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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Abstract

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 have been measured by a visual observation of the meniscus disappearance in an optical cell.

For R-32/125 system, 35 saturation density data have been measured along three different compositions, such as 10, 35, 50 mass% R-32. Nineteen saturation density data have also been measured for R-125/143a (50/50 mass%). The critical parameters such as the critical temperatures and the critical densities for these binary refrigerants have been determined, taking into consideration of the level and location of the meniscus disappearance as well as the intensity of the critical opalescence.

The correlations to represent the critical loci of these binary refrigerants for an entire range of compositions have been developed. The experimental uncertainties of saturation density data are estimated to be within 9 mK in temperature and 0.5-5.0 kg¥m^{-3} in density. The uncertainties of critical temperature and density determined are estimated to be within 12-14 mK and 4-8 kg/m^3, respectively.

Key Words

alternative refrigerant, binary R-32/125 system, binary R-125/143a system, saturation density, critical temperature, critical density, critical locus

Introduction

We have previously reported the measurements of saturation densities and critical temperatures and densities of several HFC refrigerants such as R-32[1], R-125[1] and R-143a[2]. One of the reasons why these measurements were performed was that these refrigerants are considered being promising alternatives to replace R-22 and R-502 as a component of binary and/or ternary refrigerants 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 will also provide correlations to represent the critical locus of these binary systems.

Experimentation

An experimental apparatus used for all measurements has been reported by Okazaki et al.[3] who originally built it and Tanikawa et al.[4] who reconstructed it. Our apparatus and procedure have been explained in detail in our previous papers[3,4]. Measurements of saturation densities near the critical point were performed by means of direct observation of meniscus (vapor-liquid coexisting interface) behavior. Considering the level at which meniscus was disappeared and intensity of critical opalescence, we have determined critical temperatures and densities.

We have evaluated the experimental uncertainties on the basis of the ISO recommendation[5] associated with a coverage factor being 2. The expanded uncertainties of saturation density measurement for R-32/125 are 0.5-5.0 kg/m^3, while 0.5-4.4 kg/m^3 for R-125/143a. And the expanded uncertainties of saturation temperature are 9 mK. The expanded uncertainty regarding the composition determination is estimated to be not greater than 0.04 %.

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

Results

1. Measurement of binary R-32/125 mixture

Concerning binary R-32/125 system, we have obtained 35 saturation density data along 10, 35 and 50 wt% R-32. These results are shown in Tables 1-3 and 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 are drawn with an aid of the correlation developed by Kuwabara et al.[1] in our laboratory. The line of the critical locus was determined by the present study and its details are described later. The range of measurements covers temperatures between 339.830 and 340.034 K, and densities between 474.1 and 640.1 kg/m^3 for 10 wt% R-32 mixture, whereas from 342.322 to 342.632 K in temperature and between 415.8 and 599.5 kg/m^3 in density for 35 wt% R-32 mixture. For equi-mass blend, measurements were performed at temperatures between 343.442 and 344.490 K and at densities between 401.3 and 625.4 kg/m^3.

On the basis of these measurements, we have determined the critical density and critical temperature for each mixture taking into account of the meniscus level and critical opalescence. These values are summarized in Table 5 with the estimated uncertainties determined taking the uncertainties of saturation density measurements into account.

2. Measurement of binary R-125/143a mixture

We have measured 19 saturation densities for R-125/143a (50/50 wt%), *i.e.*, R-507A, and are summarized in Table 4 and Fig. 2. The range of measurements were

between 340.403 and 343.794 K in temperature and between 291.0 and 599.6 kg/m^3 in density. The coexistence curves for pure refrigerants, R-125 and R-143a, were drawn by using our earlier correlations developed by Kuwabara et al.[1] and Aoyama et al.[2], respectively. The critical temperature and critical density have been thus determined in the similar manner as for the R-32/125 system and these values are given in Table 5.

Discussion

1. Critical locus of 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 mole fraction, *i.e.*, critical locus of the binary R-32/125 mixture, by applying the following correlation proposed by Ikeda et al.[9],

$$T_{C\mathrm{m}} = \theta_1 T_{C1} + \theta_2 T_{C2} + 2\theta_1\theta_2\Delta_T \quad (1)$$

$$V_{C\mathrm{m}} = \theta_1 V_{C1} + \theta_2 V_{C2} + 2\theta_1\theta_2\Delta_V \quad (2)$$

$$\rho_{C\mathrm{m}} = \frac{1000\mathrm{M_m}}{V_{C\mathrm{m}}} \quad (3)$$

$$\theta_\mathrm{i} = \frac{x_\mathrm{i} V_{C\mathrm{i}}^{2/3}}{\sum_\mathrm{j} x_\mathrm{j} V_{C\mathrm{j}}^{2/3}} \quad (4)$$

