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# Viscosity of Difluoromethane and Pentafluoroethane along the Saturation Line

**Li-Qun Sun, Ming-Shan Zhu,* Li-Zhong Han, and Zhao-Zhuang Lin**

Department of Thermal Engineering, Tsinghua University, Beijing 100084, P.R. China

The paper reports new measurements of the viscosity of liquid difluoromethane (HFC-32) over the temperature range 233.15 K to 333.15 K and the viscosity of pentafluoroethane (HFC-125) over the temperature range 233.15 K to 328.15 K along the saturation line. The viscosities were measured in a calibrated capillary viscometer. A new method was developed to operate the viscometer and to analyze the measured data. The uncertainty of the results is estimated to be no more than 3%. The results were correlated as a function of temperature.

## Introduction

The phase-out period for chlorodifluoromethane (HCFC-22) has been determined. A mixture of difluoromethane (HFC-32) and pentafluoroethane (HFC-125) is a potential alternative to replace chlorodifluoromethane (HCFC-22). The viscosity of HFC-32 was measured by Oliveira and Wakeham (1993), Ripple and Martar (1993), Assael et al. (1994), and Phillips and Murphy (1970). The viscosity of HFC-125 was measured by Diller and Peterson (1993), Ripple and Martar (1993), Oliveira and Wakeham (1993), and Assael and Polimatidou (1994). The differences between the results from different authors is considerable, sometimes in excess of 10%. In this paper, the viscosities of HFC-32 and HFC-125 were measured with a capillary viscometer. The measurement errors with this instrument are mainly attributed to three main effects: impurities in the samples, the precision of the calibration of the instrument, and the method of operation of the instrument during an experiment. In this paper, three viscometers were calibrated very carefully using three different liquids and two different calibrating liquid volumes in the instrument cell to eliminate the systematic errors and to verify the calibration procedure. The method to operate the instrument was also improved to reduce the measurement uncertainty to less than 3%.

## Instrument and Operation Principles

The instrument which was used in previous work (Han, 1995) and in this work is shown in Figure 1. The capillary viscosimeter is a classical method to measure the viscosity of liquids. According to the Hagen−Posieuille principle, the quantity of fluid that flows through the capillary is proportional to the pressure difference between the two ends of the capillary and the fourth power of the radius of the capillary and is inversely proportional to the length of the capillary and the viscosity of the fluid:

$$\frac{Q}{t} = \frac{\Delta P \pi R^4}{8\eta l} \tag{1}$$

Here $Q$ is the quantity of fluid (a constant for the three viscometers mentioned in this work), $t$ is the time during which the fluid of quantity $Q$ flows through the capillary, $\Delta P$ is the pressure difference between the two ends of the capillary, $R$ is the radius of the capillary, $\eta$ is the dynamic viscosity, and $l$ is the length of the capillary.

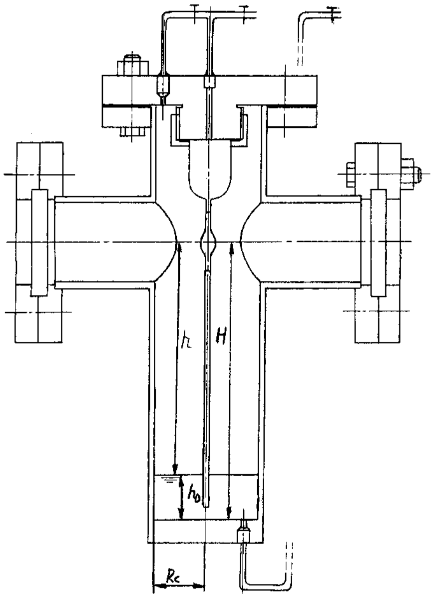

**Figure 1.** Instrument Schematic.

Including the effects of local friction and fluid surface tension, eq 1 can be rewritten in the following form:

$$\eta = \frac{gh\pi R^4\rho}{8Ql}t - \frac{\pi R^4\sigma}{4qlr}t - \frac{Q\xi}{16\pi lt} \tag{2}$$

Here $g$ is the acceleration of gravity, $h$ is the height difference of the fluid surface in the cell and the fluid surface in the viscometer, $\rho$ is the density of the measured liquid, $\sigma$ is the surface tension of the measured liquid, $r$ is the average liquid meniscus radius along the viscometer bulb, and $\xi$ is the local friction coefficient.

