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# Measurements of the Refractive Index of Alternative Refrigerants[1]

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Measurements of coexistence curves of the refractive index of HCFC-22, HFC-23, HFC-32, HFC-125, and HFC-152a have been carried out in the range from ambient to critical temperature. Near the critical temperature the refractive index has distribution in both the vapor and the liquid phases in the test cell. Thus the values at the boundary between vapor and liquid are selected at those of saturated vapor and liquid, respectively. The values of the critical temperature and critical refractive index for each substance are estimated. The refractive index is related to density by the Lorentz–Lorenz equation. In the case of HFC-32 the value of the LL function is assumed to be constant in the limited region near the critical point, and the values of density of saturated vapor and liquid are calculated and are compared with the experimental values of density obtained by *PVT* measurement.

**KEY WORDS:** alternative refrigerants; coexistence curve; critical refractive index; critical temperature; refractive index.

## 1. INTRODUCTION

The refractive index is an important optical property, and it is closely related to density by the Lorentz–Lorenz equation. In contrast to *PVT* measurements, the refractive index of a fluid can be measured locally, namely, the density distribution of a fluid in the test cell in the vertical direction can be determined. Thus the measurement of the refractive index is a powerful method to observe the behavior of a fluid in the critical

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region where properties vary significantly in the vertical direction due to gravity.

## 2. EXPERIMENTS

As shown in Fig. 1, the light beam passes through the test fluid between the prism-shaped glass and the flat glass, and is refracted. The relation between the refraction angle $\gamma$ and the refractive index $n$ of a fluid is as follows:

$$n = \{(n_1)^2 + (n_2 \sin \gamma / \sin \alpha)^2 - (2n_1 \cot \alpha)(n_2 \sin \gamma)\}^{1/2} \quad (1)$$

where $\alpha$ is the inclined angle of prism-shaped glass, and $n_1$ and $n_2$ are the refractive indices of glass and air, respectively. The inner diameter of the test cell is 30 mm. The material of the glasses is BK 7, a most stable glass with a small refractive index and dispersion ($n_1 = 1.5190$ at 293 K), and $\alpha = 30$ degree. The temperature dependence of the refractive index of BK 7 is determined by measuring the refraction angle in vacuum at each temperature.

The test cell is placed in the thermostated bath with glass windows; its temperature is controlled within 1 mK and is measured by a platinum resistance thermometer. A light beam of wavelength $\lambda = 545$ nm from a mercury lamp is used. After it passes through a vertical slit, it is made parallel by a convex lens with a diameter of 100 mm and enters the test cell. The angle of refraction is measured by a telescope mounted on the stage, which can rotate with a stepping motor. The purity of the test fluids is better than 99.5%.

The test fluid is charged into the cell so that the boundary between vapor and liquid is just in the middle of the window. Through the telescope one can see three lines, a nonrefracted line and refracted lines of the vapor and liquid. At states near the critical temperature, the lines of vapor and

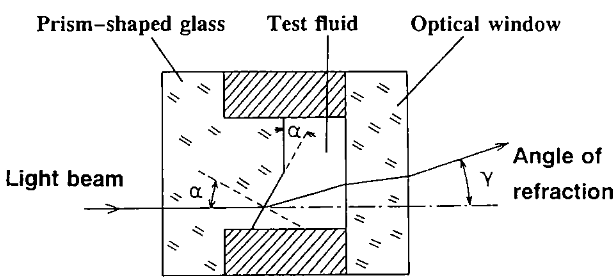


**Fig. 1.** Principle of refractive index measurements.

liquid become thick due to the variation of the refractive index along vertical direction. By placing a horizontal slit in front of the test cell and moving it up and down in the vertical direction, the lines are made thin, and it is possible to measure the refractive index of the fluid at an arbitrary height in the cell. Thus the variation of the refractive index in the vertical direction is obtained in both the vapor and the liquid phases. The values at the boundary between vapor and liquid are selected as the values of saturated vapor and liquid, respectively. The highest possible temperature is around 0.1 K lower than the critical temperature.

Limitations of optical measurements in the critical region have been discussed in the literature [1,2], and many other methods have been proposed [3–5] for the investigation of refractive index and density in the critical region. However, no further sophisticated method is used in this study.

