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# Measurements of *PVTx* Properties for Binary Mixtures of HFC-32 ($CH_2F_2$) and HFC-134a ($CH_2FCF_3$)[1]

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An experimental study of pressure–volume–temperature–composition (*PVTx*) properties for binary mixtures of HFC-32 and HFC-134a was conducted in the range of temperatures from 243 to 473 K, pressures up to 16.7 MPa, densities from 9.5 to 1065 $kg \cdot m^{-3}$, and compositions from 0.39 to 0.89 mol fraction of HFC-32, with uncertainties of 8 mK, 1.7 kPa, 0.04%, and 0.001 mol fraction, respectively. A constant-volume method was used for the present measurements either with a spherical vessel approximately 270 $cm^3$ in its inner volume or with a cylindrical vessel approximately 138 $cm^3$ in its inner volume. The present data were compared with the Piao equation of state for this substance.

**KEY WORDS:** alternative refrigerants; experimental data; HFC-32; HFC-134a; mixture; *PVTx* properties; vapor pressure.

## 1. INTRODUCTION

In a refrigeration system using a binary mixture as the working fluid, variations in their composition exist because of the effect of vapor–liquid equilibrium conditions at different temperatures and pressures. Especially, considerable composition changes exist between the inlet and the outlet of the evaporator, condenser, and expansion valve. For such reason, precise thermophysical properties are needed not only for a single composition, but also for a wide range of compositions of binary mixtures. In the present

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study, for binary mixtures of HFC-32 ($CH_2F_2$) and HFC-134a ($CH_2F$-$CF_3$) expected to be an alternative refrigerant to HCFC-22 ($CHClF_2$), an experimental study of the pressure–volume–temperature–composition (*PVTx*) properties and vapor pressures has been conducted in the range of compositions from 0.39 to 0.89 mol fraction of HFC-32.

## 2. SURVEY OF PREVIOUS EXPERIMENTAL STUDIES

### 2.1. Vapor–Liquid Equilibria

The available experimental studies of vapor–liquid equilibria for binary mixtures of HFC-32 and HFC-134a cover the temperature range of 203 to 369 K and the pressure range up to 5.4 MPa. Fujiwara et al. [1, 2] measured nine data points in the range of pressures from 0.4 to 2.6 MPa and compositions from 0.2 to 0.9 mol fraction of HFC-32 at 273 and 323 K. Higashi [3] measured 12 data points in the range of temperatures from 283 to 313 K and pressures from 0.6 to 1.9 MPa. Nagel and Bier [4] obtained 50 data points in the range of temperatures from 203 to 369 K and pressures from 0.01 to 5.4 MPa. Weber and Silva [5] obtained 33 data points in the range of temperatures from 260 to 300 K and pressures from 0.2 to 1.8 MPa.

### 2.2. *PVTx* Properties

Experimental studies of *PVTx* properties for binary mixtures of HFC-32 and HFC-134a have been conducted in the range of temperatures from 228 to 440 K, pressures from 0.2 to 10.1 MPa, densities from 7 to 1300 $kg \cdot m^{-3}$, and compositions from 0.33 to 0.89 mol fraction of HFC-32. Fukushima et al. [6] measured 128 data points in the range of temperatures from 323 to 424 K, pressures from 1.8 to 10.1 MPa, and densities from 71 to 795 $kg \cdot m^{-3}$ at a composition of 0.46 mol fraction of HFC-32. Sato et al. [7] also measured 260 data points in the range of temperatures from 320 to 440 K, pressures from 1.5 to 6.2 MPa, densities from 61 to 183 $kg \cdot m^{-3}$, and compositions from 0.33 to 0.89 mol fraction of HFC-32. Weber and Defibaugh [8] obtained 17 data points in the range of temperatures from 228 to 373 K, pressures from 0.3 to 4.3 MPa, and densities from 7 to 169 $kg \cdot m^{-3}$ at a composition of 0.5 mol fraction of HFC-32. Widiatmo et al. [9] obtained 22 data points in the range of temperatures from 280 to 330 K, pressures from 1.3 to 3.0 MPa, and densities from 993 to 1214 $kg \cdot m^{-3}$ at a composition of 0.4 mol fraction of HFC-32. Iwata et al. [10] acquired 97 data points of *PVTx* properties in the range of temperatures from 263 to 393 K, pressures from 0.2 to 1.3 MPa, densities from

200 to 1300 $kg \cdot m^{-3}$, and compositions from 0.33 to 0.75 mol fraction of HFC-32.

