International Journal of Thermophysics, Vol. 16, No. 3, 1995

Bubble-Point Pressures and Liquid Densities of Binary R-125 + R-143a System[1]

J. V. Widiatmo,[2,3] H. Sato[2] and K. Watanabe[2]

Bubble-point pressures and saturated-liquid densities of the binary R-125 (pentafluoroethane) + R-143a (1,1,1-trifluoroethane) system have been measured for several compositions at temperatures from 280 to 330 K by means of a magnetic densimeter coupled with a variable-volume cell mounted with a metallic bellows. The experimental uncertainties of the temperature, pressure, and density measurements and the composition determination were estimated to be within ±15 mK, ±12 kPa, ±0.2%, and ±0.1 wt%, respectively. The purities of the samples used throughout the measurements are 99.98 wt% for R-125 and 99.0 mol% for R-143a. Based on the present data, the thermodynamic behavior of the vapor–liquid equilibria of this binary refrigerant mixture has been evaluated by using the Peng–Robinson equation for the bubble-point pressures, and the modified Hankinson–Brobst–Thomson equation for the saturated-liquid densities. This was done to identify the optimized binary interaction parameters.

KEY WORDS: alternative refrigerants; binary mixtures; bubble-point pressure; saturated-liquid density; vapor–liquid equilibria.

1. INTRODUCTION

Recent concerns on the research and development of CFC and HCFC alternatives have forced HFC refrigerant mixtures to be considered as perspective replacements for some CFCs and HCFCs. This is due to the limited number of pure HFC refrigerants, which are nonflammable, environmentally acceptable and thus can safely be applied as working fluids. Binary and ternary mixtures of the nonflammable and flammable

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Department of Mechanical Engineering, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan.

[3] To whom correspondence should be addressed.

HFC refrigerants, by which the flammability can be avoided, are presently being considered as promising alternatives.

The nonflammable R-125 and the flammable R-143a both have vapor pressures similar to those of R-115 and of R-502 (the azeotropic mixture of R-22 and R-115). Therefore, their mixture can be expected as a promising alternative to replace R-115 and R-502. The present work aims to investigate the bubble-point pressures, the saturated-liquid densities, and the P–ρ–T–x properties of the liquid phase of the mixture.

2. MEASUREMENTS

All measurements in the present work were performed by using a magnetic densimeter coupled with a metallic bellows. The apparatus is schematically shown in Fig. 1. The apparatus is a modification of that reported by Maezawa et al. [1]. In the former apparatus, the pressure was measured through a differential pressure gauge. In the present apparatus, however, the differential pressure gauge has been replaced by a quartz pressure transducer (Paroscientific Model 31K-101) that allows a direct sample pressure measurement and produces data with higher accuracy. The density of the sample was obtained from a magnetic densimeter, while the temperature was measured by means of a 25-Ω standard platinum resistance thermometer placed in the vicinity of the magnetic densimeter. Controlling the pressure of the nitrogen gas filled in the outer part of the metal bellows allows the sample to be brought into the saturated- and/or compressed-liquid condition. The saturation condition was carefully determined by observing the dissappearance and reappearance of a bubble in liquid phase through the Pyrex glass wall of the sample cell. The detailed procedures of measurement and composition determination have been reported elsewhere [2], therefore no further explanation will be given in this paper.

The uncertainty in the temperature measurement was estimated to be no greater than ±15 mK. This uncertainty is obtained by a summation of the precision of the resistance thermometer, thermometer bridge and the possible temperature fluctuation of thermostated liquid bath. The uncertainty in the pressure measurement was estimated to be within ±2 kPa for compressed-liquid pressures. This value was obtained by considering the reproducibility of the quartz pressure transducer and the pressure stability during the measurements. The uncertainty in pressure measurement becomes ±12 kPa for bubble-point pressures due to the possible error in the saturation point determination. The uncertainty in density measurement was within ±0.2%, which included the uncertainty of the magnetic-buoy density and the reproducibility of the electric current measurements.