## 3. RESULTS

Measurements of the refractive index of HCFC-22, HFC-23, HFC-32, HFC-125, and HFC-152a at saturated states have been carried out in the

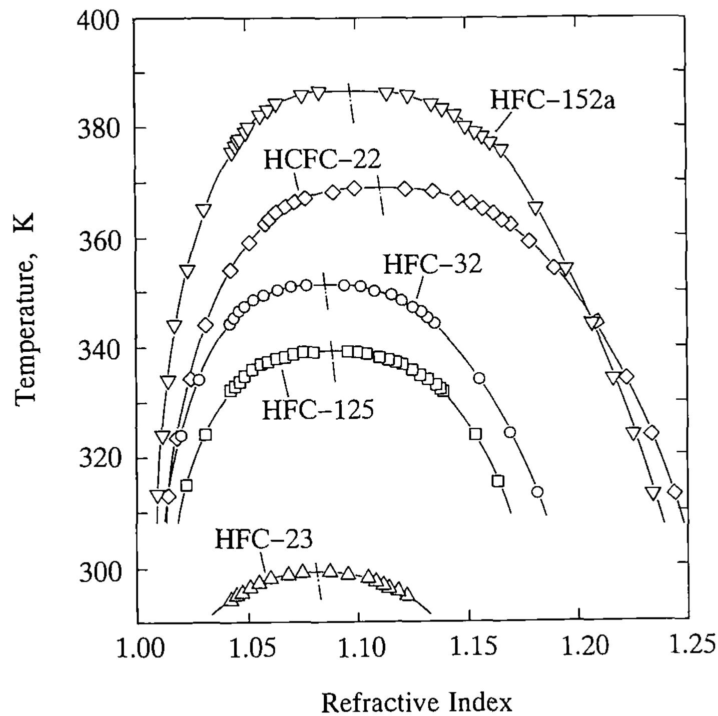


Fig. 2. Coexistence refractive index curves of five alternative refrigerants.

range from the ambient to their critical temperatures. The coexistence curves of the refractive index of these five refrigerants are shown in Fig. 2. The experimental values of the refractive index of saturated vapor and liquid are also tabulated in Table I through Table V.

**Table I.** Experimental Results of Refractive Index of HCFC-22 at Saturated States

| | Refractive index | |
|---|---|---|
| Temperature (K) | Vapor | Liquid |
| 313.974 | 1.0142 | 1.2441 |
| 323.661 | 1.0182 | 1.2339 |
| 333.902 | 1.0238 | 1.2219 |
| 344.008 | 1.0312 | 1.2079 |
| 354.285 | 1.0424 | 1.1900 |
| 359.390 | 1.0508 | 1.1783 |
| 362.436 | 1.0575 | 1.1695 |
| 363.369 | 1.0600 | 1.1664 |
| 364.396 | 1.0631 | 1.1625 |
| 365.431 | 1.0668 | 1.1582 |
| 366.461 | 1.0710 | 1.1528 |
| 367.491 | 1.0768 | 1.1463 |
| 368.629 | 1.0888 | 1.1349 |
| 368.660 | 1.0891 | 1.1345 |
| 368.688 | 1.0897 | 1.1343 |
| 368.718 | 1.0901 | 1.1338 |
| 368.753 | 1.0907 | 1.1333 |
| 368.777 | 1.0911 | 1.1329 |
| 368.819 | 1.0917 | 1.1322 |
| 368.844 | 1.0921 | 1.1318 |
| 368.859 | 1.0923 | 1.1312 |
| 368.880 | 1.0927 | 1.1308 |
| 368.904 | 1.0932 | 1.1303 |
| 368.925 | 1.0937 | 1.1299 |
| 368.947 | 1.0941 | 1.1294 |
| 368.972 | 1.0947 | 1.1288 |
| 368.992 | 1.0952 | 1.1284 |
| 369.012 | 1.0957 | 1.1278 |
| 369.049 | 1.0966 | 1.1270 |
| 369.070 | 1.0973 | 1.1261 |
| 369.091 | 1.0981 | 1.1255 |
| 369.112 | 1.0989 | 1.1247 |
| 369.136 | 1.0999 | 1.1236 |
| 369.157 | 1.1009 | 1.1227 |