## 3. METHOD

By means of the constant-volume method as described in the literature [11, 12], two kinds of vessels were used for the present measurements, namely, a spherical vessel approximately 270 $cm^3$ in its inner volume and a cylindrical vessel approximately 138 $cm^3$ in its inner volume as shown in Fig. 1. Normally, density and composition distributions exist in the vessel as a result of gravity effects. For minimizing this effect on the *PVTx* properties, especially near the critical point, a low-height vessel should be

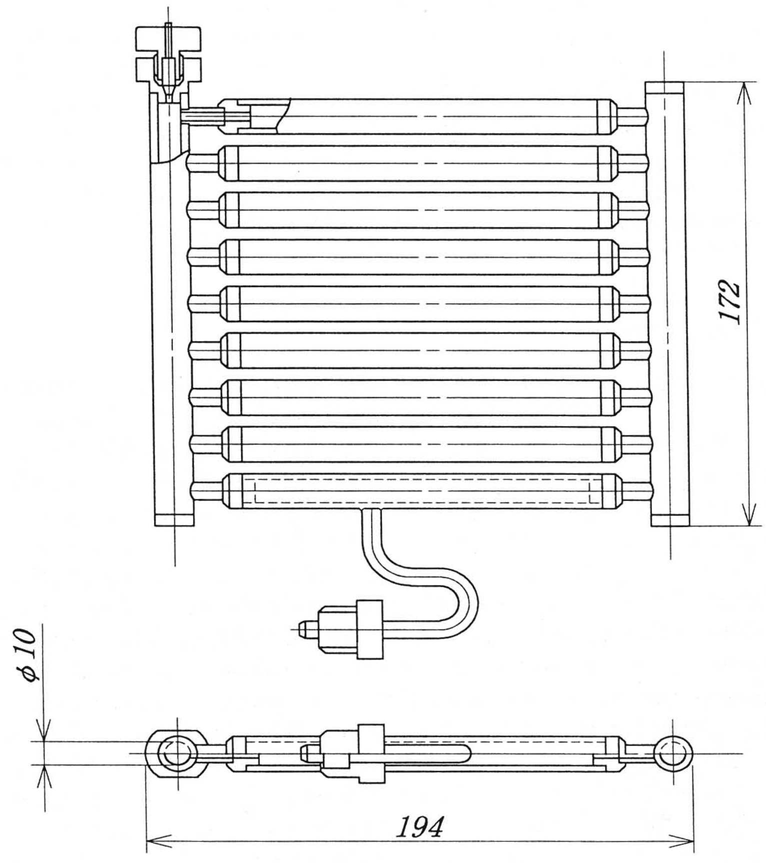


**Fig. 1.** New cylindrical vessel for mixture property measurement. Dimensions are millimeters.

considered for the mixture property measurements, and the new cylindrical vessel shown in Fig. 1 was utilized for the present measurements. The uncertainties of temperature and pressure measurements are estimated to be less than 8 mK and 1.7 kPa, respectively. The uncertainty of density measurements is less than 0.007% except for data at a 0.3971 mol fraction along the $9.5\ kg \cdot m^{-3}$ isochore, where the uncertainty is estimated to be 0.04%. Also, the uncertainty of composition measurements is less than 0.01% except data for the 0.3971 mol fraction along the $9.5\ kg \cdot m^{-3}$ isochore, where the uncertainty is estimated to be 0.1%. The purities of the sample of HFC-32 and HFC-134a are 99.9 and 99.99 mass%, respectively, as supplied by the Mitsui-du Pont Fluorochemical Co. Ltd.

## 4. RESULTS

### 4.1. Vapor Pressure

Measurements of 36 data points of vapor pressure for binary mixtures of HFC-32 and HFC-134a were conducted for different compositions from 0.39 to 0.89 mol fraction of HFC-32 in the range of temperatures from 243 to 361 K and pressures from 0.17 to 4.3 MPa, as shown in Table I.

### 4.2. *PVTx* Properties

Measurements of the *PVTx* properties of binary mixtures of HFC-32 and HFC-134a were made for compositions from 0.39 to 0.89 mol fraction of HFC-32 in the range of temperatures from 310 to 473 K, pressures from 0.29 to 16.7 MPa, and densities from 9.5 to $1062\ kg \cdot m^{-3}$, as shown in Table II.

