International Journal of Thermophysics, Vol. 20, No. 3, 1999

Measurements of Saturation Densities in Critical Region and Critical Loci for Binary R-32/125 and R-125/143a Systems[1]

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R-32/125 (difluoromethane/pentafluoroethane) and R-125/143a (pentafluoroethane/1,1,1-trifluoroethane) binary systems are promising alternative refrigerants to replace conventional refrigerants, i.e., R-22 and R-502. The saturated vapor- and liquid-density data in the critical region of these mixtures were measured using the visual observation of the meniscus disappearance in an optical cell. For the R-32/125 system, 35 saturation density data were measured at three compositions, 10, 35, and 50 mass% R-32. Nineteen saturation density data were also measured for R-125/143a (50/50 mass%). The critical temperatures and densities for these binary refrigerants were determined by taking into consideration the level and location of the meniscus disappearance as well as the intensity of the critical opalescence. Correlations to represent the critical loci of these binary refrigerants for an entire range of compositions have been developed. The experimental uncertainties of the saturation density data are estimated to be within 9 mK in temperature and 0.5 to 5.0 $kg \cdot m^{-3}$ in density. The uncertainties of the critical temperature and density are estimated to be within 12 to 14 mK and 4 to 8 $kg \cdot m^{-3}$, respectively.

KEY WORDS: alternative refrigerants; critical density; critical locus; critical temperature; R-32/125 mixture; R-125/143a mixture; saturation density.

1. INTRODUCTION

We have previously reported the measurements of saturation densities and critical temperatures and densities of several HFC refrigerants such as R-32

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

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[1], R-125 [1], and R-143a [2]. One of the reasons for performing these measurements was that these refrigerants are considered as promising alternatives to replace R-22 and R-502 as a component of binary and/or ternary refrigerant mixtures. This paper reports the measurements of saturated vapor- and liquid densities in the critical region and critical temperatures and densities of the binary R-32/125 and R-125/143a mixtures. We also provide correlations to represent the critical loci of these binary systems.

2. EXPERIMENT

The experimental apparatus and procedures used for these measurements have been described in detail by Okazaki et al. [3] and Tanikawa et al. [4]. Measurements of saturation densities near the critical point were

Table I. Experimental Saturation Densities for R-32/125

ρ'' (kg · m^{-3})[a]	T (K)	ρ' (kg · m^{-3})[b]	T (K)
	10/90 mass%		
474.1 ± 3.0	339.909	549.8 ± 0.6	340.029
479.2 ± 3.0	339.919	558.0 ± 5.0	340.014
507.8 ± 1.8	340.029	597.6 ± 3.8	340.009
513.3 ± 1.4	340.034	640.1 ± 2.4	339.830
543.9 ± 0.6	340.029	685.6 ± 0.8	339.344
	35/65 mass%		
415.8 ± 3.8	342.322	510.9 ± 0.6	342.625
445.3 ± 2.8	342.535	511.0 ± 0.6	342.632
471.5 ± 1.2	342.605	559.7 ± 1.6	342.605
477.0 ± 1.4	342.620	599.6 ± 0.6	342.386
505.0 ± 0.6	342.625		
	50/50 mass%		
401.3 ± 4.6	344.187	489.9 ± 1.4	344.470
419.8 ± 2.6	344.331	500.2 ± 1.4	344.490
429.8 ± 3.8	344.425	524.8 ± 0.6	344.470
448.6 ± 1.2	344.455	535.8 ± 0.6	344.465
457.4 ± 2.8	344.470	578.2 ± 0.6	344.182
466.7 ± 3.0	344.475	583.9 ± 1.6	344.129
467.0 ± 3.0	344.485	625.4 ± 0.6	343.442
480.5 ± 0.6	344.480		

[a] Saturated vapor density.
[b] Saturated liquid density.

performed by means of the direct observation of the meniscus (vapor–liquid coexisting interface) behavior. Considering the level at which the meniscus disappeared and the intensity of critical opalescence, we have determined the critical temperatures and densities.

We have evaluated the experimental uncertainties on the basis of the ISO recommendation [5] associated with a coverage factor of 2. The expanded uncertainties of the saturation density measurements are 0.5 to $5.0\ kg \cdot m^{-3}$ for R-32/125 and 0.5 to $4.4\ kg \cdot m^{-3}$ for R-125/143a. The expanded uncertainty of the saturation temperature is 9 mK. The expanded uncertainty for the composition is estimated to be less than 0.04%.