where $T_{C\mathrm{i}}$, $V_{C\mathrm{i}}$ are the critical temperature and critical molar volume of each component. θ_i is the surface integration ratio, x_j is mole fraction, and $T_{C\mathrm{m}}$, $V_{C\mathrm{m}}$, $\rho_{C\mathrm{m}}$ are the critical parameters for the present binary mixture, respectively, and $\mathrm{M_m}$ stands for molecular mass. For the binary R-32/125 system, we have determined the critical temperature and critical density along three composition as shown in Table 5. Using these data, parameters Δ_V and Δ_T were determined being Δ_V = -16.69 and Δ_T = -4.30. Equations (1) and (2) reproduce the input critical temperature and density data within ±0.04 % and ±0.13 %. Deviations of the present critical parameter as well as all the data and locus by other investigators from Eqs. (1) and (2) are also shown in Figs. 3 and 4. While Eq. (1)

reproduces all the critical temperature data by other investigators within ±0.12 %, Eq. (2) agrees with these data within ±1.6 %. Our locus of critical temperature in Fig.3 is very close to that reported by Higashi et al.[10], while that by Zhelezny et al.[11] behaves differently from ours. Such a significant difference seems due to the fact that Zhelezny et al.[11] developed their correlation only on the basis of two experimental data whose mole fractions are very close each other. As for the critical density in Fig.4, it is clear that the correlation by Higashi et al. [10] provides a positive deviation from Eq. (2) by 1.0-1.5 % systematically. Although Higashi et al.[10] applies similar experimental method and the same functional form as ours, difference in sample purity and other experimental factors might influence on this difference. But note that the difference is within the experimental uncertainty of critical density.

2. Critical locus of binary R-125/143a system

We have determined the critical temperature and critical density for R-125/143a (50/50 wt%), *i.e.*, R-507A, and tabulated in Table 5. Concerning the binary R-125/143a system, we have also determined the parameters Δ_V and Δ_T being Δ_V = -2.141 and Δ_T = 1.58 by means of fitting Eqs. (1) through (4) to the present experimental data of critical parameters. Figures 5 and 6 depict deviation of critical parameters and critical locus by the present study as well as those by other investigators from Eqs. (1) and (2). For R-125/143a, Eqs (1) and (2) represent the input data without any deviation, since there is only a single datum of the critical parameter. As for the critical temperature, Eq. (1) agrees with the critical temperature data by other investigators within ±0.04 %, except the value by Zhelezny et al.[11]. On the other hand, Eq. (2) reproduces the critical density data measured by others within ±3.0 %. Concerning the critical density

in Fig.5, the critical locus developed by Zhelezny et al.[11] is concave, while that by the present work and Higashi et al.[10] are convex. We have developed Eq.(2) for the R-125/143a system only at a simple composition, and therefore further measurements should be continued so as to clarify such a significant difference.

Conclusions

For binary R-32/125 system, we have measured 35 saturation densities along three different compositions, *i.e.*, 10, 35 and 50 wt% R-32, and determined critical temperatures and critical densities for these binary mixtures. Based on these results, we have developed correlations for the critical locus with high reproducibility. Concerning binary R-125/143a system, we have measured 19 saturation densities and determined critical temperature and critical density for 50 wt% R-125 mixture (R-507A) from which we have also developed a representation for the critical locus.

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References

1. Kuwabara, S.; Aoyama, H.; Sato, H.; Watanabe, K. J. Chem. Eng. Data, 1995, 40(1), 112.
2. Aoyama, H.; Kishizawa, G.; Sato, H.; Watanabe, K. J. Chem. Eng. Data, 1996, 41(5), 1046.
3. Okazaki, S.; Higashi, Y.; Takaishi, Y.; Uematsu, M.; Watanabe, K. Rev. Sci. Intrum. 1983, 54, 21.
4. Tanikawa, S.; Kabata, Y.; Sato, H.; Watanabe, K. J. Chem. Eng. Data 1990, 35(4), 381.
5. International Organization for Standardization "Guide to the Expression of Uncertainty in Measurement", 1993, Switzerland.
6. Uchida, H.; Sato, H.; Watanabe, K. Paper to be presented at the 13th Symp. on Thermophys. Prop., Boulder, Colorado, 1997.
7. Widiatmo, J.V.; Sato, H.; Watanabe, K. Int. J. Thermophys. 1995, 16(3), 801.
8. Ikeda, T.; Higashi, Y. Proc. of the 16th Japan Symp. on Thermophys. Prop. 1995, 169 [in Japanese]
9. Ikeda, T.; Kanai, K.; Higashi, Y. Proc. of the 4th Asian Thermophys. Prop. Conf. 1995, 327.
10. Higashi, Y. Proc. of 1996 JAR Annual Conf., 1996, 93 [in Japanese].
11. Zhelezny, V.; Chernyak, Y.; Zhelezny, P. Proc. of the 4th Asian Thermophys. Prop. Conf. 1995, 2, 291.
12. Bivens, D.B.; Yokozeki, A. Proc. 4th Asian Thermophys. Proc. Conf. 1995, 327.
13. Singh, R.R.; Lund, E.A.E.; Shankland, I.R. Proc. of the Int. Conf. On CFC and Halon Alternatives. Baltimore, MD, 1991, 451.
14. Nagel, M.; Bier, K. Int. J. Refrigeration 1995, 18(8), 534.
15. Nagel, M.; Bier, K. Int. J. Refrigeration 1996, 19(4), 264.