## 5. DISCUSSION

The deviations of measured densities from the equation of state proposed by Piao et al. [13] are shown in Figs. 2 to 5. The present work focused on the region where data are scarce, and most of the data shown in Table II could not be compared with available experimental data directly except near a composition of 0.39 mol fraction of HFC-32 as shown in Figs. 2 and 3.

## 6. CONCLUSION

Experimental data on *PVTx* properties and vapor pressures for binary mixtures of HFC-32 and HFC-134a were obtained with the use of a

**Table I.** Experimental Results for Vapor Pressures of Binary Mixtures of HFC-32 and HFC-134a

| Mol fraction of HFC-32 | Temp. (K) | Pressure (MPa) | Density $(kg \cdot m^{-3})$ | Type of vessel[a] |
|---|---|---|---|---|
| 0.3917 | 293.150 | 0.9032 | 491.57 | SV |
| 0.3917 | 303.150 | 1.1871 | 491.34 | SV |
| 0.3917 | 313.150 | 1.5315 | 491.11 | SV |
| 0.3917 | 333.150 | 2.4392 | 490.64 | SV |
| 0.3917 | 353.150 | 3.6954 | 490.15 | SV |
| 0.3917 | 360.150 | 4.2387 | 489.98 | SV |
| 0.3917 | 361.151 | 4.3215 | 489.95 | SV |
| 0.3939 | 273.150 | 0.4778 | 167.12 | SV |
| 0.3939 | 283.150 | 0.6459 | 167.04 | SV |
| 0.3939 | 293.150 | 0.8761 | 166.96 | SV |
| 0.3939 | 303.150 | 1.1475 | 166.89 | SV |
| 0.3939 | 313.150 | 1.4751 | 166.81 | SV |
| 0.3939 | 333.150 | 2.3247 | 166.65 | SV |
| 0.3939 | 353.150 | 3.3784 | 166.48 | SV |
| 0.3939 | 354.150 | 3.4471 | 166.48 | SV |
| 0.3951 | 308.150 | 1.3945 | 994.74 | SV |
| 0.3951 | 313.150 | 1.5511 | 994.51 | SV |
| 0.3951 | 323.150 | 1.9740 | 994.03 | SV |
| 0.3951 | 328.150 | 2.2155 | 993.79 | SV |
| 0.3951 | 329.150 | 2.2762 | 993.75 | SV |
| 0.3952 | 243.157 | 0.1735 | 1065.84 | SV |
| 0.3952 | 260.000 | 0.3276 | 1065.06 | SV |
| 0.3952 | 270.001 | 0.4609 | 1064.59 | SV |
| 0.3952 | 280.000 | 0.6331 | 1064.11 | SV |
| 0.3952 | 290.001 | 0.8512 | 1063.62 | SV |
| 0.3952 | 310.000 | 1.4537 | 1062.63 | SV |
| 0.6622 | 310.000 | 1.7818 | 428.34 | SV |
| 0.6622 | 330.000 | 2.8374 | 427.93 | SV |
| 0.6622 | 350.000 | 4.3022 | 427.50 | SV |
| 0.7466 | 310.000 | 1.9068 | 424.57 | CV |
| 0.7466 | 330.000 | 3.0345 | 424.15 | CV |
| 0.8547 | 310.000 | 2.0663 | 427.32 | SV |
| 0.8547 | 330.000 | 3.2940 | 426.91 | SV |
| 0.8547 | 350.000 | 5.0152 | 426.48 | SV |
| 0.8869 | 310.000 | 2.1180 | 424.17 | CV |
| 0.8869 | 330.000 | 3.3769 | 423.76 | CV |

[a] SV, spherical vessel; CV, cylindrical vessel.