The purities of the samples used for the measurements are 99.9811, 99.96, and 99.94 mass% for R-32, R-125, and R-143a, respectively. All have been analyzed by the chemical manufacturers.

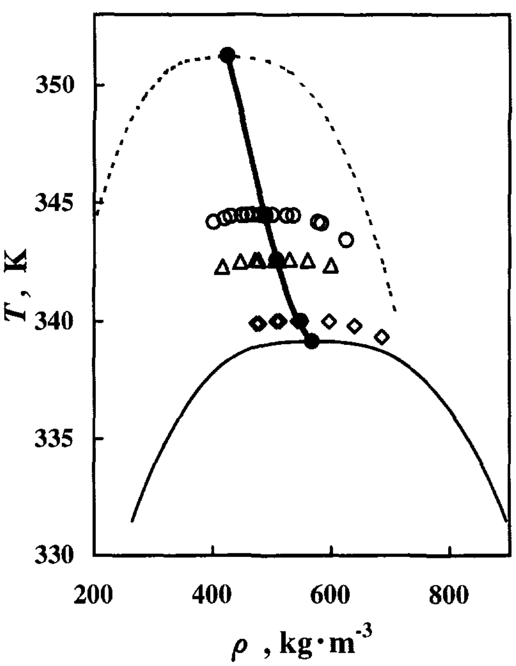

Fig. 1. Saturation densities for the R-32/125 system. (○) This work, 50/50 mass%; (△) this work, 35/65 mass%; (◇) this work, 10/90 mass%; (●) this work, critical point; (▬▬) critical locus; (——) R-125 (Kuwabara et al. [1]); (- - - -) R-32 (Kuwabara et al. [1]).

3. RESULTS

3.1. Binary R-32/125 Mixtures

For the binary R-32/125 system, we obtained 35 saturation density data at compositions of 10, 35, and 50 mass% R-32. These results are shown in Table I and in Fig. 1 on a T–ρ diagram. The vapor–liquid coexistence curves of pure refrigerants such as R-32 and R-125 in Fig. 1 were determined based on the correlation of Kuwabara et al. [1]. The critical locus was determined in the present study, and its representation is given below. The temperatures range between 339.344 and 340.034 K, and the densities between 474.1 and 685.6 $kg \cdot m^{-3}$, for the 10 mass% R-32 mixture $kg \cdot m^{-3}$. For the 35 mass% R-32 mixture, the data range from 342.322 to 342.632 K in temperature and between 415.8 and 599.6 $kg \cdot m^{-3}$ in density. For the 50 mass% mixture, measurements were performed at temperatures between 343.442 and 344.490 K and at densities between 401.3 and 625.4 $kg \cdot m^{-3}$.

On the basis of these measurements, we have determined the critical density and temperature for each mixture taking into account the meniscus level and critical opalescence. These values are summarized in Table II, along with the estimated uncertainties determined by taking into account the uncertainties of the saturation density measurements.

3.2. Binary R-125/143a Mixtures

We measured 19 saturation densities for R-125/143a (50/50 mass%), i.e., R-507A, which are summarized in Table III and Fig. 2. The measurements ranged from 340.403 to 343.794 K in temperature and from 291.0 to

Table II. Critical Parameters

	Composition (mass%)	Critical density ($kg \cdot m^{-3}$)	Critical temperature (K)
R-32/125	10/90	548 ± 4	340.029 ± 0.012
	35/65	507 ± 4	342.626 ± 0.012
	50/50	488 ± 4	344.475 ± 0.014
R-125/143a	50/50	494 ± 8	343.783 ± 0.012
R-125/143a [10]	50/50	501 ± 5^a	343.760 ± 0.02^a
R-32 [1]		424 ± 1^a	351.255 ± 0.010^a
R-125 [1]		568 ± 1^a	339.165 ± 0.010^a
R-143a [2]		434 ± 1^a	345.860 ± 0.010^a

[a] These uncertainty values were not evaluated on the basis of the ISO recommendation in terms of the expanded uncertainty.