Equation 2 can be simplified to

$$\nu = At - B\frac{\sigma}{\rho}t - \frac{C}{t} \tag{3}$$

Here

$$A = gh\pi R^4/8Ql \tag{4}$$

$$B = \pi R^4/4Qlr \tag{5}$$

$$C = Q\xi/16\pi l \tag{6}$$

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* To whom correspondence should be addressed.

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**Table 1. Calibration Results of the Instrument**

| $R$/mm | $V$/cm$^3$ | $A \times 10^4$/mPa | $B \times 10^5$/(kg·m$^{-4}$) | $C$/(mPa·s$^2$) | $h$/mm |
|---|---|---|---|---|---|
| 0.210 | 200 | 1.8889 | 3.5963 | 1.3564 | 83.97 |
| 0.210 | 250 | 1.5718 | 3.5471 | 1.3485 | 69.88 |
| 0.196 | 200 | 1.5154 | 2.8883 | 1.4858 | 88.21 |
| 0.196 | 250 | 1.2732 | 2.8622 | 1.4378 | 74.11 |
| 0.370 | 200 | 20.116 | 35.094 | 1.4745 | 92.76 |
| 0.370 | 250 | 17.059 | 34.581 | 1.4258 | 78.66 |

**Table 2. Verification of the Instrument Calibration Results with Acetone**

| $R$/mm | $V$/cm$^3$ | $t$/°C | $\eta_{\mathrm{lit}}$/(mPa·s) | $\eta_{\mathrm{exp}}$/(mPa·s) | $100(\eta_{\mathrm{exp}} - \eta_{\mathrm{lit}})/\eta_{\mathrm{lit}}$ |
|---|---|---|---|---|---|
| 0.210 | 200 | 50 | 0.2490 | 0.2477 | −0.52 |
| 0.210 | 250 | 50 | 0.2490 | 0.2483 | −0.26 |
| 0.196 | 200 | 50 | 0.2490 | 0.2477 | −0.52 |
| 0.196 | 250 | 50 | 0.2490 | 0.2508 | 0.70 |
| 0.370 | 200 | 20 | 0.3250 | 0.3262 | 0.34 |
| 0.370 | 250 | 20 | 0.3250 | 0.3255 | 0.11 |

In general, $r$ is not a constant and cannot be measured accurately. After observing the flow of various fluids such as water, acetone, alcohol, hexane, HFC-32, and HFC-125 through the viscometer, the authors found that $r$ did not change greatly and can be treated as approximately constant for these liquids in the viscometers used in this study. Comparison of the three parts of eq 3, $At$, $B\sigma t/\rho$, and $C/t$, using the calibrated values of $A$, $B$, and $C$ shown in Table 1 and the density and surface tension values for the liquids mentioned above showed that the effect of surface tension is very small for these liquids. Therefore, treating $r$ as a constant does not lead to significant errors. Thus, in eq 5, $B$ and $C$ can be treated as constants which can be obtained by calibration.

According to eq 4, $A$ is proportional to $h$. During an experiment, the total mass of the saturated liquid and saturated vapor coexisting in the cell was constant. When the fluid temperature varies, the height of the liquid surface in the cell changes because of the changes in the density of the saturated liquid and saturated vapor. Therefore, $A$ depends on the density of the saturated liquid and saturated vapor. Only when the liquid surface height in the cell is kept constant can the coefficient $A$ be treated as a constant. At temperatures well below the critical temperature, the densities do not change greatly, so the value of $h$ will change little. Once the quantity of fluid in the cell is determined, the value of $A$ can be treated as a constant without introducing significant error. For the fluids measured in this work, it is difficult to repeatedly set the liquid surface level to a given height, though the total mass in the cell can be measured accurately. Therefore, $A$ cannot be treated as a constant and the value of $A$ obtained by calibration cannot be used directly. For this reason, the following method was adopted in order to increase measurement accuracy.

