Measurements of Gaseous *PVTx* Properties and Saturated Vapor Densities of Refrigerant Mixture R-125 + R-143a¹

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The experimental *PVTx* properties of a binary refrigerant mixture, R-125 (pentafluoroethane) + R-143a (1,1,1-trifluoroethane), have been measured for a composition of 50 mass % R-125 by a constant-mass method coupled with an expansion procedure in a range of temperatures from 305 to 400 K, pressures from 1.5 to 6.1 MPa, and densities from 92 to 300 kg · m⁻³. The experimental uncertainties of the present measurements are estimated to be within ± 7.2 mK in temperature, ± 3.0 kPa in pressure, ± 0.12 kg · m⁻³ in density, and ± 0.040 mass % in composition. The sample purities are 99.953 mass % for R-125 and 99.998 % for R-143a. Seven saturated vapor densities and dew point pressures of the R-125 + R-143a system were determined, on the basis of rather detailed *PVTx* properties measured in the vicinity of the saturation boundary as well as the thermodynamic behavior of isochores near saturation. The second and third virial coefficients for temperatures from 330 to 400 K were also determined.

KEY WORDS: alternative refrigerants; binary refrigerant mixtures; dew point pressures; HFC-125 + HFC-143a system; PVTx properties; saturated vapor densities; virial coefficients.

1. INTRODUCTION

One of the urgent issues to be solved in the refrigeration industry is to identify the optimum alternative refrigerants to replace the conventional refrigerant R-502 (an azeotropic refrigerant mixture of R-22 (chlorodi-fluoromethane) + R-115 (monochloropentafluoroethane)), which is being

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used in refrigeration equipment for low-temperature applications. One of the candidates to replace R-502 is a refrigerant mixture of R-125 (penta-fluoroethane) + R-143a (1,1,1-trifluoroethane). R-125 and R-143a contain no chlorine, and their ozone depletion potential (ODP) is zero.

Reliable information about the thermodynamic properties of this blend is important for the design and operation of advanced refrigeration equipment with the binary R-125 + R-143a system. This paper deals with an experimental study of the PVTx properties, saturated vapor densities, dew point pressures, and second and third virial coefficients for this refrigerant mixture.

2. MEASUREMENTS

The constant-mass method coupled with an expansion procedures was used for the present measurements of PVTx properties. The apparatus and



Fig. 1. Experimental apparatus. (A) Sample cell; (B) expansion cell; (C) vacuum pump; (D) main heater; (E) subheater; (F) cooler; (G) platinum resistance thermometer; (H) thermometer bridge; (I) PID controller; (J) DC power supply; (J1, J2) joints; (K) stirrer; (L) thermostated fluid bath; (M) differential pressure detector; (N) electric tester; (O) nitrogen cylinder; (P) precise pressure controller; (Q) digital quartz pressure transducer; (R) digital quartz pressure controller; (V1–V10) valves.

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procedure have been reported in detail by Takaishi et al. [1] and Kiyoura et al. [2].

The apparatus shown in Fig. 1 consists of a sample cell (A), an expansion cell (B), a differential pressure detector (M), a platinum resistance thermometer (G) calibrated against ITS-90, a thermostated fluid bath (L), temperature control/measuring devices, and pressure measuring instruments. The inner volumes of the sample cell and expansion cell were carefully calibrated with pure water; they were 283.368 ± 0.027 and 55.583 ± 0.007 cm³, respectively, at 273.15 K. The temperature in the silicone oil-filled thermostated fluid bath was controlled within ± 2 mK. When thermal equilibrium was reached with the pressure remaining unchanged over several hours, the temperature and pressure of the sample fluid were measured. After a series of measurements along a prescribed isochore was completed, a part of the sample fluid was expanded into the expansion cell in the single-phase gas to reach another isochore, with composition unchanged.