Table III. Experimental Saturation Densities for R-125/143a (50/50 mass%)

ρ'' ($kg \cdot m^{-3}$)	T (K)	ρ' ($kg \cdot m^{-3}$)	T (K)
291.0 ± 1.4	340.403	503.3 ± 0.6	343.780
331.2 ± 1.9	342.101	516.7 ± 0.6	343.780
382.4 ± 4.4	343.273	519.0 ± 2.3	343.780
409.6 ± 3.6	343.621	522.6 ± 3.4	343.770
438.7 ± 2.8	343.770	559.8 ± 1.5	343.675
450.3 ± 2.7	343.780	599.6 ± 0.5	343.203
455.8 ± 1.2	343.789	635.6 ± 2.4	342.478
460.9 ± 1.2	343.794	680.9 ± 0.8	341.019
482.4 ± 1.3	343.780		
487.9 ± 4.4	343.785		
488.3 ± 0.5	343.789		

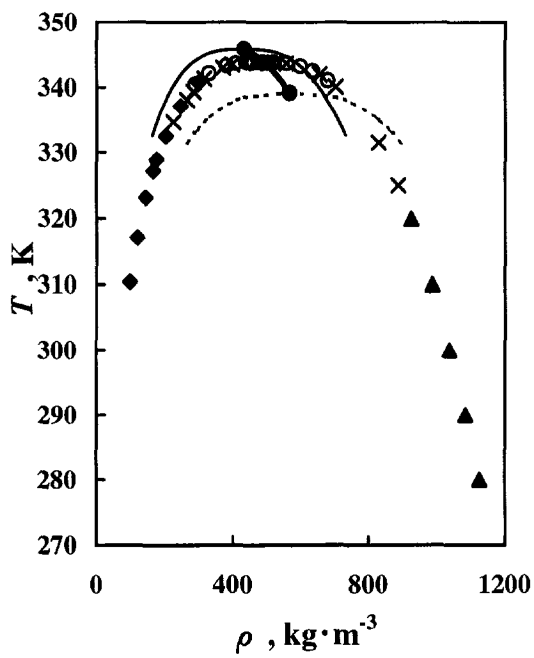

Fig. 2. Saturation densities for the R-125/143a system. (○) This work (50/50 mass%); (×) Ikeda et al. (50/50 mass%) [8]; (●) this work, critical point; (▲) Widiatmo et al. (50/50 mass%) [7]; (◆) Uchida et al. (50/50 mass%) [6]; (——) critical locus; (——) R-143a (Aoyama et al. [2]); (- - - -) R-125 (Kuwabara et al. [1]).

580.9 k kg $\cdot$ m^{-3} in density. The coexistence curves for the pure refrigerants, R-125 and R-143a, were determined based on earlier correlations developed by Kuwabara et al. [1] and Aoyama et al. [2], respectively. The critical temperature and density were determined in the same manner as for the R-32/125 system, and these values are given in Table II.

4. DISCUSSION

4.1. Critical Locus of the Binary R-32/125 System

Based on the present measurements, we have developed a correlation representing the critical temperature and/or the critical density in terms of the mole fraction, i.e., the critical locus of the binary R-32/125 mixture, by applying the following correlation proposed by Ikeda et al. [9]:

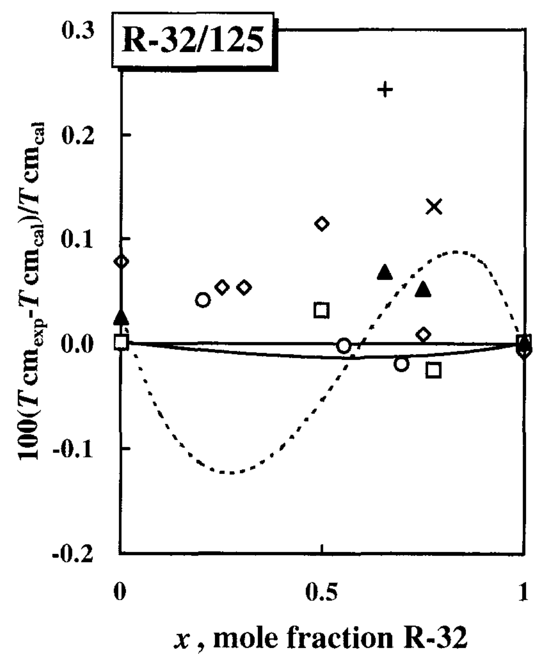

Fig. 3. Deviations of critical temperatures from Eq. (1) for the R-32/125 system. (○) This work; (□) Higashi [10]; (▲) Zhelezny et al. [11]; (×) Singh et al. [13]; (+) Bivens et al. [12]; (◇) Nagel and Bier [14]; (——) Higashi [10]; (- - - -) Zhelezny et al. [11].

