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Analysis of *PVTx* Measurements for Binary Mixtures of R115 and R114[1]

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We have made *PVTx* measurements of R115 and R114 at temperatures from 296 to 443 K, pressures from 0.4 to 9.8 MPa, and densities from 153 to 1387 $\text{kg} \cdot \text{m}^{-3}$, for four compositions, namely, 25, 50, 75, and 100 wt% R115. The data were obtained along isochores. The uncertainties in temperature, pressure and density are less than ±8 mK, ±2.2 kPa and ±0.1%, respectively. Using the experimental measurements on 100 wt% R115, we have validated our experimental apparatus and measurements. Furthermore, from the *PVTx* measurements for 75 wt% R115, 50 wt% R115, and 25 wt% R115, we have determined dew points and bubble points enabling us to construct the dew- and bubble-point curves for each composition. Our measurements also yield the critical point of R115 and R114 as a function of the concentration of the mixture.

KEY WORDS: bubble point; critical phenomena; dew point; mixtures; refrigerants; R114; R115.

1. INTRODUCTION

Some of the advantages of using binary refrigerant mixtures for refrigeration and heat pumps as well as for Rankine cycle applications with small temperature differences have been pointed out and discussed in many references [1, 2]. In practical applications, the relationship among the pressure P, volume V, temperature T, and concentration x should be known accurately for those binary refrigerant mixtures in order to design the system and examine the cycle performance with high reliability.

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Although the binary refrigerant R115 ($CClF_2CF_3$; monochloropentafluoroethane) + R114 ($CClF_2CClF_2$, 1,2-dichloro-1,1,2,2-tetrafluoroethane) system is one of the technically important mixtures, experimental investigations for its thermodynamic properties are not available. In previous publications we have reported *PVTx* measurements for the R12 + R22 system [3], the R22 + R114 system [4], the R13B1 + R114 system [5], and the R152a + R114 system [6, 7]. Here we present information on the thermophysical properties of the R115 + R114 system at a wide range of temperatures from 296 to 443 K, pressures from 0.4 to 9.8 MPa, and densities from 153 to 1387 $kg \cdot m^{-3}$. We have measured the *PVTx* properties along isochores for four compositions, namely, 25, 50, 75, and 100 wt% R115. The actual experimental data will be presented in another publication [8]. For 100 wt% R115, we have submitted a paper for publication [9], so we do not discuss the results for 100 wt% R115 in detail in this paper. Figure 1 shows all the *PVTx* measurements obtained for this mixture including the data for 100 wt% R115. Based on these experimental data, we have determined the dew points, the bubble points, and the critical point for each composition.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

The method, apparatus, and procedure used for the *PVTx* measurements have been described in detail in our previous publications

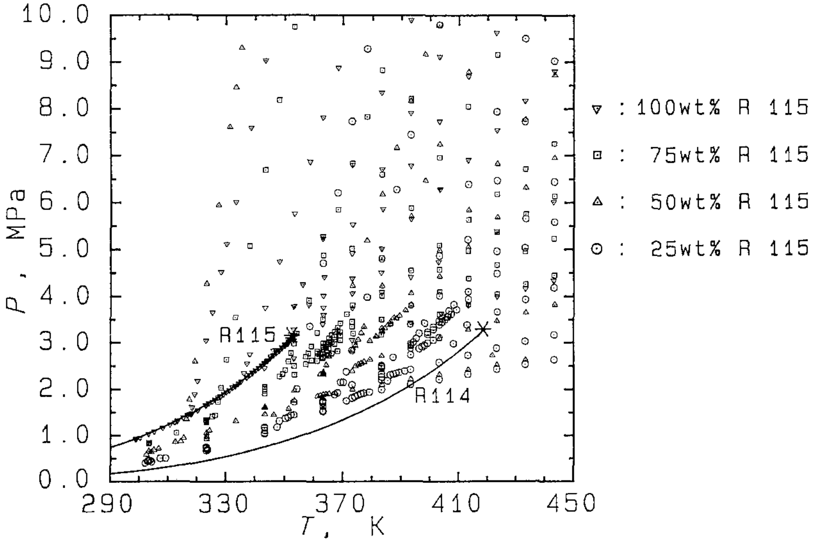

Fig. 1. Distribution of the measurements for the R115 + R114 system in a pressure–temperature diagram.