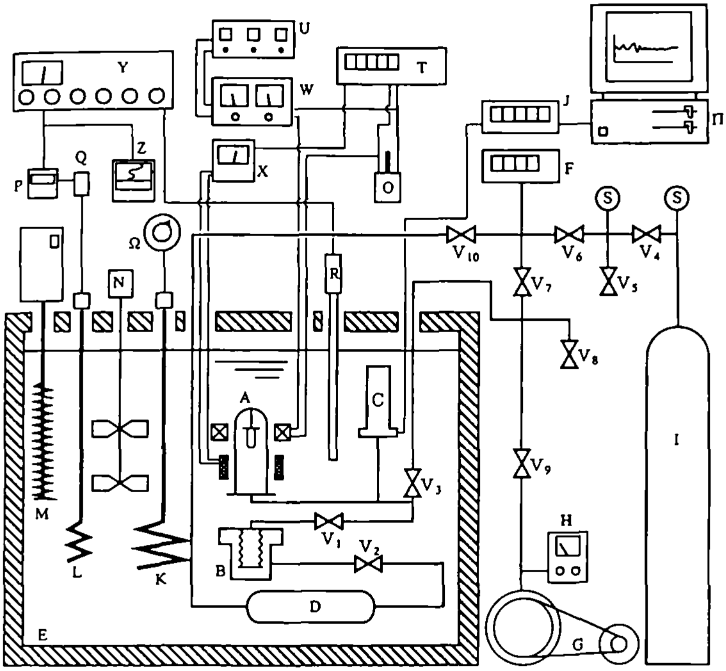

Fig. 1. Experimental apparatus. (A) Magnetic densimeter, (B) variable-volume cell, (C) digital quartz pressure transducer, (D) damper, (E) thermostat, (F) digital pressure gauge, (G) vacuum pump, (H) vacuum gauge, (I), nitrogen gas, (J) digital quartz pressure computer, (K) main heater, (L) subheater, (M) cooler, (N) stirrer, (O) standard resistor, (P) PID controller, (Q) thyristor, (R) platinum resistance thermometer, (S) pressure gauge, (T) digital multimeter, (U) current controller, (V_1-V_{10}) valves, (W) DC power supply, (X) galvanometer, (Y) thermometer bridge, (Z) pen recorder, (Ω) transformer, and (Π) personal computer.

The experimental uncertainty in composition was estimated to be within ±0.1 wt% R-125, as calculated from the sample remaining in the supplying vessels after sample expansions into the metal bellows. The purities of R-125 and of R-143a were 99.98 wt% and 99.0 mol%, respectively, according to the analysis performed by the manufacturers. The reproducibility of the apparatus has also been confirmed by performing measurements of vapor pressures and saturated-liquid densities of R-22. The measured results have also been examined by comparing them with vapor pressure and saturated-liquid density correlations by McLinden [3] for R-22.

3. RESULTS

Bubble-point pressures and saturated-liquid densities of the binary system have been measured in the temperature range from 280 to 320 K in 10 K intervals and compositions of 10, 30, 45, 50, 70, and 90 wt% R-125. The compressed-liquid densities (P–ρ–T–x properties) were obtained at a composition of 45 wt% R-125 and temperatures of 280 and 290 K. The experimental results are presented in Tables I and II.

Table I. Measured Bubble-Point Pressures and Saturated-Liquid Densities

T (K)	P (MPa)	ρ (kg · m^{-3})	x (mol · mol^{-1})
279.987	0.774	1021.7	0.0726
289.989	1.026	983.8	0.0726
299.987	1.338	942.8	0.0726
299.987	1.342	942.9	0.0726
309.986	1.722	898.0	0.0726
319.985	2.172	841.7	0.0726
279.987	0.779	1071.3	0.2305
279.988	0.781	1071.3	0.2305
289.988	1.034	1031.6	0.2305
299.987	1.349	988.7	0.2305
309.985	1.731	941.5	0.2305
319.987	2.190	880.5	0.2305
279.988	0.777	1113.7	0.3637
279.988	0.786	1115.9	0.3637
289.988	1.029	1072.4	0.3637
289.988	1.033	1072.2	0.3637
279.988	0.779	1115.6	0.3637
279.988	0.779	1115.2	0.3644
279.988	0.773	1127.0	0.4118
289.988	1.033	1085.1	0.4118
299.987	1.352	1039.1	0.4118
309.985	1.741	987.1	0.4118
319.986	2.211	925.2	0.4118
279.988	0.789	1202.1	0.6780
289.989	1.054	1156.4	0.6780
299.987	1.380	1106.6	0.6780
309.986	1.779	1049.8	0.6780
319.985	2.257	981.4	0.6780
329.985	2.829	884.9	0.6780
279.988	0.807	1252.5	0.8631
289.988	1.078	1201.7	0.8631
299.989	1.414	1147.7	0.8631
309.985	1.820	1087.4	0.8631
319.986	2.311	1013.7	0.8631