Table I Experimental Result of Saturation Density for R-32/125 (10/90 wt%)

ρ" / kg•m^{-3}	T / K	ρ' / kg•m^{-3}	T / K
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

Table II Experimental Result of Saturation Density for R-32/125 (35/65 wt%)

ρ" / kg•m^{-3}	T / K	ρ' / kg•m^{-3}	T / K
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		

Table III Experimental Result of Saturation Density for R-32/125 (50/50 wt%)

ρ" / kg•m^{-3}	T / K	ρ' / kg•m^{-3}	T / K
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		

Table IV Experimental Result of Saturation Density for R-125/143a (50/50 wt%)

ρ" / kg•m^{-3}	T / K	ρ' / kg•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		

Table V Critical parameters

	Component [wt%]	Critical Density [kg•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 (Higashi [10])	50/50	501±5*	343.76 ±0.02 *
R-32 (Kuwabara et al.[1])		424±1*	351.255±0.010*
R-125 (Kuwabara et al.[1])		568±1*	339.165±0.010*
R-143a (Aoyama et al.[2])		434±1*	345.860±0.010*

* These uncertainty values were established in the basis of past concept

Figure Captions

Figure 1 Experimental Result of Saturation Density for R-32/125 system

○ 50/50 wt% Δ 35/65 wt% ◊ 10/90 wt% ● Critical Point
Critical Locus R-125 (Kuwabara et al. [1])
R-32 (Kuwabara et al. [1])

Figure 2 Experimental Result of Saturation Density for R-125/143a system

○ This work 50/50 wt% x Ikeda et al. (50/50 wt%) [8] ● Critical Point
▲ Widiatmo et al.(50/50 wt%) [7] ◆ Uchida et al. (50/50 wt%) [6]
Critical Locus Critical Locus R-143a (Aoyama et al. [2])
R-125 (Kuwabara et al. [1])

Figure 3 Deviation of Critical Temperature from Equation (1) for R-32/125 system
○ This work □ Higashi [10] ▲ Zhelezny et al.[11] x Singh et al. [13]
+ Bivens and Yokozeki [12] ◊ Nagel and Bier [14]
Higashi [10] Zhelezny et al. [11]

Figure 4 Deviation of Critical Density from Equation (2) for R-32/125 system
○ This work □ Higashi [10] ▲ Zhelezny et al.[11] x Singh et al. [13]
+ Bivens and Yokozeki [12] ◊ Nagel and Bier [14]
Higashi [10] Zhelezny et al. [11]

Figure 5 Deviation of Critical Temperature from Equation (1) for R-125/143a system
○ This work □ Higashi [10] ▲ Zhelezny et al.[11] ◊ Nagel and Bier [14]
Higashi [10] Zhelezny et al. [11]

Figure 6 Deviation of Critical Density from Equation (2) for R-125/143a system
○ This work □ Higashi [10] ▲ Zhelezny et al.[11] ◊ Nagel and Bier [14]
Higashi [10] Zhelezny et al. [11]