**Table II.** Experimental Results for *PVTx* Properties of Binary Mixtures of HFC-32 and HFC-134a

| Mol fraction of HFC-32 | Temp. (K) | Pressure (MPa) | Density ($kg \cdot m^{-3}$) | Type of vessel[a] |
|---|---|---|---|---|
| 0.3917 | 370.150 | 5.1383 | 489.73 | SV |
| 0.3917 | 371.150 | 5.2346 | 489.70 | SV |
| 0.3917 | 383.150 | 6.4063 | 489.40 | SV |
| 0.3917 | 393.150 | 7.3926 | 489.14 | SV |
| 0.3917 | 403.150 | 8.3857 | 488.89 | SV |
| 0.3917 | 413.151 | 9.3806 | 488.63 | SV |
| 0.3917 | 423.151 | 10.3756 | 488.36 | SV |
| 0.3917 | 433.150 | 11.3715 | 488.10 | SV |
| 0.3917 | 443.150 | 12.3663 | 487.84 | SV |
| 0.3917 | 453.150 | 13.3594 | 487.57 | SV |
| 0.3917 | 463.150 | 14.3495 | 487.30 | SV |
| 0.3917 | 473.150 | 15.3379 | 487.03 | SV |
| 0.3939 | 364.150 | 3.6870 | 166.39 | SV |
| 0.3939 | 383.150 | 4.1919 | 166.24 | SV |
| 0.3939 | 403.150 | 4.6996 | 166.07 | SV |
| 0.3939 | 423.151 | 5.1899 | 165.90 | SV |
| 0.3939 | 443.150 | 5.6664 | 165.72 | SV |
| 0.3939 | 473.150 | 6.3629 | 165.46 | SV |
| 0.3952 | 320.000 | 4.3785 | 1062.05 | SV |
| 0.3952 | 330.000 | 9.5550 | 1061.40 | SV |
| 0.3952 | 335.000 | 12.1525 | 1061.07 | SV |
| 0.3952 | 340.000 | 14.7419 | 1060.75 | SV |
| 0.3952 | 343.150 | 16.3811 | 1060.54 | SV |
| 0.3971 | 310.000 | 0.2857 | 9.55 | SV |
| 0.3971 | 320.000 | 0.2976 | 9.55 | SV |
| 0.3971 | 330.000 | 0.3078 | 9.54 | SV |
| 0.3971 | 340.001 | 0.3175 | 9.54 | SV |
| 0.3971 | 350.000 | 0.3276 | 9.53 | SV |
| 0.3971 | 360.000 | 0.3376 | 9.53 | SV |
| 0.3971 | 370.001 | 0.3483 | 9.52 | SV |
| 0.3971 | 380.001 | 0.3570 | 9.52 | SV |
| 0.3971 | 390.001 | 0.3672 | 9.51 | SV |
| 0.3971 | 400.000 | 0.3775 | 9.51 | SV |
| 0.3971 | 410.001 | 0.3873 | 9.50 | SV |
| 0.3971 | 420.001 | 0.3978 | 9.50 | SV |
| 0.3971 | 430.001 | 0.4071 | 9.49 | SV |
| 0.3971 | 440.001 | 0.4169 | 9.49 | SV |
| 0.3971 | 450.001 | 0.4268 | 9.48 | SV |
| 0.3971 | 460.000 | 0.4364 | 9.48 | SV |
| 0.3971 | 470.000 | 0.4463 | 9.48 | SV |
| 0.6622 | 370.000 | 6.2110 | 427.07 | SV |
| 0.6622 | 390.000 | 8.1752 | 426.62 | SV |
| 0.6622 | 410.000 | 10.1372 | 426.16 | SV |

**Table II.** *(Continued)*

| Mol fraction of HFC-32 | Temp. (K) | Pressure (MPa) | Density ($kg \cdot m^{-3}$) | Type of vessel[a] |
|---|---|---|---|---|
| 0.6622 | 430.000 | 12.0831 | 425.70 | SV |
| 0.6622 | 450.000 | 14.0204 | 425.26 | SV |
| 0.7466 | 350.000 | 4.6045 | 423.73 | CV |
| 0.7466 | 370.001 | 6.6292 | 423.29 | CV |
| 0.7466 | 390.001 | 8.7029 | 422.84 | CV |
| 0.7466 | 410.000 | 10.7775 | 422.39 | CV |
| 0.7466 | 430.001 | 12.8469 | 421.93 | CV |
| 0.7466 | 450.000 | 14.9053 | 421.46 | CV |
| 0.8547 | 370.001 | 7.2292 | 426.04 | SV |
| 0.8547 | 390.000 | 9.4965 | 425.59 | SV |
| 0.8547 | 410.001 | 11.7727 | 425.13 | SV |
| 0.8547 | 430.001 | 14.0399 | 424.67 | SV |
| 0.8869 | 350.000 | 5.1481 | 423.33 | CV |
| 0.8869 | 370.000 | 7.4094 | 422.89 | CV |
| 0.8869 | 390.001 | 9.7197 | 422.41 | CV |
| 0.8869 | 410.001 | 12.0354 | 421.98 | CV |
| 0.8869 | 430.001 | 14.3509 | 421.52 | CV |
| 0.8869 | 450.001 | 16.6536 | 421.05 | CV |

[a] SV, spherical vessel; CV, cylindrical vessel.