$$T_{\mathrm{Cm}} = \theta_1 T_{\mathrm{C1}} + \theta_2 T_{\mathrm{C2}} + 2\theta_1 \theta_2 \Delta_T \tag{1}$$

$$V_{\mathrm{Cm}} = \theta_1 V_{\mathrm{C1}} + \theta_2 V_{\mathrm{C2}} + 2\theta_1 \theta_2 \Delta_V \tag{2}$$

$$\rho_{\mathrm{Cm}} = \frac{1000 M_{\mathrm{m}}}{V_{\mathrm{Cm}}} \tag{3}$$

$$\theta_i = \frac{x_i V_{\mathrm{C}i}^{2/3}}{\sum_j x_j V_{\mathrm{C}j}^{2/3}} \tag{4}$$

where $T_{\mathrm{C}i}$ and $V_{\mathrm{C}i}$ are the critical temperature and critical molar volume of each component. θ_i is the integrated surface fraction ratio, x_j is the mole fraction of each component, T_{Cm}, V_{Cm}, and ρ_{Cm} are the critical parameters for the binary mixture, and M_{m} is the molar mass. For the binary R-32/125 system, we determined the critical temperature and density for three compositions (see Table II). Using these data, the fitted parameters, $\Delta_V = -16.69$ and $\Delta_T = -4.30$, were determined. Equations (1) and (2) reproduce

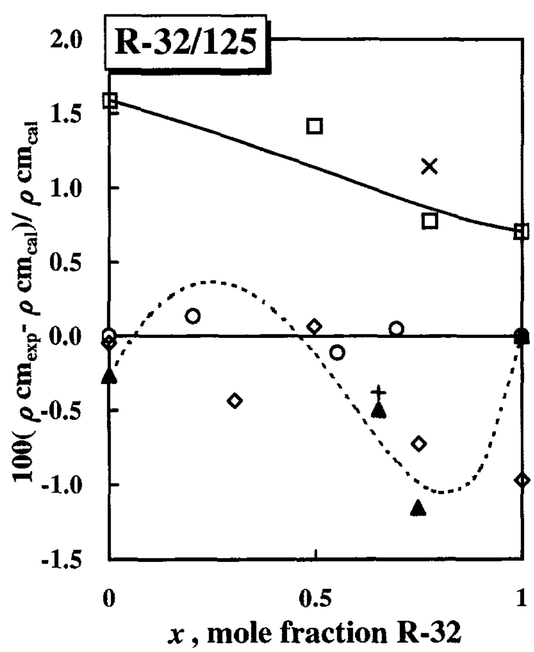

Fig. 4. Deviations of critical densities from Eq. (2) for the R-32/125 system. (○) This work; (□) Higashi [10]; (▲) Zhelezny et al. [11]; (×) Singh et al. [13]; (+) Bivens et al. [12]; (◇) Nagel and Bier [14]; (——) Higashi [10]; (- - - -) Zhelezny et al. [11].

the critical temperature and density data within ±0.13 and ±0.04%, respectively. Deviations of the present critical parameters and literature data from Eqs. (1) and (2) are shown in Figs. 3 and 4, respectively. Equation (1) reproduces literature critical temperature data within ±0.12%. Equation (2) agrees with literature critical volume data within ±1.6%. Our locus of critical temperatures in Fig. 3 is very close to that reported by Higashi [10], while that by Zhelezny et al. [11] shows significant differences from ours. This difference may be due to the fact that Zhelezny et al. [11] developed their correlation on the basis of only two experimental data whose mole fractions are very close to each other. For the critical density in Fig. 4, the correlation of Higashi [10] shows systematic deviations from Eq. (2) of 1.0 to 1.5%. Although Higashi et al. [10] use a similar experimental method and the same functional form as used here, differences in sample purity and other experimental factors might explain this difference. However, the difference is within the estimated experimental uncertainty of the critical density.

