

# Vapor–Liquid Equilibrium, Coexistence Curve, and Critical Locus for Pentafluoroethane + 1,1,1-Trifluoroethane (R125/R143a)

Yukihiro Higashi<sup>†</sup>

Department of Mechanical Engineering, Iwaki Meisei University, 5-5-1, Iino, Chuodai, Iwaki 970-8551, Japan

The vapor–liquid equilibrium for pentafluoroethane (R125) + 1,1,1-trifluoroethane (R143a) was measured by the static method in the temperature range between 273.15 K and 313.15 K. The vapor–liquid coexistence curve near the critical point was measured by observation of the meniscus disappearance. The critical temperatures and critical densities of the 0.4118 and 0.6208 mole fraction of R125 were determined from the saturation densities along the coexistence curve in the critical region. In addition, the critical locus for the R125/R143a mixture is correlated as a function of composition.

## Introduction

Because of their low ozone-depletion potentials, hydrofluorocarbon (HFC) mixtures are considered as alternative refrigerants for R22 and R502 as the working fluid of air conditioning and heat pump systems. Binary mixtures of pentafluoroethane (R125) and 1,1,1-trifluoroethane (R143a), especially the near-azeotropic mixture R507A (50 mass % R125 + 50 mass % R143a), are of interest as candidates for replacing R502. However, reliable information on the thermophysical properties of this mixture is insufficient.

The present author has previously measured the vapor–liquid equilibrium and the vapor–liquid coexistence curve near the critical point for the difluoromethane (R32) + 1,1,1,2-tetrafluoroethane (R134a) mixture (Higashi, 1995), those for the difluoromethane + pentafluoroethane mixture (Higashi, 1997), and those for the pentafluoroethane + 1,1,1,2-tetrafluoroethane mixture (Higashi, 1999). This paper reports for the R125/R143a mixture.

## Experimental Section

**Chemicals.** The samples of pure components were furnished by Asahi Glass Co. Ltd. (To describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturer's name or label. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the particular material or equipment is necessarily the best available for the purpose.) The stated sample purity was 99.99 mass % R125 and 99.995 mass % R143a. These samples were used without further purification.

**Apparatus.** The experimental apparatus for measuring the vapor–liquid equilibrium and the vapor–liquid coexistence curve near the critical point at Iwaki Meisei University has been described in detail previously (Higashi, 1999).

With respect to the apparatus for vapor–liquid equilibrium, temperatures were measured with a 100  $\Omega$  platinum resistance thermometer calibrated against ITS-90 using a 25  $\Omega$  standard platinum resistance thermometer. The uncertainty of temperature measurements is estimated to be within  $\pm 10$  mK. The pressure of the sample was

measured with a diaphragm semiconductor strain-gauge pressure transducer. This pressure transducer was checked against a quartz crystal pressure transducer after each series of experiments. The uncertainty of the pressure measurement is estimated to be within  $\pm 3$  kPa. Compositions of the vapor phase (dew-point composition) and the liquid phase (bubble-point composition) for the mixtures were determined using a gas chromatograph equipped with a thermal conductivity detector. The uncertainty of the composition measurement is estimated to be within  $\pm 0.4$  mol %.

As for the apparatus for vapor–liquid coexistence curve measurements, temperature measurements were made with a 25  $\Omega$  standard platinum resistance thermometer calibrated against ITS-90 with the aid of a thermometer bridge. The uncertainty of temperature measurement is estimated to be within  $\pm 10$  mK. The sample density in the optical cell can be calculated from the mass of the sample and the inner volume of three vessels. The uncertainty of the density measurements is estimated to be within  $\pm 0.5$ %. The uncertainty of the mass of the sample obtained was not greater than  $\pm 0.1$ %. In addition, the uncertainty of the composition of the sample was estimated to be within  $\pm 0.05$ %. In this experiment, a gas chromatograph is not used to determine the composition.