Table II. Measured Compressed-Liquid Densities

T (K)	P (MPa)	ρ (kg · m^{-3})	x (mol · mol^{-1})
279.988	0.999	1115.1	0.3637
279.988	1.505	1118.4	0.3637
279.988	1.993	1122.3	0.3637

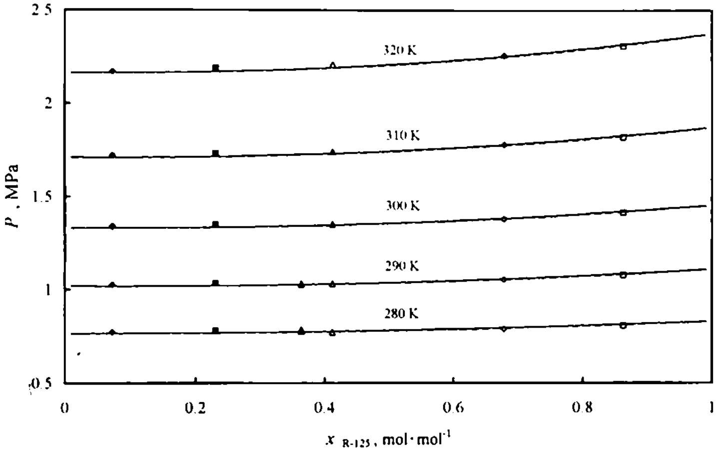

Fig. 2. Measured bubble-point pressures: (- —) bubble-point; (· - -) dew-point.

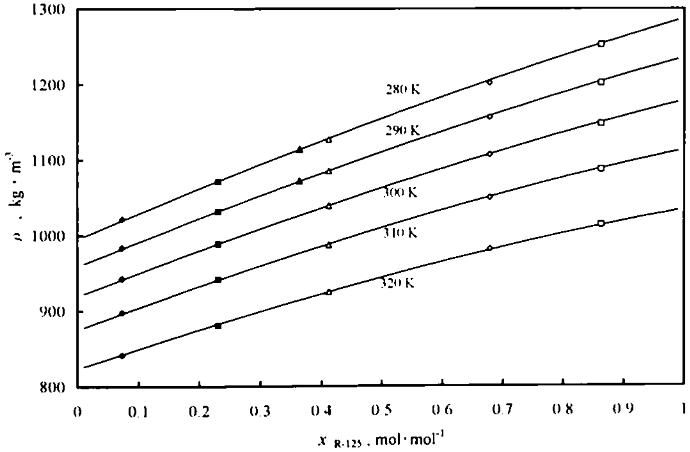

Fig. 3. Measured saturated-liquid densities.

Figure 2 depicts the measured results of bubble-point pressures for the different compositions. The solid lines were calculated from the Peng–Robinson (PR) equation [4] with the optimized binary interaction parameter discussed later. The calculated dew-point pressures are also displayed in Fig. 2, although they almost overlap with the bubble-point pressures. This fact implies that this binary system is nearly azeotropic for a wide range of compositions. The real azeotropic composition may exist in the vicinity of 1 mol% R-125 as indicated by a bubble-point pressure lower than the vapor pressure of R-143a; this was calculated using the optimized PR equation. Some more detailed measurements near the calculated azeotropic composition are needed to determine the exact azeotropic composition.

Figure 3 represents the composition dependence of the measured saturated-liquid densities. Solid lines were calculated from the Hankinson–Brobst–Thomson (HBT) equation originally modified by Maezawa et al. [5], which are discussed later.

4. DISCUSSION

The Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) equations have been applied to analyze the bubble-point pressures obtained in the present work. The binary interaction parameter, k_{ij}, of those equations have been optimized for the binary system along each isotherm as listed in Table III. The critical parameters of R-125 and R-143a used in all equations cited in this paper are given in Table IV. The critical temperature and density of R-125 are those determined by Kuwabara et al. [6], while the critical pressure is the value proposed by Sagawa et al. [7]. The critical temperature, pressure, and density of R-143a are those determined by Fukushima [8].