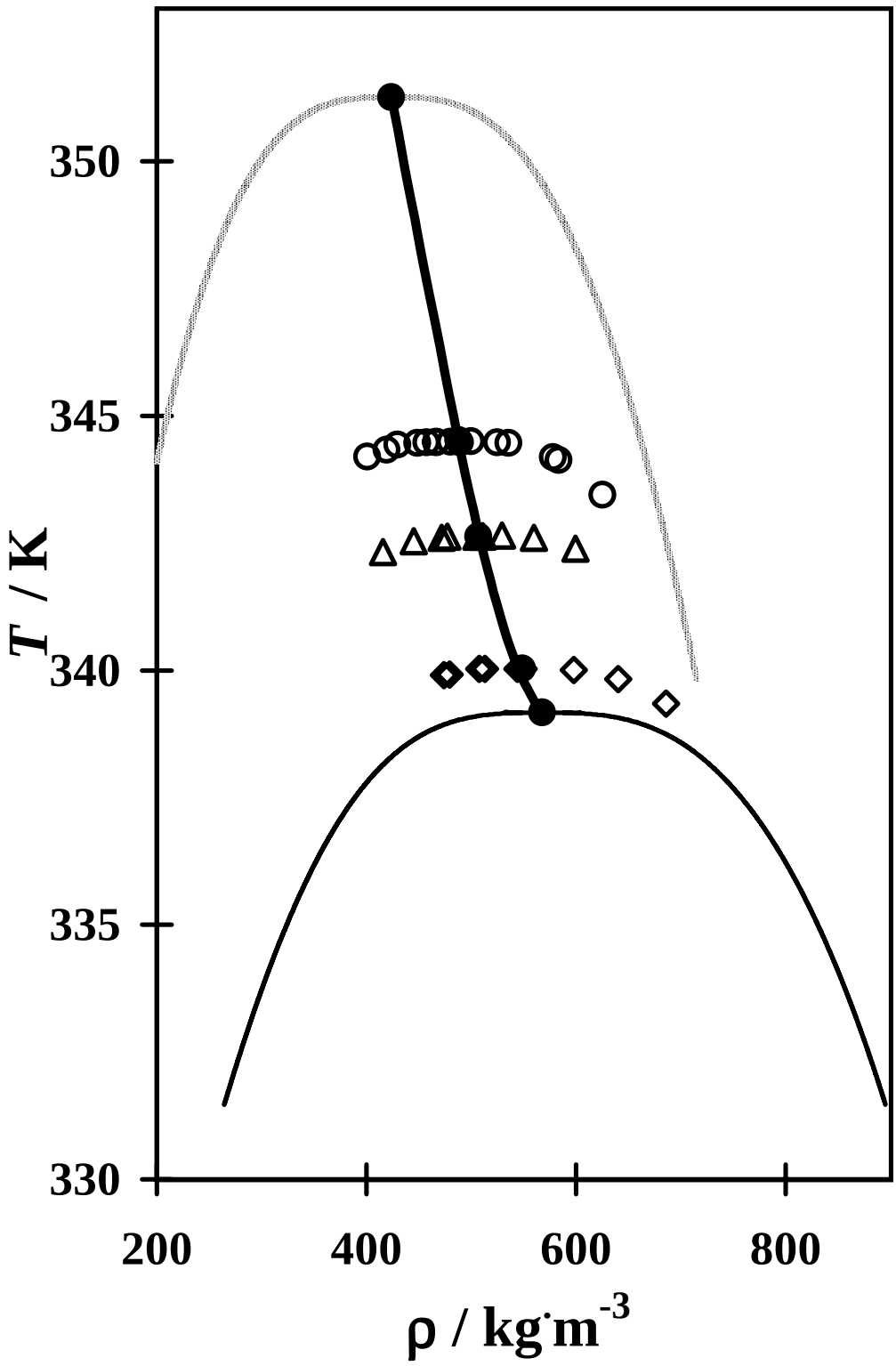


Figure 1