## Calibration and Determination of *A*, *B*, and *C*

On the basis of the discussion above, liquids with a high critical temperature such as alcohol, hexane, and pure water were used to calibrate the instrument with calibrating liquid volumes of 200 cm$^3$ and 250 cm$^3$. During the experiment, the time in which the liquid with quantity $Q$ flowed through the viscometer was accurately measured. The three coefficients in eq 3 were obtained by measuring the time, $t$, for the three different liquids with a fixed liquid surface height in the cell. Knowing the values of $\nu$, $\sigma$, and $\rho$ for each calibrating fluid, the values of $A$, $B$, and $C$ were obtained for a fixed liquid surface height. The calibration results are given in Table 1. To check the results, the viscosity of acetone, which is very close to the viscosity of HFC-32 and HFC-125, was measured and compared with the values given in the literature. The comparison results are given in Table 2. The density, surface tension, and viscosity data for the four fluids were provided by Beaton and Hewitt (1988).

Calibration and verification results for the other two different viscometers which differ only in the radius of the capillaries and in $H$, the height of the liquid surface in the viscometer bulb to the bottom of the cell, are also given in Tables 1 and 2 to further verify the calibration procedure. From eqs 4 and 5, $A \propto R^4h$ and $B \propto R^4$. Therefore, for two different capillary radii, when the values of the liquid surface height in the cell are equal, the values of $A_1(R_1,h_{11})/A_1(R_2,h_{12})$ and $A_2(R_1,h_{21})/A_2(R_2,h_{22})$ should be equal to $(R_1{}^4h_{11})/(R_2{}^4h_{12})$ and $(R_1{}^4h_{21})/R_2{}^4h_{22})$, respectively, and the values of $B_1(R_1)/B_1(R_2)$ and $B_2(R_1)/B_2(R_2)$ should be equal to $(R_1/R_2)^4$. $A_1$ and $B_1$ refer to the coefficient values when the calibrating liquid volume was 200 cm$^3$. $A_2$ and $B_2$ correspond to the calibrating liquid volume of 250 cm$^3$. $R_1$ and $R_2$ refer to the capillary radii. $h_{11}$ and $h_{12}$ refer to the values of $h$ for the viscometers with capillary radii of $R_1$ and $R_2$, respectively, when the calibrating liquid volume in the cell was 200 cm$^3$. $h_{21}$ and $h_{22}$ correspond to the calibrating liquid volume of 250 cm$^3$ for the viscometers with capillary radii of $R_1$ and $R_2$, respectively. The values of $A$ and $B$ in Table 1 agree well with the expected results of these ratios.

As discussed before, $A$ cannot be treated as a constant at temperatures near the critical temperature; therefore, a method was used here to modify the value of $A$ for different temperatures.

During the calibration procedure, the viscometer was calibrated using two calibrating liquid volumes, $V_1$ (200 cm$^3$) and $V_2$ (250 cm$^3$), to obtain two groups of coefficients, $A_1$, $B_1$, and $C_1$ and $A_2$, $B_2$, and $C_2$. From eq 4, $A_1$ is proportional to $h_1$ and $A_2$ is proportional to $h_2$, where $h_1$ and $h_2$ are the values of $h$ for the calibrating liquid volumes of $V_1$ and $V_2$. For the two calibrating volumes $V_1$ and $V_2$, the height difference between $h_1$ and $h_2$, $\Delta h$, can be obtained from $V_1$, $V_2$, and the cell radius, $R_c$. Therefore

$$\Delta h = h_1 - h_2 \tag{7}$$

$$A_1/A_2 = h_1/h_2 \tag{8}$$

$$\Delta h = \frac{V_2 - V_1}{\pi R_c{}^2} \tag{9}$$

Solving the three equations gives the values of $h_1$ and $h_2$. Thus, $h_1$ and $h_2$ can be obtained through the calibration results since they cannot be accurately measured directly.