Table III. Binary Interaction Parameters of the PR, SRK, HBT, and Rackett Equations

T	k_{ij}			
(K)	PR	SRK	HBT	Rackett
280	−0.009	−0.017	−0.010	−0.002
290	−0.012	−0.023	−0.008	−0.004
300	−0.013	−0.025	−0.008	−0.006
310	−0.014	−0.027	−0.009	−0.010
320	−0.015	−0.025	−0.006	−0.009

Table IV. Parameters Used in the PR, SRK, HBT, and Rackett Equations

	R-125	R-143a
T_c (K)	339.165	345.97
P_c (MPa)	3.620	3.769
ρ_c ($kg \cdot m^{-3}$)	568	429
M ($g \cdot mol^{-1}$)	120.02	84.04
ω	0.299	0.259
V^* ($cm^3 \cdot mol^{-1}$)	209.4	192
Z_{RA}	0.267	0.2567

The k_{ij} of both the PR and the SRK equations, as summarized in Table III, show similar temperature dependence although there exist differences between their absolute values. Figure 4 shows that the optimized PR equation can reproduce the measured data satisfactorily within ±10 kPa (±0.1 %), smaller than the estimated uncertainty of the present pressure measurement. The systematic deviation of the absolute pressure values from the PR equation for different compositions could be due to the mixing rule applied to the PR equation. The SRK equation with optimized binary parameter is also found to reproduce the measured bubble-point pressures fairly well within ±12 kPa.

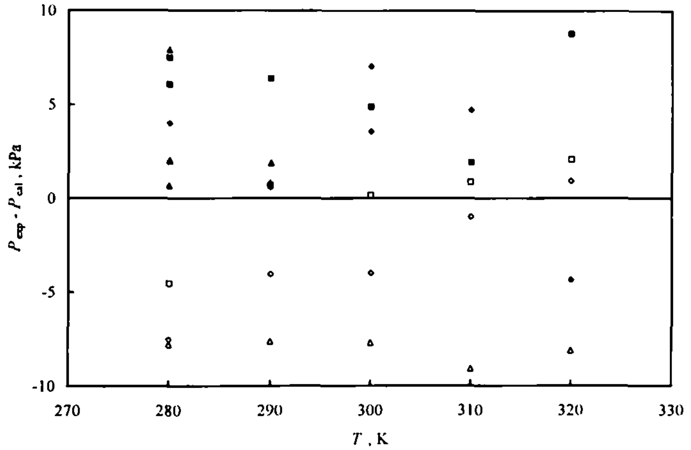

Fig. 4. Deviation of measured bubble-point pressures from the PR equation: (◆) 10 wt% R-125; (■) 30 wt% R-125; (▲) 45 wt% R-125; (□) 50 wt% R-125; (◇) 75 wt% R-125; (△) 90 wt% R-125.

The PR and the SRK equations, which are widely being employed in industrial applications, are confirmed effective only in reproducing the bubble-point pressures but not the liquid densities. Although these equations were applicable in reproducing the present bubble-point pressures, as shown in Fig. 4, they showed the deviations up to ten percent from the saturated-liquid densities. Therefore instead, we applied the modified HBT and the modified Rackett equations to reproduce the liquid densities.

The HBT equation applied to represent the present saturated-liquid densities is that originally modified by Maezawa et al. [5], which includes two binary interaction parameters, k_{ij} and l_{ij}, in its mixing rule. In the present study, l_{ij}, appearing in the mixing rule for the acentric factor of the mixture, was considered to be zero for all temperatures. The optimized k_{ij} for each temperature are listed in Table III. Also listed in Table III are the optimized k_{ij} for the modified Rackett equation [9]. The temperature dependence of k_{ij} for the HBT equation is different from that for the Rackett equation, i.e., it increases with the increasing temperature in the HBT equation, while in the Rackett equation it behaves inversely.

Figure 5 depicts the deviation of measured saturated-liquid densities from the optimized HBT equation. The midified HBT equation represents the measured densities accurately within ±0.3%. In the case of the present binary system, the modified Rackett equation is also able to reproduce the measured data within ±0.3%.