The experimental uncertainties of the present measurements are estimated to be within ± 7.2 mK in temperature, ± 3.0 kPa in pressure, ± 0.12 kg·m⁻³ in density, and ± 0.040 mass% in composition. The sample purities are 99.953 mass% for R-125 and 99.998% for R-143a, as determined by the chemical manufacturers.

3. RESULTS

Measurements of the PVTx properties of refrigerant mixture R-125 + R-143a were made along seven isochores at temperatures from 305 to 400 K, pressures up to 6.1 MPa, and densities from 92 to 300 kg·m⁻³, for 50.043 and 49.998 mass% compositions of R-125. Figure 2 shows the distribution of the PVTx data on a pressure-temperature plane. The vapor pressure curves are calculated from the correlations of both pure components [3], and the critical temperatures are adopted from earlier studies of our laboratory [4, 5].

4. DISCUSSION

4.1. Saturated Vapor Densities and Dew Point Pressures

In this study, seven saturated vapor densities and dew point pressures of the R-125 + R-143a system for a composition of 50 mass % R-125 have been determined on the basis of rather detailed PVTx properties measured in the vicinity of the saturation boundary as well as the thermodynamic



Fig. 2. Distribution of the *PVTx* measurements of R-125 + R-143a (50/50 mass%). (×) This work (50.043 mass% R-125); (\bigcirc) this work (49.998 mass% R-125); (\longrightarrow) vapor pressure curve of R-125 [3]; (---) vapor pressure curve of R-143a [3]; (\blacktriangle) critical point of R-125 [4]; (\blacklozenge) critical point of R-143a [5].

behavior of gaseous isochores near saturation. Figure 3 shows a typical isochore in the two-phase region correlated with the following relation:

$$\ln P_{\rm r} = \mathbf{A} - \mathbf{B}T_{\rm r} \tag{1}$$

and a gaseous isochore near saturation correlated with the following relation:

$$Z = C + (D/T_r) + (E/T_r^2) + F \exp(1/T_r)$$
(2)

where P_r , T_r , and Z denote reduced pressure, reduced temperature, and the compressibility factor. A, B, C, D, E, and F are numerical constants of the correlations. The *PVTx* measurements used to determine the saturated vapor densities and dew point pressures are those within 5 K below the saturation temperature for Eq. (1) and those within 5 K above the saturation temperature for Eq. (2). The critical pressure and critical temperature



Fig. 3. Determination of the saturated vapor densities. (\bigcirc) Present measurements; (\blacksquare) saturated vapor determined; (-) Eq. (1); (---) Eq. (2).

for this refrigerant mixture R-125 + R-143a (50/50 mass%), reported by Higashi [6] are used for the correlations of Eqs. (1) and (2). Each correlation represents the *PVTx* measurements of this work within experimental uncertainty.

After determining the numerical constants A through F along each isochore, the saturated vapor densities and dew point pressures were

<i>T</i> ″ (K)	$\rho'' (\mathrm{kg} \cdot \mathrm{m}^{-3})$	x (mass% R-125)
340.80	299.93	49.998
337.32	247.00	49.998
332.75	203.42	49.998
326.89	164.77	50.043
320.98	135.71	50.043
314.62	111.77	50.043
308.12	92.06	50.043

Table I. Experimental Saturated Vapor Densities of R-125 + R-143aSystem (50/50 mass%)

<i>P</i> " (kPa)	<i>T</i> " (K)	x (mass% R-125)
3467.5	340.80	49.998
3217.3	337.32	49.998
2915.7	332.75	49.998
2561.0	326.89	50.043
2239.1	320.98	50.043
1931.0	314.62	50.043
1648.2	308.12	50.043

Table II. Experimental Dew Point Pressures of R-125 + R-143aSystem (50/50 mass %)

calculated with the aid of the Newton–Raphson method. Saturated vapor density and dew point pressure values thus determined are shown in Tables I and II. The uncertainties of these values are estimated to be within ± 0.10 K in temperature, ± 4.2 kPa in pressure, and ± 0.12 kg \cdot m⁻³ in density.