[10–12]. In principle, the *PVTx* measurements are made with the constant-volume method coupled with isothermal expansion procedures. Prescribed quantities of 99.97 wt% pure R114, an isomeric blend of 95% $CClF_2CClF_2$ and 5% CCl_2FCF_3, and that of 99.999 wt% pure R115 were prepared in two independent vessels which had been evacuated in advance. The amount of the pure component in each vessel is adjusted to the prescribed mass and then weighed by a precision chemical balance with a sensitivity of 2 mg. The temperature is measured by a 25-Ω platinum resistance thermometer (Chino Model R800-1) calibrated on IPTS-68 within ±3 mK. The temperature in the thermostated bath is controlled within ±5 mK. Since the temperature of the sample is not measured directly in the present measurements, careful attention has been given to verifying the existence of thermodynamic equilibrium between the sample and the thermostated bath fluid during the experiments. Thus the uncertainty of the temperature measurements was less than ±8 mK. The sample pressure is transmitted to an external pressure measuring system through a diaphragm-type differential-pressure detector by balancing the sample pressure with the pressure of the nitrogen gas applied as the pressure transmitting medium. The sensitivity of the pressure measurements is about 0.1 kPa. The nitrogen pressure is measured with two different pressure gauges: an air piston gauge (Ruska Model 2465) for pressures below 4 MPa and an oil-operated dead weight pressure gauge (Futaba Model TL-2) for pressures between 4 and 10 MPa. The uncertainty of the pressure measurements was less than ±0.6 kPa for pressures below 4 MPa and less than ±2.2 kPa for those above 4 MPa. The uncertainty of the density measurements after the expansion procedure may be accumulated by repeating the expansion procedure. Since the expansion procedures did not exceed three times in the present work, the uncertainty in the density measurements is estimated as less than ±0.1%. The uncertainty of the mass-fraction measurements is also estimated to be less than ±0.1%.

3. RESULTS

The experiments have been performed for four compositions, namely, 25, 50, 75, and 100 wt% R115, as summarized in Table I. The distribution of the measured points is shown in Fig. 1. These 597 experimental data of *PVTx* properties have been submitted for publication [8]. It should be noted that we have not made any new measurements for pure R114, since they have already been obtained by Hasegawa et al. [4] using the same apparatus. However, we did make new measurements for pure R115 along two isochores to check the data reported previously [9].

Table I. Range and Number of Measurements

Composition of R115	Temperature range (K)	Pressure range (MPa)	Density range ($kg \cdot m^{-3}$)	Isochores	Data points
100 wt%	296 ~ 443	0.8 ~ 9.6	235 ~ 1244	13	186
75 wt% (76.8 mol%)	303 ~ 443	0.8 ~ 9.8	270 ~ 1267	10	144
50 wt% (52.5 mol%)	302 ~ 443	0.6 ~ 9.3	153 ~ 1387	8	124
25 wt% (26.9 mol%)	302 ~ 443	0.4 ~ 9.8	163 ~ 1273	10	143
Total	296 ~ 443	0.4 ~ 9.8	153 ~ 1387	41	597

Analyzing these *PVTx* measurements graphically for three compositions, we determined the dew and bubble points by finding the breaking point of each isochore in the *P–T* plane. We determined the bubble point as the breaking point where the slope of the isochore increases, while we determined the dew point as the breaking point where the slope of the isochore decreases. For the isochores near the critical density, however, it is difficult to find the breaking point of each isochore; hence, we determined dew points, bubble points, and critical points by referring to the vapor–liquid coexistence curve in the T–ρ plane observed by Tanikawa et al. [13]. They determined the vapor–liquid coexistence curve by observing the disappearance of the meniscus for the same samples used in this study.