## Experimental Results

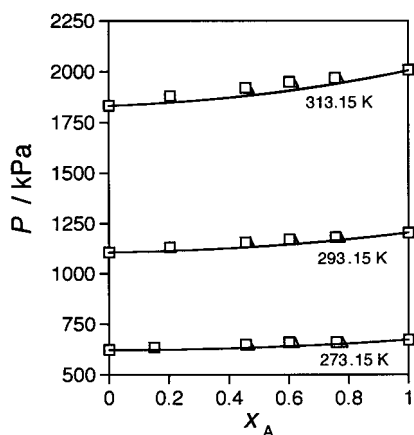
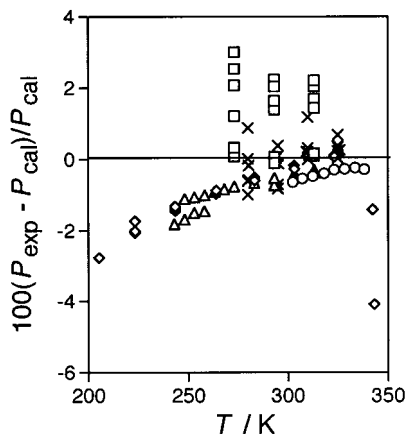
**Vapor–Liquid Equilibrium.** The experimental results for the vapor–liquid equilibrium (VLE) for an R125/R143a mixture are given in Table 1. Measurements were made along three isotherms, i.e., (273.15, 293.15, and 313.15) K, and the vapor pressure for each pure component was measured. The distribution of VLE results for the R125/R143a mixture is shown in Figure 1 on a pressure–composition diagram. In this figure, the solid lines are the predictions of REFPROP 6.0 (McLinden et al., 1998) at the same three temperatures.

Experimental results for the vapor–liquid equilibrium for the R125/R143a mixture measured by Nagel and Bier (1996), Kleemiss (1996), Gorenflo et al. (1996), and Holcomb et al. (1997) were available for comparison. The bubble-point pressure comparisons between the available VLE data and the calculated results of the Helmholtz free energy model equation of state (Lemmon and Jacobsen, 1998) are shown in Figures 2–4 using REFPROP 6.0.

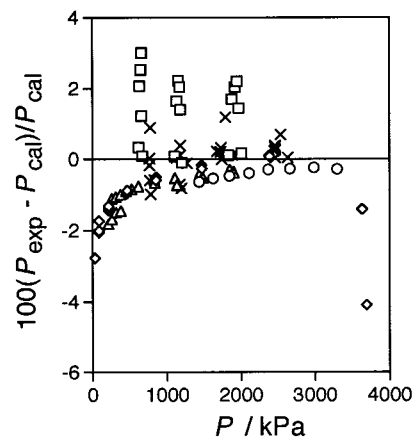
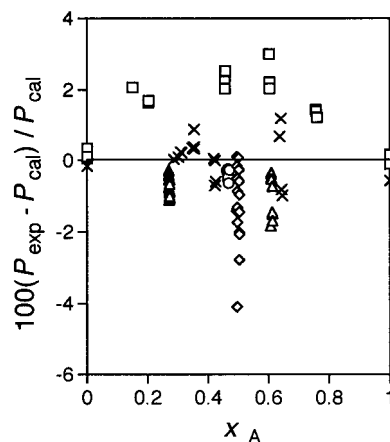
<sup>†</sup> Present address: Guest Researcher at the Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, Colorado 80303.

**Table 1. Isothermal Vapor–Liquid Equilibrium Data of the R125(A)/R143a(B) Mixture**

$T/K$	$P/\text{kPa}$	$x_A$	$y_A$
273.16	622.1	0.0	0.0
273.15	634.3	0.1506	0.1502
273.15	647.2	0.4564	0.4677
273.15	658.3	0.6011	0.6188
273.15	657.9	0.7589	0.7789
273.15	671.0	1.0	1.0
293.13	1106.0	0.0	0.0
293.16	1131.7	0.2022	0.2060
293.15	1156.6	0.4559	0.4687
293.16	1170.3	0.6023	0.6175
293.15	1182.4	0.7565	0.7717
293.15	1202.8	1.0	1.0
313.14	1833.6	0.0	0.0
313.15	1879.3	0.2036	0.2061
313.15	1919.7	0.4559	0.4665
313.15	1949.7	0.6020	0.6153
313.15	1968.7	0.7551	0.7682
313.15	2008.4	1.0	1.0

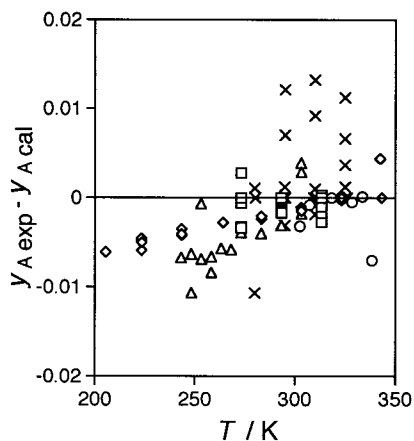
**Figure 1.** Vapor–liquid equilibria of the R125 (A)/R143a (B) mixture in a pressure–temperature diagram: (□) bubble-point; (△) dew-point, (–) REFPROP 6.0 predictions.**Figure 2.** Bubble-point pressure deviations between the experimental VLE data and the predictions of REFPROP 6.0 for the R125 (A)/R143a (B) mixture vs temperature: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).