Figure 4 shows the vapor-liquid saturation curve for R-125 + R-143a (50/50 mass%). This figure includes results reported by Ikeda et al. [7],



Fig. 4. Saturation curve for R-125 + R-143a (50/50 mass%). (•) This work; (×) Ikeda et al. [7]; (\triangle) Widiatmo et al. [8]; (+) Fujimine et al. [9]; (\Box) Kishizawa et al. [10].

Widiatmo et al. [8], Fujimine et al. [9], and Kishizawa et al. [10]. Among those reported measurements, Ikeda et al. [7] and Kishizawa et al. [10] reported measurements of the saturated vapor densities. The present results agree better with those of Kishizawa et al.

4.2. Second and Third Virial Coefficients

The compressibility factors, Z, of the present binary R-125 + R-143a mixtures with a composition 50 mass% R-125 were derived from the measurements using the following relations:

$$Z = MP/(\rho RT) \tag{3}$$

and

$$M = \sum_{i=1}^{n} x_i M_i \tag{4}$$

where P, ρ , and T denote the pressure, mass density, and temperature, respectively. R is the universal gas constant ($R = 8.31451 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), while M_i and x_i are the molar mass and respective mole fraction of each component.



Fig. 5. Relation of $(Z-1)/\rho$ vs ρ for R-125 + R-143a (50/50 mass%).

T (K)	$B(L \cdot mol^{-1})$	$C (L^2 \cdot \mathrm{mol}^{-2})$
330	-0.306	0.031
340	-0.283	0.0286
350	-0.262	0.026
360	-0.244	0.0244
370	-0.227	0.0227
380	-0.212	0.0212
390	-0.198	0.0199
400	-0.185	0.0187

Table III.Experimental Second and Third Virial Coefficients of
R-125 + R-143a System (50/50 mass %)



Fig. 6. Temperature dependence of second virial coefficients for R-125 + R-143a (50/50 mass %). (\bullet) This work (50/50 mass %); (×) Zhang et al. (R-125) [11]; (*) Zhang et al. (R-143a) [11]; (···) Zhang et al. (50/50 mass %) [12]; (—) Zhang et al. (R-125) [12]; (—) Zhang et al. (R-143a) [12].

The PVTx property measurements were represented within the estimated experimental uncertainty by the following truncated virial expression:

$$(Z-1)/\rho = B + C\rho \tag{5}$$

Straight lines can be drawn by plotting the values $(Z-1)/\rho$ versus ρ along isotherms, as shown in Fig. 5. The intersection with the ordinate corresponds to the second virial coefficient *B*, while the slope of each isotherm represents the third virial coefficient *C*. The second and third virial coefficients thus determined from the present measurements are listed in Table III. In this analysis, all of the measurements in the gaseous phase are used to normalize the virial coefficients for the 50.0 mass % R-125 mixture, although they have been measured at two slightly different compositions, 50.043 mass % R-125 and 49.998 mass % R-125. Note that the difference in composition is sufficiently small to have negligible effect within the estimated uncertainties of determining the virial coefficients.

Figures 6 and 7 show the temperature dependences of B and C. Note that the solid and dashed curves in Figs. 6 and 7 are the calculated results



Fig. 7. Temperature dependence of third virial coefficients for R-125 + R-143a (50/50 mass%). (\bullet) This work (50/50 mass%); (\cdots) Zhang et al. (50/50 mass%) [12]; (-) Zhang et al. (R-125) [12]; (-) Zhang et al. (R-143a) [12].

from correlations by Zhang et al. [11] developed for each mixture and pure component. The solid curves denote the correlations for the pure components, whereas the dashed lines are for the mixture. Figure 6 includes the second virial coefficients for the pure refrigerants reported by Zhang et al. [12]. This correlation represents the virial coefficient values of the present work within $\pm 0.7\%$ for B and $\pm 10.0\%$ for C.

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