Table II contains the critical parameters as a function of composition; they were deduced from the vapor–liquid coexistence curve obtained by Tanikawa et al. [13]. Table II also includes the critical parameters for the two pure components, R115 and R114, from our previous measurements [8, 14]. Table III shows the breaking points of the isochores, i.e., dew points at each composition for the R115 + R114 system. The data given with an asterisk are the values determined with the aid of the data of

Table II. Determined Critical Points

Composition	ρ_c ($kg \cdot m^{-3}$)	T_c (K)	P_c (MPa)
100 wt% R115 [9]	604 ± 3	352.945 ± 0.010	3.118 ± 0.002
75 wt% R115	594 ± 5	366.2 ± 1.8	3.20 ± 0.15
50 wt% R115	585 ± 5	387.07 ± 0.05	3.43 ± 0.10
25 wt% R115	577 ± 5	403.71 ± 0.05	3.52 ± 0.15
0 wt% R115 [14]	576 ± 3	418.78 ± 0.02	4.520 ± 0.001

Tanikawa et al., as mentioned above. The uncertainties of the dew and bubble points listed in Table III are estimated as ±2.0 K in temperature, ±0.17 MPa in pressure, and ±5.0 kg·m^{-3} in density for 75 wt% R115. The uncertainties for the other compositions are estimated as ±1.5 K in temperature, ±0.15 MPa in pressure, and ±3.0 kg·m^{-3} in density.

Table III. Determined Dew and Bubble Points[a]

	ρ (kg·m^{-3})	T (K)	P (MPa)
75 wt% R115			
Bubble point	1265.7	326.3	1.45
Bubble point	1091.5	350.1	2.36
Bubble point	993.8	358.1	2.75
Bubble point	844.2	367.0	3.19
Bubble point	662.2	368.7	3.26
Dew point	556.7	367.7	3.15
Dew point	437.8	367.2	3.02
Dew point	344.3	365.6	2.92
Dew point	270.8	364.4	2.72
50 wt% R115			
Bubble point	1387.2	315.2	0.93
Bubble point	1088.4	363.4	2.38
Bubble point	* 998.8	373.7	2.85
Bubble point	* 785.1	382.4	3.18
Bubble point	* 617.3	387.0	3.43
Dew point	* 583.1	387.2	3.41
Dew point	248.6	375.5	2.55
Dew point	153.9	361.7	1.86
25 wt% R115			
Bubble point	1269.9	352.3	1.43
Bubble point	1169.2	369.5	1.98
Bubble point	* 996.9	388.8	2.77
Bubble point	* 918.4	394.7	3.04
Bubble point	* 722.0	402.8	3.44
Dew point	* 567.7	404.6	3.47
Dew point	332.2	398.7	2.98
Dew point	205.6	385.4	2.30
Dew point	163.4	376.7	1.92

[a] Data given with an asterisk are from Ref. 13.

4. DISCUSSION

4.1. Pure R115

For 100 wt% R115, we made some measurements to reconfirm our earlier experiments [9]. Our new vapor pressure can be compared with a correlating vapor pressure equation presented previously [9]:

$$\ln(P/P_c) = (A\tau + B\tau^{1.9} + C\tau^{2.4})T_c/T \tag{1}$$

with T in K, P in MPa, and $\tau = 1 - T/T_c$. The assigned critical-point values are $T_c = 352.945$ K and $P_c = 3.118$ MPa, and the numerical constants in Eq. (1) are $A = -7.14372$, $B = 4.63333$, and $C = -6.29645$, respectively. Figure 2 shows the deviations of the present experimental pressures, other available experimental data [14, 15] and reported vapor pressure correlations [15, 16] from Eq. (1). It is seen from Fig. 2 that the present results are in good agreement with Eq. (1). Furthermore, the present PVT data for 100 wt% R115 are also in good agreement with our previously proposed equation of state for R115 [17].