These deviations are plotted against temperature, pressure, and composition in Figures 2–4, respectively. As shown in Figures 2–4, the bubble-point pressure deviations of the present data are higher by approximately 1–3% than the calculated results of the Helmholtz free energy model equation of state, although those of both pure components are in better agreement. The data sets of Nagel and Bier, Kleemiss, and Gorenflo et al. are in good agreement with

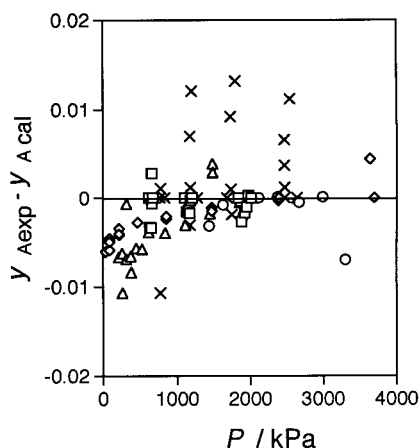
**Figure 3.** Bubble-point pressure deviations between the experimental VLE data and the prediction of REFPROP 6.0 for the R125 (A)/R143a (B) mixture vs pressure: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).**Figure 4.** Bubble-point pressure deviations between the experimental VLE data and the prediction of REFPROP 6.0 for the R125 (A)/R143a (B) mixture vs bubble-point composition of R-125: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).

each other. These data sets were obtained using a standard mixture charged into their apparatus. The liquid composition was nearly constant as the temperature was varied. This is shown in Figure 4. Although the data of this work and that of Holcomb et al. show more scatter than the other sources, this is partially due to the wider range of compositions that they measured. Because the data of this work and that of Holcomb et al. measure the liquid composition and because the slope ( $dP/dx$ ) is different at each experimental composition, the overall uncertainty of the bubble-point pressure varies from point to point.

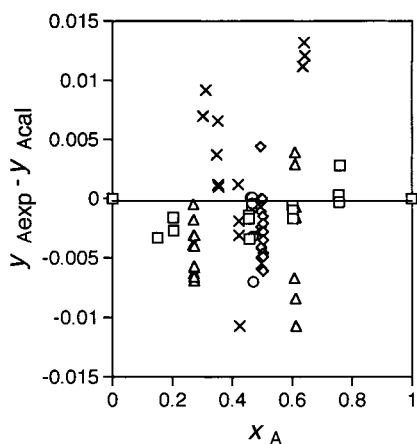
The dew-point composition comparisons between the available VLE data and the calculated results of the Helmholtz free energy model equation of state are also shown in Figures 5–7. To calculate the dew-point compositions, the mixture parameters of the Helmholtz free energy model equation of state were adopted from REFPROP 6.0. As for the dew-point composition, the Helmholtz free energy model equation of state adopted in REFPROP 6.0 can reproduce the present data very well. Although some of the data of Holcomb et al. have a large positive deviation compared to the model, most of the data show deviations in mole fraction between +0.005 and –0.010 which is within the stated uncertainty of the measurements.



**Figure 5.** Dew-point composition deviations between the experimental VLE data and the prediction of REFPROP 6.0 for the R125 (A)/R143a (B) mixture vs temperature: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).



**Figure 6.** Dew-point composition deviations between the experimental VLE data and the prediction of REFPROP 6.0 for the R125 (A)/R143a (B) mixture vs pressure: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).