The calibrating liquid surface heights in the cell are $h_{10}$ and $h_{20}$ for the liquid volumes $V_1$ and $V_2$. As shown in Figure 1, $H$ is a constant even though the liquid surface height, $h_0$, in the cell may change. Therefore, the height of the liquid surface in the viscometer bulb to the cell bottom is

$$H = h_1 + h_{10} = h_2 + h_{20} \tag{10}$$

The values of $h_{10}$ and $h_{20}$ can be obtained from

$$h_{10} = V_1/(\pi R_c{}^2) \quad \text{and} \quad h_{20} = V_2/(\pi R_c{}^2)$$

The mass of fluid in the cell and the cell volume were both determined accurately. The vapor and liquid volumes

**Table 3. Coefficients of Eq 14 for HFC-32 and HFC-125**

| | *D* | *E* | *F* | *G* |
|---|---|---|---|---|
| HFC-32 | 2.212577 | −476.858550 | $-1.986062 \times 10^{-2}$ | $1.531689 \times 10^{-5}$ |
| HFC−125 | 1.350405 | −251.616723 | $-2.111787 \times 10^{-2}$ | $2.186299 \times 10^{-5}$ |

can then be determined from

$$V_l + V_v = V \tag{11}$$

$$\rho_l V_l + \rho_v V_v = m \tag{12}$$

where $V_l$ and $V_v$ are the volumes of saturated liquid and saturated vapor and $\rho_l$ and $\rho_v$ are the densities of the saturated liquid and saturated vapor, respectively. After solving for the values of $V_l$ and $V_v$, the liquid surface height can be obtained from $h_0 = V_l/(\pi R_c^2)$. Using eq 9, the coefficient $A$ can be expressed by

$$A = \frac{A_1(H - h_0)}{h_1} = \frac{A_2(H - h_0)}{h_2} \tag{13}$$

Therefore, $A$ is a function of $h_0$ which will change with temperature even though a certain mass of fluid is input into the cell. Equation 13 can eliminate the systematic errors caused by the changes of the liquid surface height in the cell. For a certain viscometer, since $Q$, $l$, $r$, $R$, and $\xi$ do not change with the liquid surface height in the cell, eqs 5 and 6 suggest that the constants $B_1$ and $C_1$ for the lqiuid surface height $h_1$ should be equal to the constants $B_2$ and $C_2$ for the liquid surface height $h_2$, respectively. There are small differences between the two groups of calibration data. But the difference between $B_1$ and $B_2$ does not exceed 1%, and the estimated difference between $C_1$ and $C_2$ does not exceed 4% in Table 1. The resultant error in the measured viscosity is no more than 0.05%. In principle, either group of data can be adopted.

During the course of an experiment, some of the vapor must be vented and the mass in the cell changes. The quantity of vented vapor is very small and will not significantly affect the measured results. To reduce the effect of vapor venting on the measured results, the measurements were started at a high temperature and proceeded to the lower temperatures.

## Results and Analysis

The viscosities of HFC-32 and HFC-125 were measured along the saturation line. The uncertainty of the temperature measurements was within ±10 mK, and the thermal gradient of the bath used in the experiment was less than ±5 mK. The temperature range was 233.15 K to 333.15 K for HFC-32 and 233.15 K to 328.15 K for HFC-125. The density values for HFC-32 were provided by Fu et al. (1995). The surface tension values for HFC-32 were calculated with the equation provided by Zhu and Lu (1994) with an accuracy of 0.5%. The density and surface tension values for HFC-125 were calculated with NIST program REFPROP and the equation provided by Liu et al. (1994) with estimated accuracies of 0.2% and 0.5%, respectively.

The experimental results were fitted to the equation

$$\log(\eta/\mathrm{Pa{\cdot}s}) = D + E/(T/K) + F(T/K) + G(T/K)^2 \tag{14}$$

The values of the coefficients in eq 14 for HFC-32 and HFC-125 are given in Table 3. The standard deviation of experimentally measured results from eq 14 is 0.46% for HFC-32 and 0.28% for HFC-125. The experimentally measured viscosity values of HFC-32 and HFC-125 are given in Figure 2 and Tables 4 and 5, respectively. Figures 3 and 4 compare the results for HFC-32 and HFC-125 from different authors with eq 14, where $\eta_{\mathrm{EXP}}$ represents the experimental results and $\eta_{\mathrm{EQ}}$ are the values calculated from eq 14.