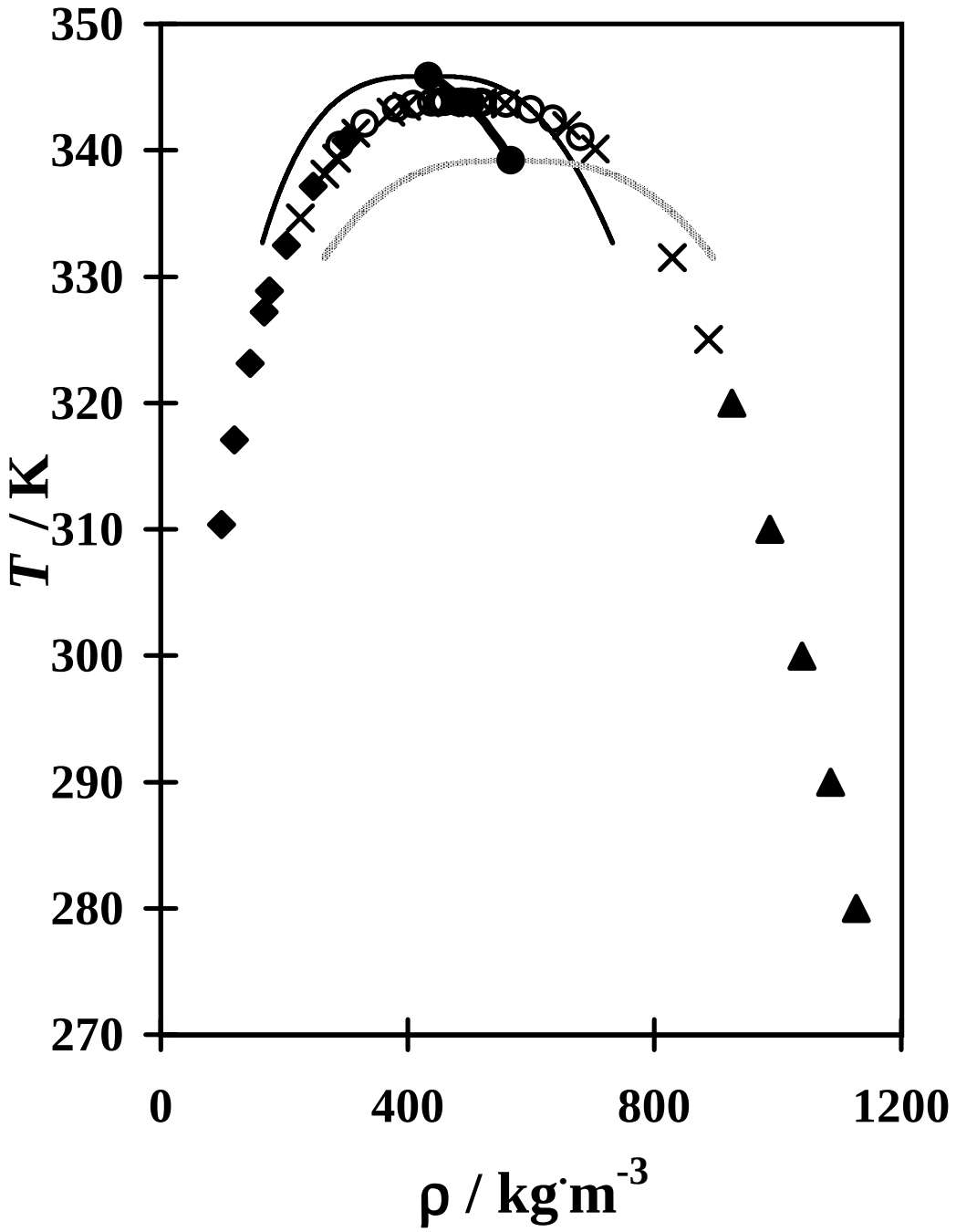
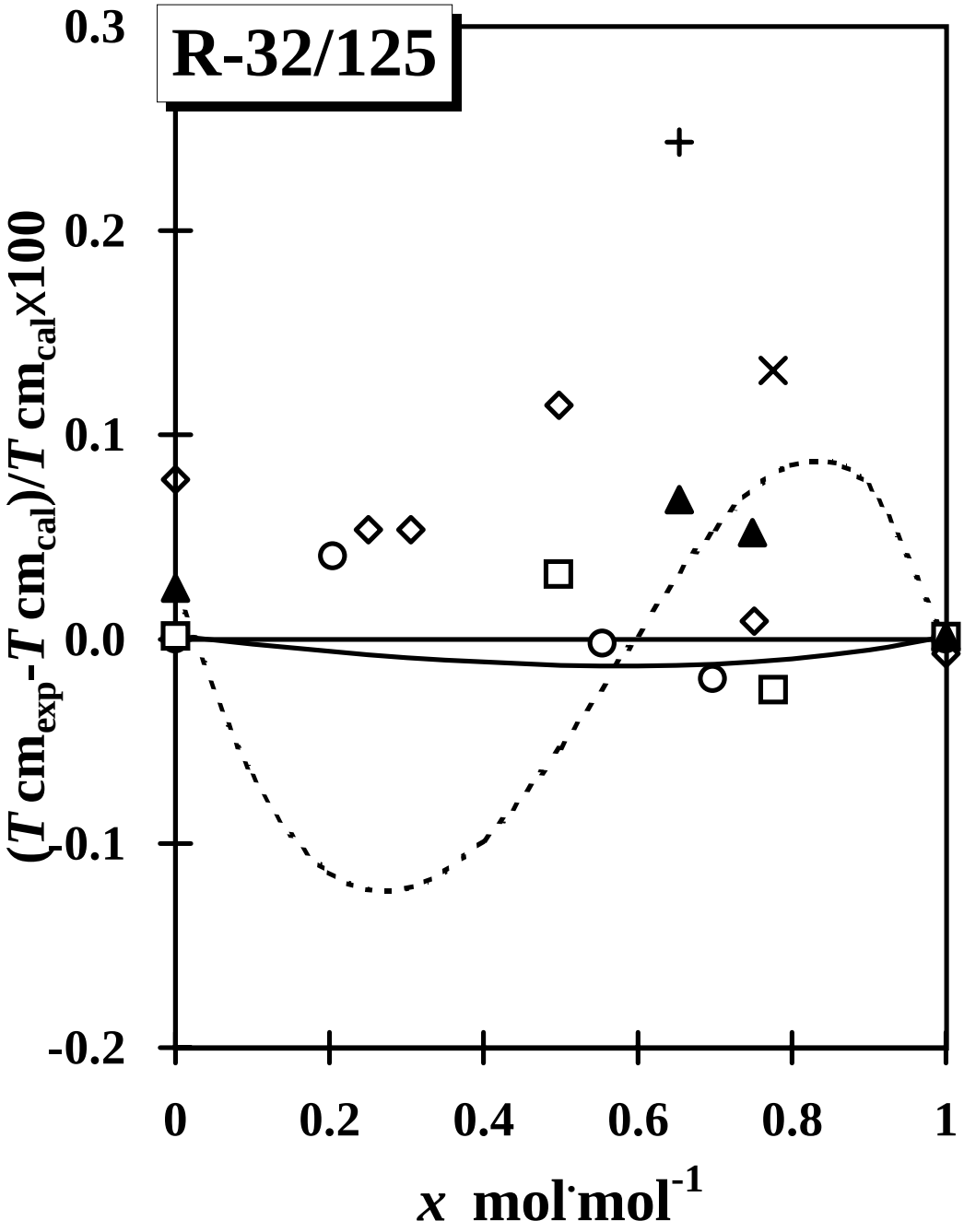