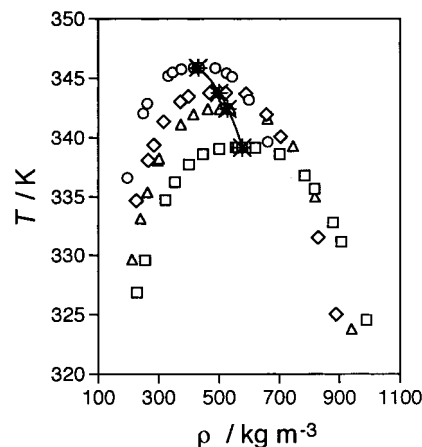


**Figure 7.** Dew-point composition deviations between the experimental VLE data and the prediction of REFPROP 6.0 for the R125 (A)/R143a (B) mixture vs bubble-point composition of R125: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).

**Vapor–Liquid Coexistence Curve near the Critical Point.** The vapor–liquid coexistence curve near the critical point for the 41.18 mol % R125 + 58.82 mol % R143a mixture and the 62.08 mol % R125 + 37.92 mol % R143a

**Table 2.** Vapor–Liquid Coexistence Curve Data of the R125(A)/R143a(B) Mixture near the Critical Point

$x_A = 0.4118$		$x_A = 0.6208$	
$T/K$	$\rho/\text{kg m}^{-3}$	$T/K$	$\rho/\text{kg m}^{-3}$
325.02	$887.9 \pm 0.9$	323.77	$939.8 \pm 0.9$
331.51	$828.8 \pm 0.8$	334.97	$817.8 \pm 0.8$
340.09	$704.0 \pm 1.2$	339.28	$745.1 \pm 1.3$
341.95	$657.3 \pm 1.8$	341.59	$659.6 \pm 0.7$
343.69	$558.6 \pm 1.8$	342.42	$538.4 \pm 0.5$
343.76	$521.5 \pm 1.6$	342.44	$531.9 \pm 1.7$
343.76	$502.6 \pm 1.6$	342.43	$523.4 \pm 0.9$
343.77	$469.3 \pm 1.5$	342.43	$502.6 \pm 0.5$
343.48	$398.8 \pm 1.6$	342.42	$463.1 \pm 1.5$
343.02	$372.4 \pm 1.5$	341.99	$415.3 \pm 1.3$
341.35	$316.5 \pm 1.7$	341.11	$373.7 \pm 1.2$
339.37	$284.8 \pm 1.5$	338.26	$301.4 \pm 1.6$
338.11	$265.9 \pm 1.4$	338.07	$296.6 \pm 1.2$
334.66	$226.0 \pm 1.4$	335.37	$262.5 \pm 1.4$
		333.12	$239.2 \pm 1.5$
		329.60	$211.8 \pm 1.1$



**Figure 8.** Vapor–liquid coexistence curve of the R125 (A)/R143a (B) mixture in the critical region: (\*) critical point; (–) critical locus; (○)  $x_A = 0.0$ ; (◇)  $x_A = 0.4118$ ; (△)  $x_A = 0.6208$ ; (□)  $x_A = 1.0$ .

**Table 3.** Critical Parameters of the R125(A)/R143a(B) Mixture

$x_A$	$T_c/K$	$\rho_c/\text{kg m}^{-3}$	$V_c/\text{cm}^3 \text{mol}^{-1}$
0	$345.88 \pm 0.01$	$431 \pm 3$	$195 \pm 2$
0.4118	$343.76 \pm 0.02$	$501 \pm 5$	$197 \pm 2$
0.6208	$342.43 \pm 0.02$	$528 \pm 5$	$201 \pm 2$
1	$339.17 \pm 0.01$	$577 \pm 5$	$208 \pm 2$

mixture was determined by visual observation of meniscus disappearance. The experimental data obtained are given in Table 2 and shown in Figure 8 in the temperature–density plane. The experimental results of pure components reported by the author (Higashi, 1994; Higashi and Ikeda, 1996) are also shown in Figure 8. The asterisk denotes the critical point, determined by taking into consideration the meniscus disappearance level and also the intensity of the critical opalescence. The solid line in Figure 8 shows the critical locus for the R125/R143a mixture. The critical temperature  $T_c$ , critical density  $\rho_c$ , and critical molar volume  $V_c$  of this mixture are summarized in Table 3.