**Table 4. Saturated Liquid Viscosity and the Density of the Liquid and Vapor Phases for HFC-32**

| *T*/K | $\rho_v$/(kg·m$^{-3}$) | $\rho_l$/(kg·m$^{-3}$) | $\eta$/(mPa·s) |
|---|---|---|---|
| 233.15 | 5.0344 | 1179.2 | 0.2351 |
| 238.15 | 6.2091 | 1165.1 | 0.2235 |
| 243.15 | 7.5916 | 1150.5 | 0.2122 |
| 248.15 | 9.2086 | 1135.6 | 0.2014 |
| 253.15 | 11.089 | 1120.3 | 0.1911 |
| 258.15 | 13.266 | 1104.6 | 0.1818 |
| 263.15 | 15.776 | 1088.5 | 0.1716 |
| 268.15 | 18.660 | 1071.9 | 0.1619 |
| 273.15 | 21.965 | 1054.8 | 0.1530 |
| 278.15 | 25.745 | 1037.2 | 0.1445 |
| 283.15 | 30.155 | 1018.6 | 0.1362 |
| 288.15 | 34.994 | 1000.1 | 0.1285 |
| 293.15 | 40.629 | 980.4 | 0.1209 |
| 298.15 | 47.078 | 960.0 | 0.1130 |
| 303.15 | 54.479 | 938.6 | 0.1065 |
| 308.15 | 63.007 | 916.0 | 0.0993 |
| 313.15 | 72.844 | 892.1 | 0.0935 |
| 318.15 | 84.452 | 866.4 | 0.0879 |
| 323.15 | 98.174 | 838.7 | 0.0827 |
| 328.15 | 114.57 | 808.1 | 0.0774 |
| 333.15 | 134.08 | 773.5 | 0.0740 |

**Table 5. Saturated Liquid Viscosity and Density of the Liquid and Vapor Phases for HFC-125**

| *T*/K | $\rho_v$/(kg·m$^3$) | $\rho_l$/(kg·m$^{-3}$) | $\eta$/(mPa·s) |
|---|---|---|---|
| 233.15 | 9.859 | 1484 | 0.3383 |
| 238.15 | 12.10 | 1465 | 0.3130 |
| 243.15 | 14.73 | 1447 | 0.2902 |
| 248.15 | 17.81 | 1427 | 0.2692 |
| 253.15 | 21.38 | 1407 | 0.2511 |
| 258.15 | 25.52 | 1387 | 0.2343 |
| 263.15 | 30.27 | 1366 | 0.2189 |
| 268.15 | 35.75 | 1344 | 0.2042 |
| 273.15 | 42.03 | 1321 | 0.1915 |
| 278.15 | 49.23 | 1297 | 0.1797 |
| 283.15 | 57.46 | 1272 | 0.1683 |
| 288.15 | 66.87 | 1246 | 0.1575 |
| 293.15 | 77.65 | 1219 | 0.1477 |
| 298.15 | 90.01 | 1190 | 0.1384 |
| 303.15 | 104.2 | 1159 | 0.1295 |
| 308.15 | 120.6 | 1125 | 0.1221 |
| 313.15 | 139.6 | 1090 | 0.1155 |
| 318.15 | 161.8 | 1051 | 0.1089 |
| 323.15 | 188.2 | 1008 | 0.1037 |
| 328.15 | 219.7 | 959.3 | 0.0996 |

The results for liquid HFC-32 along the saturation line deviate from eq 14 with a maximum deviation of about 0.9%. The results of Oliveira and Wakeham (1993) are very close to our values with average deviations from eq 14 within 1% and the greatest deviation being about 2%. The deviations of the values of Ripple and Martar (1993) and Assael et al. (1994) from eq 14 remain within 5%. The results of Phillips and Kevin (1970) show discrepancies from 5% to 15%.

Viscosities for HFC-125 along the saturation line have been reported by four researchers. At higher temperatures, the results of Diller and Peterson (1993) are lower than the results of other authors, and the greatest deviation from the values expressed by eq 14 is about 25%. The results of Ripple and Martar (1993), Diller and Peterson (1993), and Assael and Polimatidou (1994) are very close

