our data are within 2.5%, although the results at lower pressures have

Table I. Vapor-Liquid Equilibrium Data of HFC-32/134a Mixtures

Pressure (kPa)	Mole fraction of HFC-32	
	Liquid	Vapor
	$T = 263.150$ K	
251.6	0.1384	0.3054
304.7	0.2863	0.5180
320.3	0.3239	0.5631
357.6	0.4289	0.6504
397.4	0.5408	0.7468
432.2	0.6110	0.7996
447.0	0.6682	0.8293
465.2	0.7064	0.8544
488.2	0.7554	0.8907
542.7	0.8967	0.9509
551.8	0.9233	0.9672
	$T = 273.150$ K	
361.1	0.1425	0.2930
432.2	0.2768	0.4927
454.3	0.3173	0.5381
503.3	0.4191	0.6391
558.1	0.5356	0.7329
604.9	0.6099	0.7912
627.6	0.6550	0.8235
651.2	0.6985	0.8454
683.3	0.7567	0.8820
757.9	0.8963	0.9533
770.1	0.9216	0.9653
	$T = 283.150$ K	
503.3	0.1362	0.2704
596.7	0.2748	0.4706
626.5	0.3166	0.5200
691.7	0.4142	0.6216
826.5	0.6094	0.7822
856.7	0.6531	0.8126
929.9	0.7565	0.8727
1032.2	0.8946	0.9498
1048.9	0.9192	0.9628
	$T = 293.150$ K	
684.8	0.1350	0.2564
805.2	0.2751	0.4587
844.9	0.3181	0.5024
927.0	0.4138	0.5992
1021.5	0.5179	0.7031
1103.6	0.6095	0.7645
1142.3	0.6507	0.8034
1375.1	0.8948	0.9473
1396.6	0.9211	0.9608

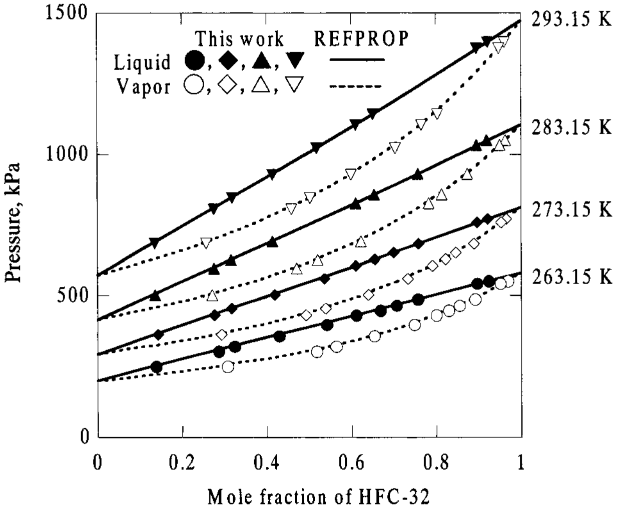

Fig. 3. Vapor-liquid equilibria of HFC-32/134a mixtures.

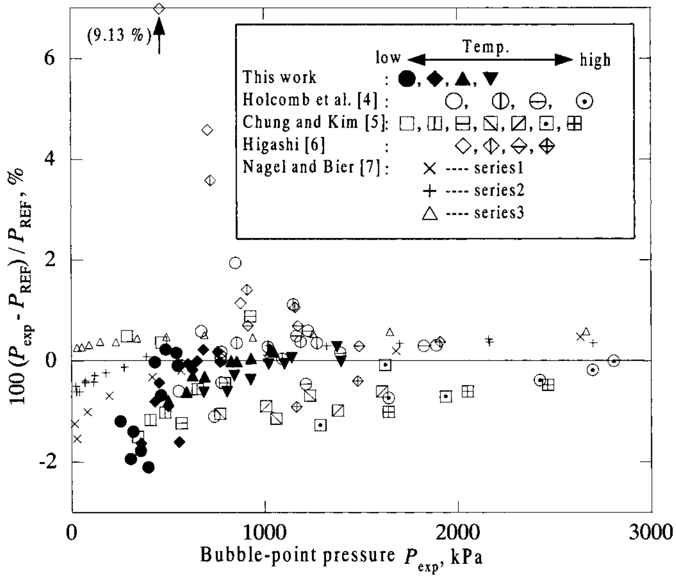

Fig. 4. Relative deviations of bubble-point pressure P_{exp} from P_{REF} as a function of P_{exp}. P_{REF} was calculated from REFPROP (Ver. 6.01). The relative deviations of this work are within 2%.

larger deviations. The deviations of other studies are also qualitatively similar to those of our work except for those of Higashi [6]. It is thought that the tendency of larger deviations at lower pressures originates from the predictions of REFPROP for the HFC-32+HFC-134a system. However, these deviations are within the uncertainties of the composition and pressure measurements.

4. CONCLUSION

A new apparatus for precise measurements of vapor-liquid equilibria was developed in this study. This apparatus consists of a high-stability temperature-control system and a helium pressurization system. With these new components, temperature control of ±0.5 mK at the target temperature and accurate composition measurements with a small amount of sample were realized.

Using this apparatus, vapor-liquid equilibria of HFC-32 and HFC-134a mixtures were measured. The results at all temperatures are in good agreement with values calculated with REFPROP, i.e., within 2% in the relative pressure difference.

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