## Discussion

**Correlation of the Critical Locus.** To represent the composition dependence of the critical parameters of the system, a correlation of the critical locus was formulated. The functional form of this correlation is as follows (Higashi et al. 1986; Higashi 1997, 1999):

$$T_{cm} = \theta_1 T_{c1} + \theta_2 T_{c2} + 2\theta_1\theta_2\Delta T \quad (1)$$

$$V_{cm} = \theta_1 V_{c1} + \theta_2 V_{c2} + 2\theta_1\theta_2\Delta_V \quad (2)$$

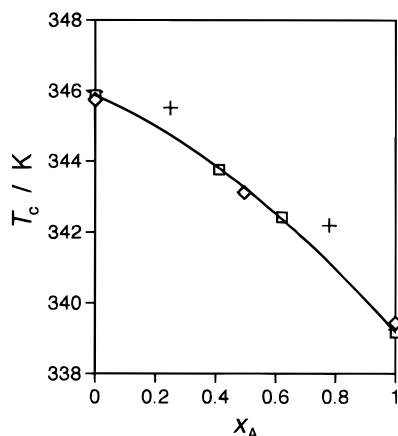
$$\rho_{cm} = M_m/V_{cm} \quad (3)$$

$$P_{cm} = \theta_1 P_{c1} + \theta_2 P_{c2} + 2\theta_1\theta_2\Delta_P \quad (4)$$

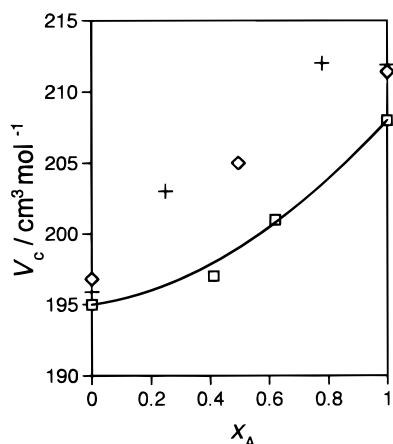
$$\theta_i = \frac{x_i V_{ci}^{2/3}}{\sum_j x_j V_{cj}^{2/3}} \quad (5)$$

Here,  $T_{cm}$ ,  $V_{cm}$ ,  $\rho_{cm}$ , and  $P_{cm}$  denote the critical temperature of the mixture, the critical molar volume of the mixture, the critical density of the mixture, and the critical pressure of the mixture, respectively.  $M_m$  denotes the molar mass of mixture and is  $M_m = x_1 M_1 + (1 - x_1) M_2$ . The surface fraction  $\theta_i$  is defined in eq 5 in terms of the composition and critical molar volumes of the pure components.  $\Delta_T$  in eq 1,  $\Delta_V$  in eq 2, and  $\Delta_P$  in eq 4 are the adjustable parameters used to fit eqs 1, 2, and 4 to the data. The  $\Delta_T$  and  $\Delta_V$  values were determined from the present measured critical parameters of the two mixtures listed in Table 3. With respect to the R125/R143a mixture,  $\Delta_T$  and  $\Delta_V$  are 1.56 K and  $-5.16 \text{ cm}^3 \text{ mol}^{-1}$ , respectively.

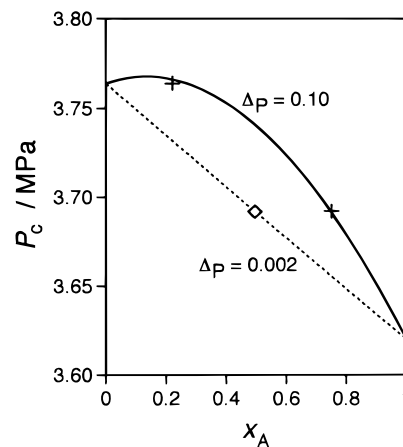
The comparisons of the critical temperature and critical molar volume for the R125/R143a mixture between the present results, the results by Nagel and Bier (1996), and those by Zhelezny et al. (1995) are shown in Figures 9 and



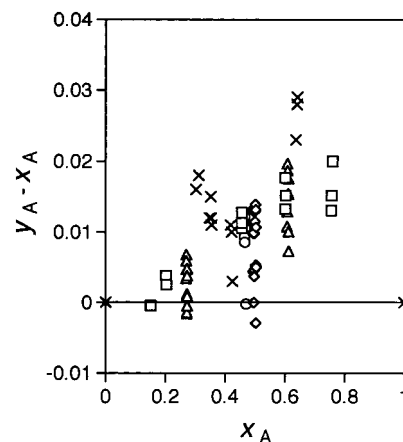
**Figure 9.** Composition dependence of the critical temperatures of the R125 (A)/R143a (B): (□) present author; (+) Zhelezny et al. (1996); (◇) Nagel and Bier (1996); (—) eq 1.