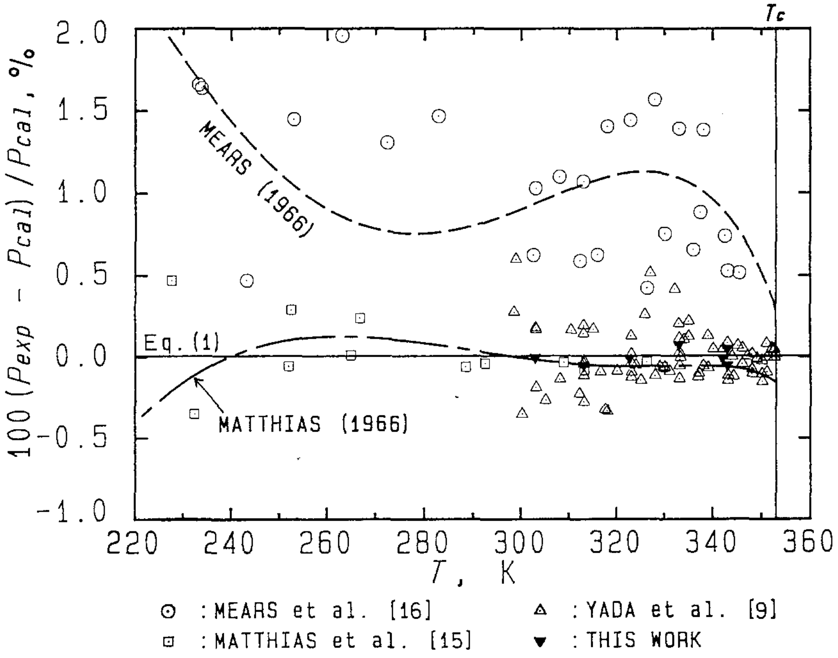

Fig. 2. Deviations of the vapor pressure data from Eq. (1).

4.2. R115 + R114 Mixtures

The dew points, bubble points, and critical points listed in Tables II and III are shown in the *P–T* plane in Fig. 3 together with the vapor pressure curves and critical points of R115 and R114. Connecting the dew and bubble points smoothly, we can obtain dew- and bubble-point curves from which dew points and bubble points at arbitrary temperatures and pressures can be deduced. In Fig. 3, the dashed line indicates the critical curve connecting the critical points of the three compositions observed in the present study. We find that the dew- and bubble-point curves of the R115 + R114 system are distributed almost evenly with their difference in weight fractions. For example, Fig. 3 shows that the dew- and bubble-point curves of 50 wt% R115 + 50 wt% R114 lie in the middle of the vapor pressure curves of the two pure components, while those of 25 wt% R115 + 75 wt% R114 and those of 75 wt% R115 + 25 wt% R114 also lie in an evenly distributed location with their weight fractions.

On the other hand, from the envelope of the dew- and bubble-point curves in Fig. 3, it is seen that this mixture is a nonazeotropic one that has different dew-point curves and bubble-point curves. Among the three compositions, the composition which has the largest envelope of dew- and bubble-point curves is 50 wt% R115. The spread of the phase-boundary envelope for 25 wt% R115 is as large as that for 75 wt% R115. It is interesting to note that the largest spread of each dew- and bubble-point curve for each composition exhibits lower pressures than the critical pressure by about 1–2 MPa.

The critical curve becomes convex and it exhibits a higher pressure than the pressure along the straight tie line between two critical points of

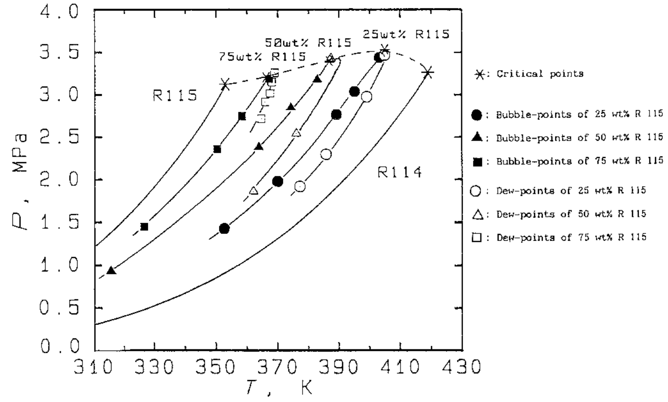

Fig. 3. Dew and bubble points of the R115 + R114 system.

the components. We note the following characteristics of the binary mixture considered here. First, the two components have a similar molecular structure. Second, the difference in their critical temperatures is large (about 65 K), while that in the critical pressures is small. Third, both R115 and R114 have a fairly low polarity.

5. CONCLUSIONS

We have measured the *PVTx* properties of R115 and R114 mixtures for a wide range of temperatures, pressures, and densities for four compositions including 100 wt% R115. We have confirmed the reliability of our earlier measurements [9] by repeating vapor pressure and *PVT* measurements for 100 wt% R115. Based upon our *PVTx* measurements for 75 wt% R115, 50 wt% R115, and 25 wt% R115, we have determined dew points, bubble points, and critical points for the respective compositions, from which deduced the critical curve and dew- and bubble-point curves of the R115 + R114 system.

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