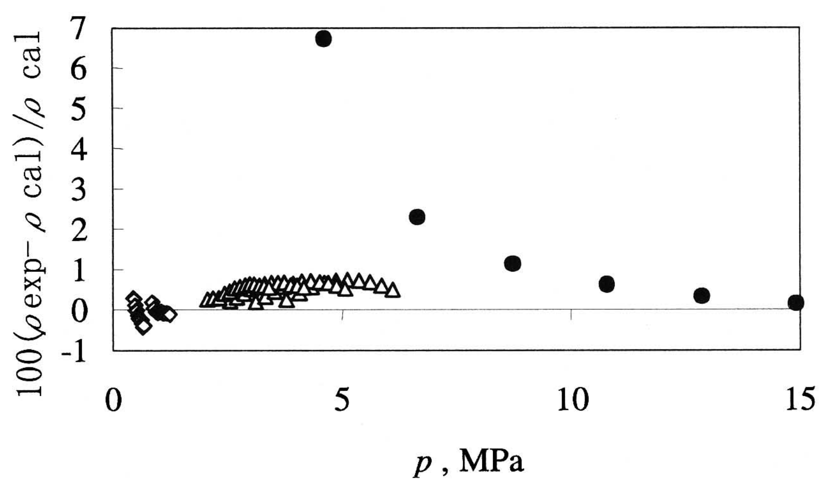


**Fig. 2.** Deviation of measured densities for a composition of 0.39 mol fraction of HFC-32 from equation of state by Piao et al. [13]. (●) This work: $x = 0.3917$ to $0.3971$, $\rho = 9.48$ to $1062.05\ kg \cdot m^{-3}$. (△) Sato et al. [7]: $x = 0.3953$, $\rho = 82.29$ to $164.76\ kg \cdot m^{-3}$. (□) Widiatmo et al. [9]: $x = 0.3953$, $\rho = 993.1$ to $1206.5\ kg \cdot m^{-3}$.

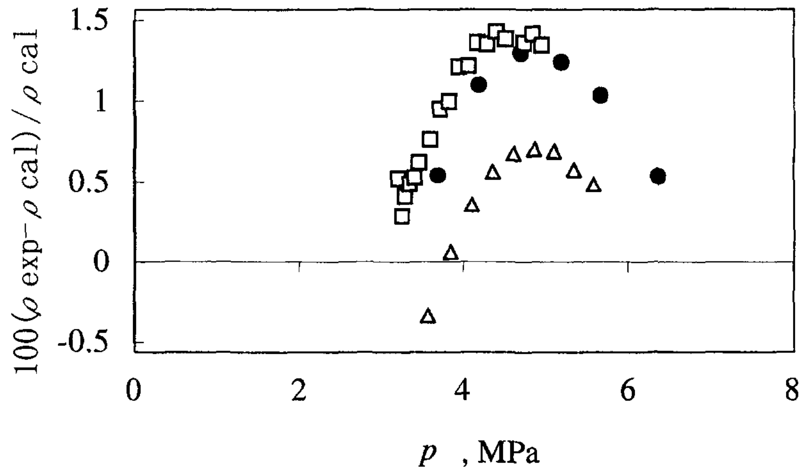


**Fig. 3.** Deviation of measured densities near a composition of 0.39 mol fraction of HFC-32 and densities of 160 kg · m$^{-3}$ from equation of state by Piao et al. [13]. (●) This work: $x = 0.3939$, $\rho = 165.46$ to 166.40 kg · m$^{-3}$. (△) Sato et al. [7]: $x = 0.3953$, $\rho = 164.10$ to 164.76 kg · m$^{-3}$. (□) Fukushima et al. [6]: $x = 0.4536$, $\rho = 147.81$ to 148.35 kg · m$^{-3}$.