Figure 2


R-32/125
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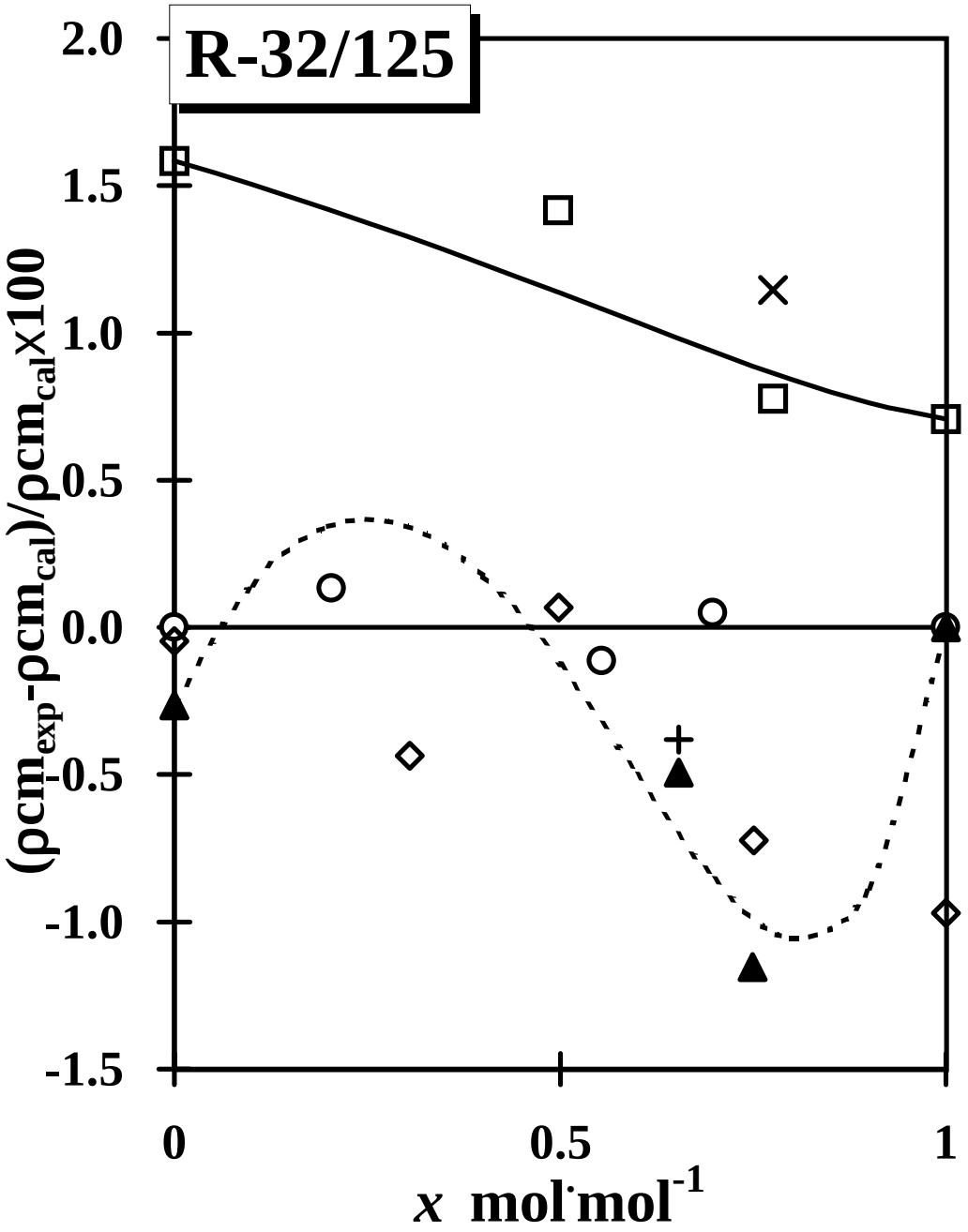
0.2
0.1
0.0
-0.1
-0.2
0
0.2
0.4
0.6
0.8
1
(T cm_exp-T cm_cal)/T cm_cal×100
x mol·mol^-1