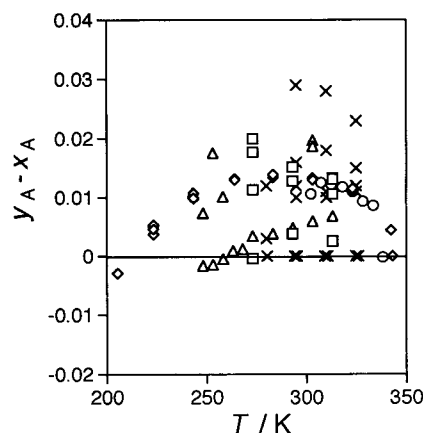
**Figure 10.** Composition dependence of the critical molar volume of the R125 (A)/R143a (B): (□) present author; (+) Zhelezny et al. (1996); (◇) Nagel and Bier (1996); (—) eq 2.



**Figure 11.** Composition dependence of the critical pressure of the R125 (A)/R143a (B): (+) Zhelezny et al. (1996); (◇) Nagel and Bier (1996); (—) eq 4 by using  $\Delta_P = 0.10$  MPa; (---) eq 4 by using  $\Delta_P = 0.002$  MPa.



**Figure 12.** Plot of the difference between dew-point composition and bubble-point composition ( $y_A - x_A$ ) vs bubble-point composition  $x_A$  for the R125 (A)/R143a (B) mixture: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).



**Figure 13.** Plot of the difference between dew-point composition and bubble-point composition ( $y_A - x_A$ ) versus  $t$  temperature for the R125 (A)/R143a (B) mixture: (□) present work; (◇) Nagel and Bier (1996); (○) Kleemiss (1996); (△) Gorenflo et al. (1996); (×) Holcomb et al. (1997).

10, respectively. As for the critical temperature, the present results and Nagel and Bier's results are in good agreement. The critical temperatures determined by Zhelezny et al. are slightly higher than others. The present correlation for the critical temperature of the R125/R143a can reproduce

the present results within  $\pm 0.05$  K. The critical molar volumes for the R125/R143a are scattered and do not agree with each other. The present correlation for the critical molar volume of the R125/R143a can reproduce the present results within an uncertainty of  $\pm 2$  kg m<sup>-3</sup>.

The critical pressure of the R125/143a mixture could not be measured with this apparatus. As for the critical pressure data, two experimental data sets were available. One is by Zhelezny et al. (1995), and another is by Nagel and Bier (1996). Zhelezny et al. determined two critical pressures of the R125/R143a system, i.e., 3.7640 MPa at 22.14 mol % R125 and 3.6922 MPa at 75.05 mol % R125. Nagel and Bier also reported a critical pressure for this system, i.e., 3.692 MPa at 49.57 mol % R125. Figure 11 shows the distribution of the measured critical pressures of this mixture versus mole fraction of R125. As shown in Figure 11, the critical pressures by Zhelezny et al. do not agree with the critical pressure reported by Nagel and Bier. When the  $\Delta_P$  value in eq 4 was determined based on the critical pressures by Zhelezny et al., the  $\Delta_P$  value became 0.10 MPa. However, the  $\Delta_P$  value became 0.002 MPa when the  $\Delta_P$  value was determined based on the critical pressure by Nagel and Bier.

**Possibility of an Azeotrope.** The mixture composed of 50 mass % R125 and 50 mass % R143a is named R507A and was believed to be an azeotropic mixture. To determine the existence of an azeotrope, the relationship of the difference between dew-point composition and bubble-point composition ( $y_A - x_A$ ) versus the bubble-point composition  $x_A$  is shown in Figure 12. In addition, the relationship of the ( $y_A - x_A$ ) against temperature  $T$  is also shown in Figure 13. If the R125/R143a mixture is an azeotrope, the region where the value of ( $y_A - x_A$ ) is negative must exist. As shown in Figures 12 and 13, the experimental data of the present work, of Holcomb et al. (1997), and of Kleemiss (1996) do not show azeotropic behavior in the experimental temperature range. However, the data obtained by Nagel and Bier (1996) and by Gorenflo et al. (1996) show azeotropic behavior in the very low-temperature range. This means that an azeotrope for the R125/R143a mixture may exist at temperatures below 260 K and at R143a-rich compositions.

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