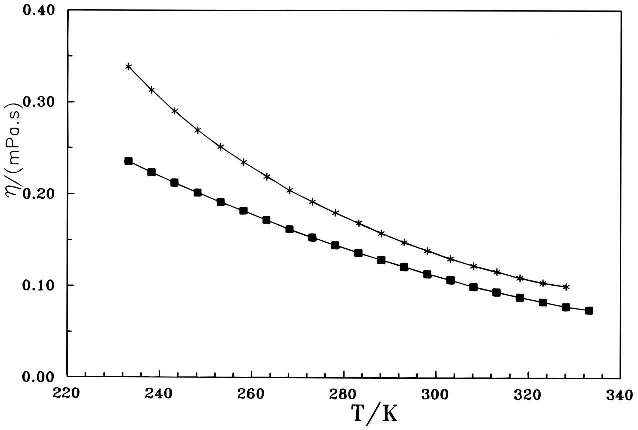

**Figure 2.** Viscosity of HFC-32 and HFC-125 as a function of temperature: (■) HFC-32; (*) HFC-125.

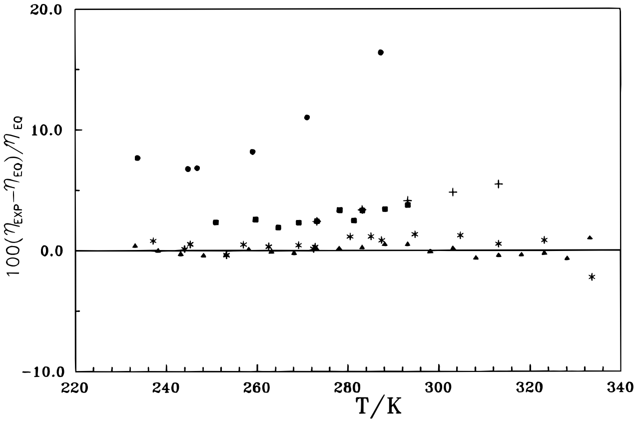

**Figure 3.** Comparison of the viscosity of HFC-32 of different authors with eq 14: (*) Oliveira and Wakeham (1993); (▲) this work; (■) Ripple and Martar (1993); (●) Phillips and Murphy (1970); (+) Assael et al. (1994).

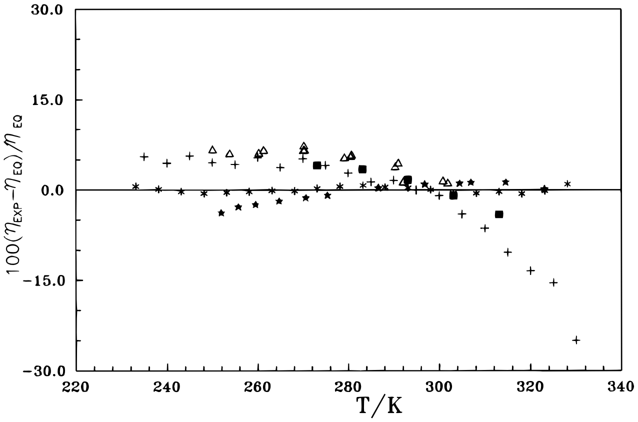

**Figure 4.** Comparison of the viscosity of HFC-125 of different authors with eq 14: (*) this work; (★) Oliveira and Wakeham (1993); (■) Assael and Polimatidou (1994); (△) Ripple and Martar (1993); (+) Diller and Peterson (1993).

in the temperature range from 250 K to 290 K and are 5% higher than the values of this work. The values of Oliveira and Wakeham (1993) are nearly in accordance with eq 14 in the temperature range from 270 K to 330 K and are a little lower in a lower temperature range, with the greatest difference being 3%.

The estimated errors caused by vapor venting a different temperatures are shown in Figure 5 for HFC-32 and HFC-125. In addition, the estimated errors arising from assuming that $A$ is the constant value for the calibrating