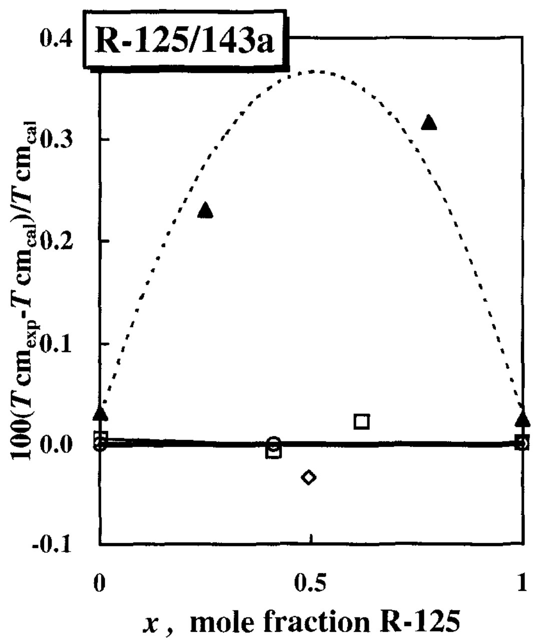

Fig. 5. Deviations of critical temperatures from Eq. (1) for the R-125/143a system. (○) This work; (□) Higashi [10]; (▲) Zhelezny et al. [11]; (◇) Nagel and Bier [14]; (——) Higashi [10]; (- - - -) Zhelezny et al. [11].

4.2. Critical Locus of the Binary R-125/143a System

We have determined the critical temperature and density for R-125/143a (50/50 mass%), i.e., R-507A (see Table II). The fitted parameters in Eqs. (1) and (2) are $\Delta_V = -2.141$ and $\Delta_T = 1.58$, found by means of fitting Eqs. (1) through (4) to the experimental critical parameters. Figures 5 and 6 show deviations of critical parameters from the present study and other investigators compared to calculated values from Eqs. (1) and (2). Equations (1) and (2) represent our single point exactly. Equation (1) agrees with critical temperature data of other investigators within $\pm 0.04\%$, except for the value by Zhelezny et al. [11]. Equation (2) agrees with critical density data measured by others within $\pm 3.0\%$. In Fig. 5, the critical locus developed by Zhelezny et al. [11] is concave, while those of the present work and Higashi [10] are convex. Since our correlation is based on only one composition, further measurements are needed to understand these differences better.

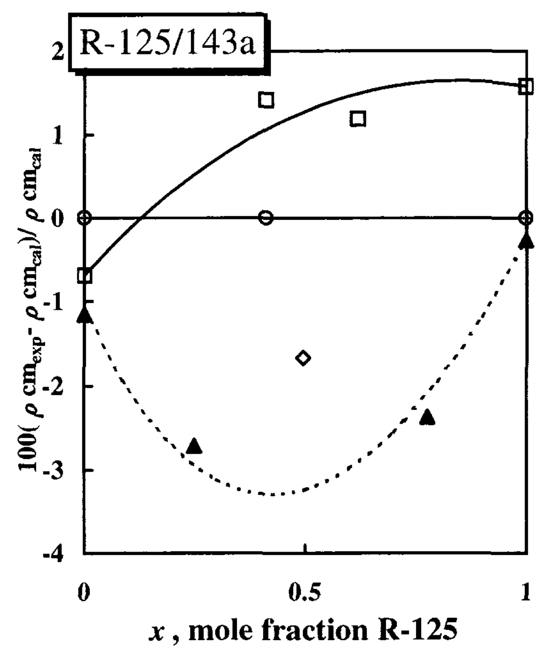

Fig. 6. Deviations of critical densities from Eq. (2) for the R-125/143a system. (○) This work; (□) Higashi [10]; (▲) Zhelezny et al. [11]; (◇) Nagel and Bier [14]; (——) Higashi [10]; (- - - -) Zhelezny et al. [11].

5. SUMMARY

For the binary R-32/125 system, we have measured 35 saturation densities at three compositions, i.e., 10, 35, and 50 mass% R-32, and determined the critical temperatures and densities for these binary refrigerants. For the binary R-125/143a system, we have measured 19 saturation densities and determined the critical temperature and density for 50 mass% R-125 mixture (R-507A).

On the basis of the measurements, correlations to represent the critical loci of these binary refrigerants for an entire range of compositions have been developed.

ACKNOWLEDGMENTS

We are grateful to Asahi Glass Co. Ltd., Tokyo, and Daikin Industries, Ltd., Osaka, for furnishing the research-grade samples. Special thanks go to Hidehiro Goto for his valuable contribution to a series of measurements.

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