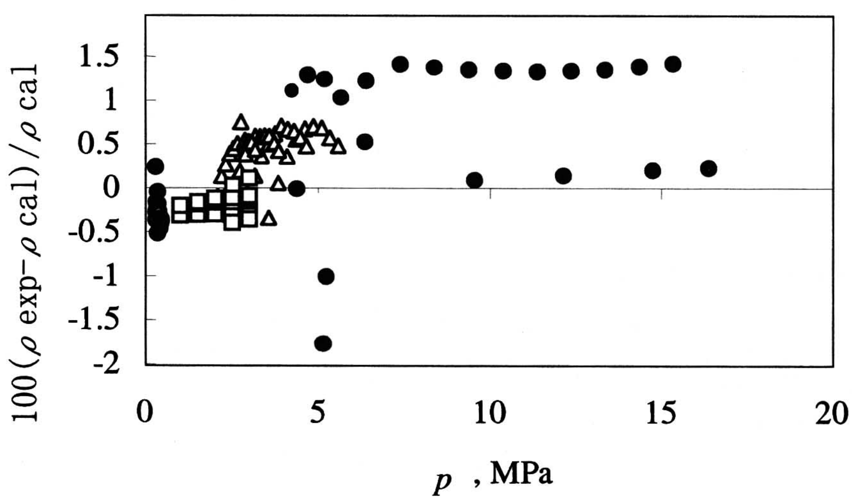


**Fig. 4.** Deviation of measured densities near a composition of 0.75 mol fraction of HFC-32 and for different densities from equation of state by Piao et al. [13]. (●) This work: $x = 0.7466$, $\rho = 421.46$ to 423.73 kg · m$^{-3}$. (△) Sato et al. [7]: $x = 0.7463$, $\rho = 68.51$ to 137.22 kg · m$^{-3}$. (◇) Iwata et al. [10]: $x = 0.7462$ to 0.7463, $\rho = 13.45$ to 26.02 kg · m$^{-3}$.

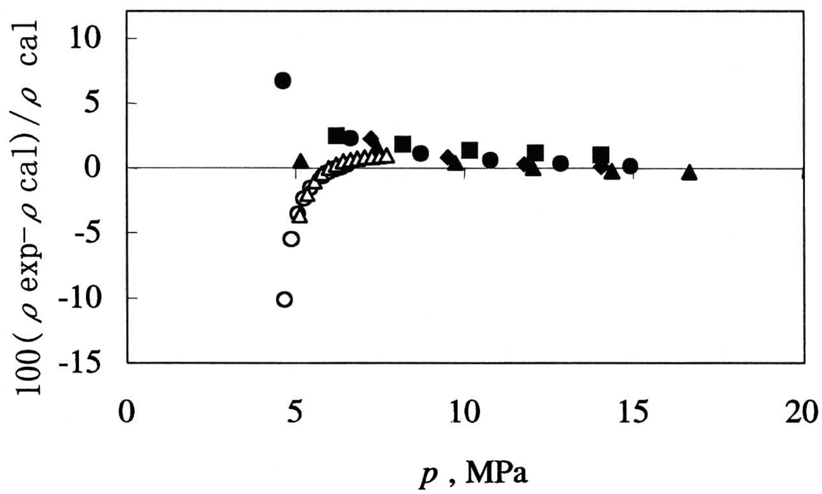


**Fig. 5.** Deviation of measured densities for different compositions (mol fractions of HFC-32) and near densities of 400 kg · m$^{-3}$ from equation of state by Piao et al. [13]. (■) This work: $x =$ = 0.6622, $\rho = 424.77$ to 427.07 kg · m$^{-3}$. (●) This work: $x = 0.7465$, $\rho = 421.46$ to 423.73 kg · m$^{-3}$. (◆) This work: $x = 0.8547$, $\rho = 424.20$ to 426.04 kg · m$^{-3}$. (▲) This work: $x = 0.8869$, $\rho = 421.05$ to 423.33 kg · m$^{-3}$. (○) Iwata et al. [10]: $x = 0.3288$, $\rho = 397.89$ to 398.37 kg · m$^{-3}$. (△) Iwata et al. [10]: $x = 0.5667$, $\rho = 397.79$ to 398.36 kg · m$^{-3}$.

constant-volume apparatus for compositions from 0.39 to 0.89 mol fraction of HFC-32 in the range of temperatures from 243 to 473 K, pressures from 0.17 to 16.7 MPa, and densities from 9.5 to 1062 kg · m$^{-3}$. For developing the equation of state for this mixture, more precise experimental data should be measured over a wide range of densities and compositions.

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