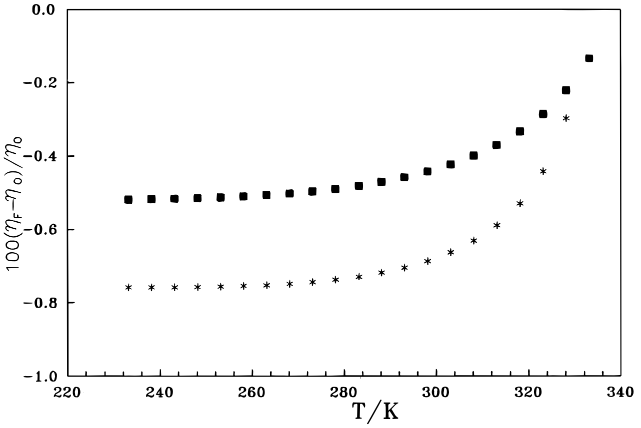

**Figure 5.** Estimated uncertainty caused by vapor venting for HFC-32 and HFC-125: (■) HFC-32; (*) HFC-125.

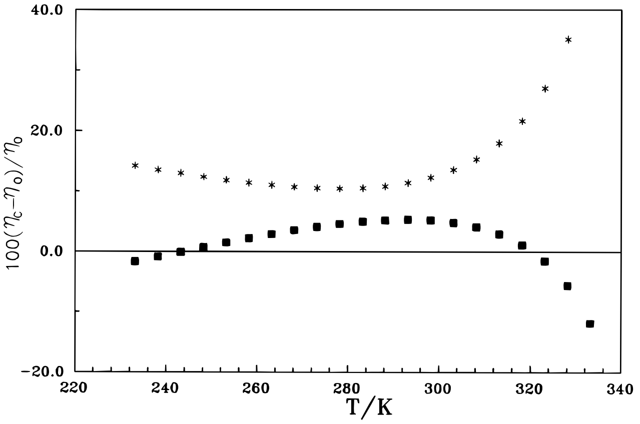

**Figure 6.** Estimated uncertainty when the coefficient $A$ is regarded as a constant for HFC-32 and HFC-125: (■) HFC-32; (*) HFC-125.

liquid volume of 200 cm$^3$ are shown in Figure 6. $\eta_C$ represents the values assuming $A$ is a constant; $\eta_o$ represents the values using $A$ as defined in eq 13. $\eta_F$ represents the values when considering the effect of vapor venting during the course of the experiment. Figure 6 clearly shows that $A$ needs to be modified.

## Conclusion

An improved method was developed for measuring the viscosity of saturated liquids. The viscosity of liquid HFC-32 and HFC-132 over a wide temperature range was measured with an uncertainty of less than 3%. The results compared well with literature values.

## Acknowledgment

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## Literature Cited

Assael, M. J.; Polimatidou, S. K. Measurements of the Viscosity of Liquid R22, R124 and R125 in the Temperature Range 273−333 K at Pressures up to 17 MPa. *Int. J. Thermophys.* **1994**, *15*, 779−790.

Assael, M. J.; Dymond, J. H.; Polimatidou, S. K. Measurements of the Viscosity of R134a and R32 in the Temperature Range 270−340K at Pressures up to 20 MPa. *Int. J. Thermophys.* **1994**, *15*, 591−601.

Beaton, C. F.; Hewitt, G. F. *Physical Property Data for the Design Engineer*; Hemisphere Publishing Corp.: New York, 1988.

Diller, D. E.; Peterson, S. M. Measurements of the Viscosities of Saturated and Compressed Fluid 1-Chloro-1,2,2,2-Tetrofluoroethane(R124) and Pentafluoroethane(R125)at Temperatures Between 120 and 420 K. *Int. J. Thermophys.* **1993**, *14*, 55−67.

Fu, Y. D.; Han, L. Z.; Zhu, M. S. PVT Properties, Vapor Pressures and Critical Parameters of HFC-32. *Fluid Phase Equilib.* **1995**, *111*, 273−286.

Han, L. Z.; Zhu, M. S.; Li, X. Y.; Luo, D. Viscosity of Saturated Liquid for 1,1,1,2-Tetrafluoroethane. *J. Chem. Eng. Data* **1995**, *40*, 650−652.

Liu, M. F.; Han, L. Z.; Zhu, M. S. Surface tension of Pentafluoroethane. *Int. J. Thermophys.* **1994**, *15*, 941−948.

Oliveira, C. M. B. P.; Wakeham, W. A. The Viscosity of R32 and R125 at saturation. *Int. J. Thermophys.* **1993**, *14*, 1131−1143.

Phillips, T. W.; Murphy, K. P. Fluid Viscosity of Halocarbons. *J. Chem. Eng. Data* **1970**, *15*, 304−307.

Ripple, D.; Martar, O. Viscosity of the Saturated Liquid Phase of Six Halogenated Compounds and Three Mixtures. *J. Chem. Eng. Data* **1993**, *38*, 560−564.

Zhu, M. S.; Lu, C. X. Surface tension of Difluoromethane. *J. Chem. Eng. Data* **1994**, *15*, 205−206.

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