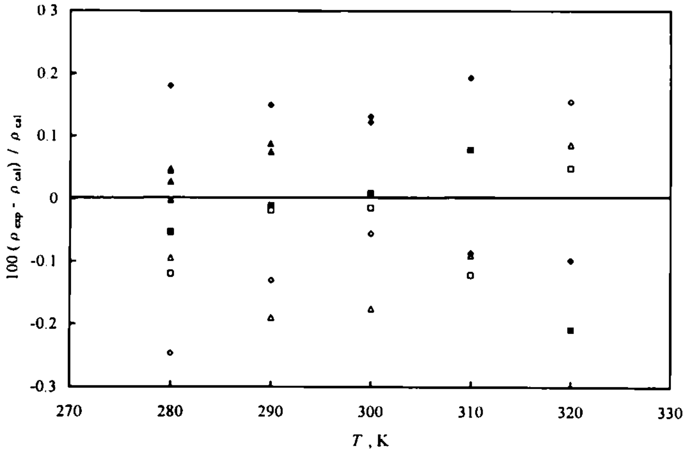

Fig. 5. Deviation of measured saturated-liquid densities from the HBT equation: (◆) 10 wt% R-125; (■) 30 wt% R-125; (▲) 45 wt% R-125; (□) 50 wt% R-125; (◇) 75 wt% R-125; (△) 90 wt% R-125.

The compressed-liquid densities (P–ρ–T–x properties) are analyzed by applying the following Tait equation proposed by Thomson et al. [10].,

$$v = v_s\left(1 - C\ln\frac{B+P}{B+P_s}\right) \tag{1}$$

We have adopted this equation for representing the compressed-liquid densities of binary R-32 + R-134a system [11], which resulted in good agreement within ±0.3%. In Eq. (1), v_s is saturated-liquid molar volume, in which we used the values calculated from the modified HBT equation, parameters B and C are functions of acentric factor and the corresponding temperature, while P_s is the vapor pressure of the mixture, which was originally proposed as a function of calculated critical parameters and the acentric factor for the mixture. In the present study, we replaced the calculated P_s values by the measured bubble-point pressures. If the bubble-point data are not available, bubble-point pressure calculated from the PR equation described in the previous subsection can be used as P_s. This modified Tait equation represented the measured data within ±0.3%.

5. CONCLUSIONS

Thirty-four bubble-point pressures and saturated-liquid densities of the binary R-125/143a system have been measured over the temperature range of 280–320 K at compositions of 10, 30, 45, 50, 75, and 90 wt% R-125. Three compressed-liquid densities at composition of 45 wt% have also been determined. The applicability of the Peng–Robinson and the Soave–Redlich–Kwong equations for representing the bubble-point pressures of the system have been confirmed by optimizing their binary interaction parameters. The measured saturated-liquid densities are reproduced satisfactorily within ±0.3% by using the modified Hankinson–Brobst–Thomson and the modified Rackett equations with their optimized binary interaction parameters.

ACKNOWLEDGMENTS

We are indebted to the Grant-in-Aid for Scientific Research Fund (No. 04402025) of the Ministry of Education, Science and Culture, Japan, and to Du Pont-Mitsui Fluorochemicals and Daikin Industries, Ltd., for their valuable cooperations in furnishing the research-grade samples of R-125 and R-143a. The assistance by Shinya Ueda is also greatly acknowledged.

REFERENCES

1. Y. Maezawa, H. Sato, and K. Watanabe, *J. Chem. Eng. Data* **35**(3):225 (1990).
2. Y. Maezawa, H. Sato, and K. Watanabe, *Fluid Phase Equil.* **61**:263 (1991).
3. M. O. McLinden, *Int. J. Refrig.* **13**:149 (1990).
4. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.* **15**(1):59 (1976).
5. Y. Maezawa, H. Sato, and K. Watanabe, *Trans. JAR* **10**(1):125 (1993).
6. S. Kuwabara, H. Sato, and K. Watanabe, *High Temp. High Press.* **26**:35 (1994).
7. T. Sagawa, H. Sato, and K. Watanabe, *High Temp. High Press.* **26**:193 (1994).
8. M. Fukushima, *Trans. JAR* **10**(1):87 (1993).
9. C. F. Spencer and R. P. Dannar, *J. Chem. Eng. Data* **18**:230 (1973).
10. G. H. Thomson, K. R. Brobst, and R. W. Hankinson, *AIChE J.* **28**(4):671 (1982).
11. J. V. Widiatmo, H. Sato, nd K. Watanabe, *Fluid Phase Equil.* **99**:199 (1994).