Figure 3


R-32/125
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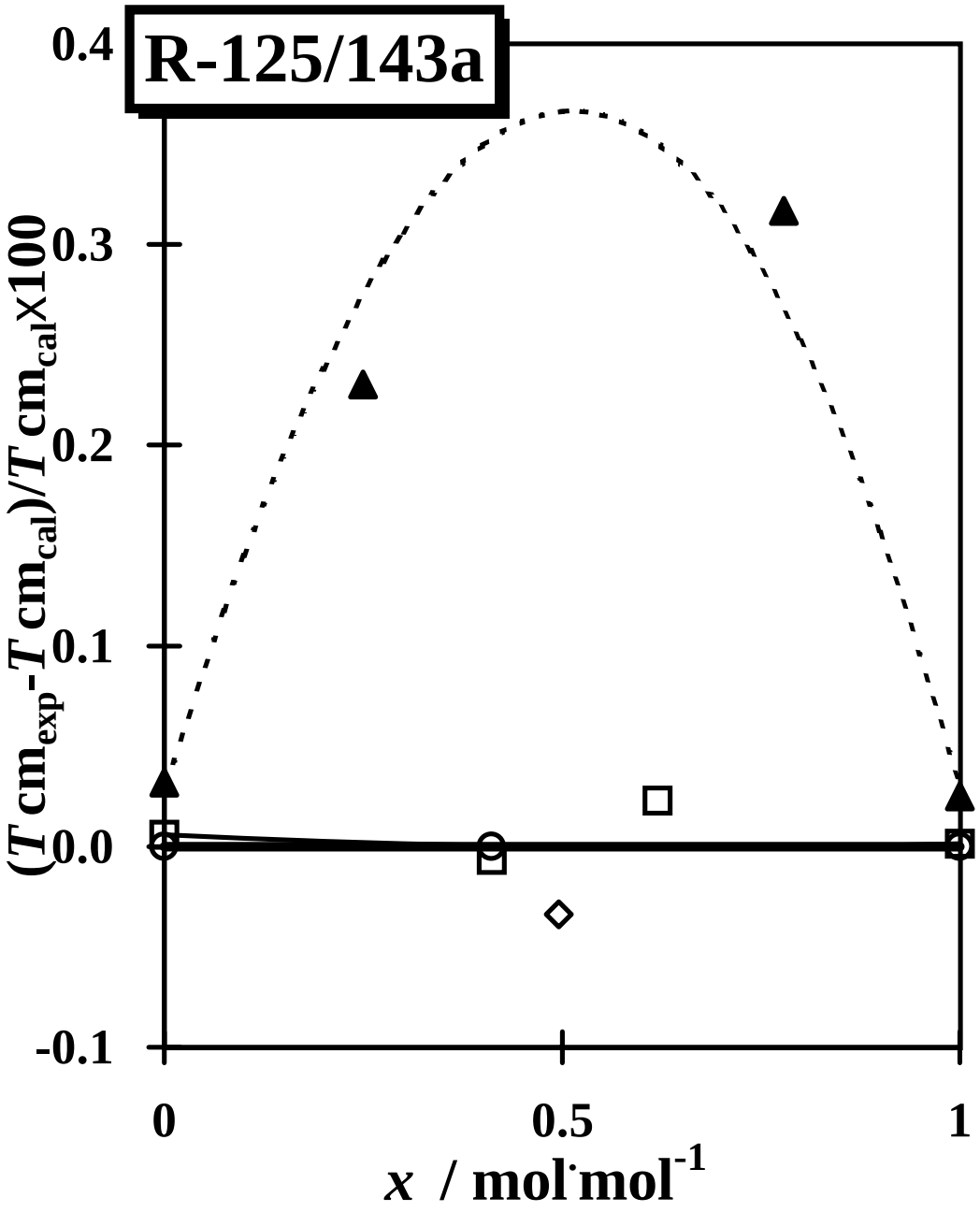
1.0
0.5
0.0
-0.5
-1.0
-1.5
(ρcm_exp-ρcm_cal)/ρcm_cal×100
0
0.5
1
x mol·mol^-1

Figure 4


R-125/143a
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0.3
0.2
0.1
0.0
-0.1
0
0.5
1
x / mol·mol-1
(T cmexp-T cmcal)/T cmcal×100

Figure 5

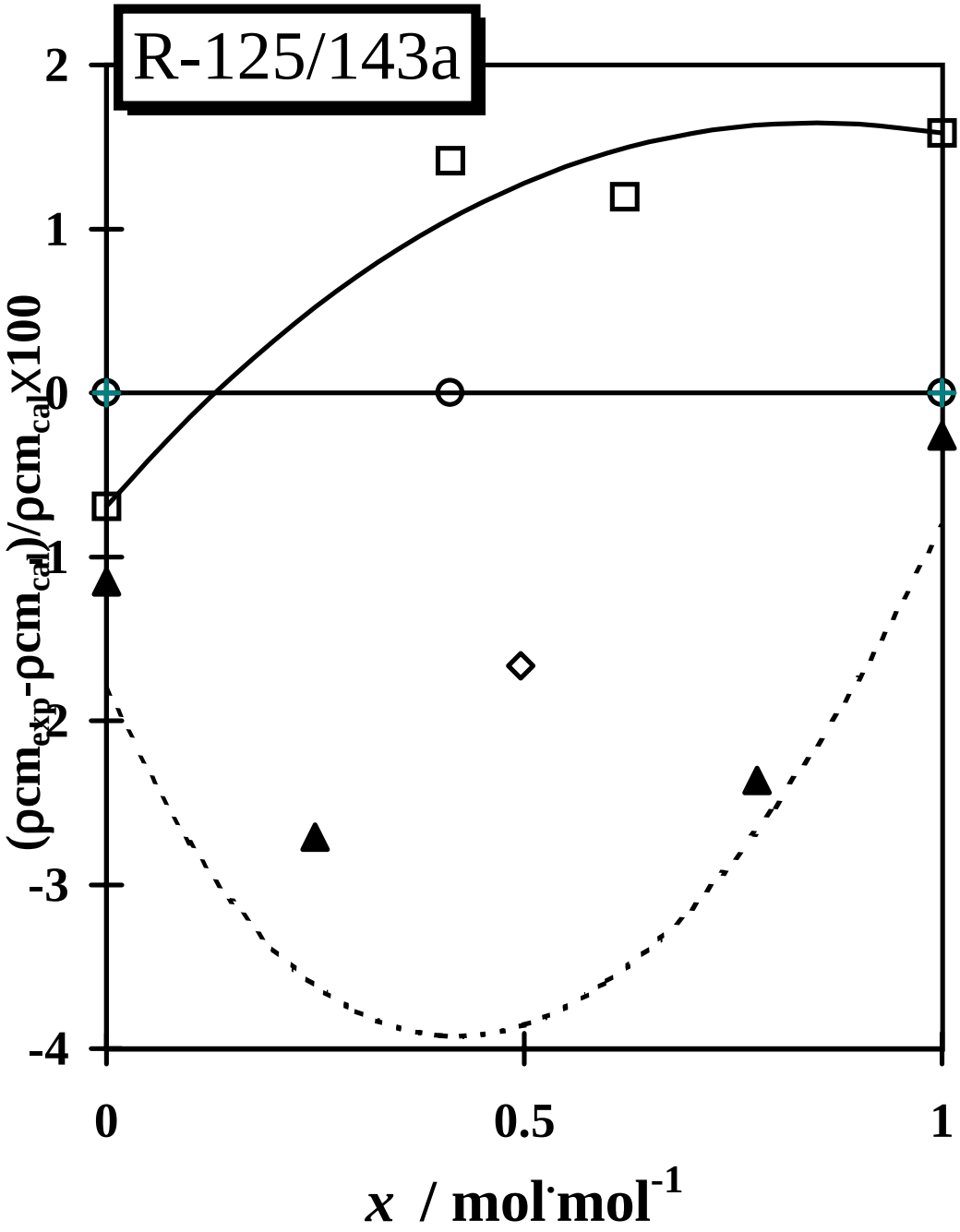

Figure 6