**Table II.** Experimental Results of Refractive Index of HFC-23 at Saturated States

| Temperature (K) | Refractive index | |
|---|---|---|
| | Vapor | Liquid |
| 293.550 | 1.0417 | 1.1252 |
| 294.569 | 1.1442 | 1.1220 |
| 295.568 | 1.0471 | 1.1184 |
| 296.598 | 1.0509 | 1.1139 |
| 297.711 | 1.0562 | 1.1078 |
| 298.776 | 1.0659 | 1.0962 |
| 298.800 | 1.0663 | 1.0958 |
| 298.819 | 1.0668 | 1.0955 |
| 298.839 | 1.0673 | 1.0950 |
| 298.855 | 1.0676 | 1.0946 |
| 298.878 | 1.0681 | 1.0942 |
| 298.897 | 1.0686 | 1.0936 |
| 298.920 | 1.0692 | 1.0930 |
| 298.940 | 1.0699 | 1.0923 |
| 298.961 | 1.0705 | 1.0916 |
| 298.982 | 1.0715 | 1.0905 |
| 299.004 | 1.0722 | 1.0896 |
| 299.028 | 1.0734 | 1.0882 |
| 299.049 | 1.0747 | 1.0864 |

**Table III.** Experimental Results of Refractive Index of HFC-32 at Saturated States

| Temperature (K) | Refractive index | |
|---|---|---|
| | Vapor | Liquid |
| 313.379 | 1.0149 | 1.1811 |
| 323.850 | 1.0202 | 1.1694 |
| 334.049 | 1.0280 | 1.1553 |
| 344.240 | 1.0417 | 1.1348 |
| 345.258 | 1.0438 | 1.1319 |
| 346.281 | 1.0463 | 1.1287 |
| 347.306 | 1.0492 | 1.1251 |
| 348.333 | 1.0527 | 1.1209 |
| 349.355 | 1.0572 | 1.1155 |
| 350.371 | 1.0641 | 1.1078 |
| 350.714 | 1.0678 | 1.1035 |
| 350.725 | 1.0680 | 1.1033 |
| 350.737 | 1.0682 | 1.1032 |
| 350.756 | 1.0684 | 1.1029 |
| 350.772 | 1.0686 | 1.1026 |

**Table III.** *(Continued)*

| Temperature (K) | Refractive index | |
|---|---|---|
| | Vapor | Liquid |
| 350.790 | 1.0689 | 1.1024 |
| 350.816 | 1.0693 | 1.1020 |
| 350.834 | 1.0696 | 1.1016 |
| 350.852 | 1.0699 | 1.1013 |
| 350.871 | 1.0702 | 1.1010 |
| 350.889 | 1.0706 | 1.1006 |
| 350.906 | 1.0710 | 1.1002 |
| 350.925 | 1.0714 | 1.0999 |
| 350.947 | 1.0716 | 1.0993 |
| 350.993 | 1.0730 | 1.0981 |
| 351.047 | 1.0745 | 1.0964 |
| 351.070 | 1.0755 | 1.0955 |
| 351.093 | 1.0767 | 1.0944 |

**Table IV.** Experimental Results of Refractive Index of HFC-125 at Saturated States

| Temperature (K) | Refractive index | |
|---|---|---|
| | Vapor | Liquid |
| 315.030 | 1.0226 | 1.1663 |
| 323.967 | 1.0306 | 1.1535 |
| 332.104 | 1.0422 | 1.1370 |
| 332.696 | 1.0435 | 1.1354 |
| 333.781 | 1.0462 | 1.1324 |
| 334.846 | 1.0490 | 1.1289 |
| 335.871 | 1.0522 | 1.1250 |
| 336.902 | 1.0562 | 1.1204 |
| 337.412 | 1.0586 | 1.1177 |
| 337.932 | 1.0616 | 1.1143 |
| 338.443 | 1.0655 | 1.1100 |
| 338.957 | 1.0721 | 1.1029 |
| 339.017 | 1.0733 | 1.1018 |
| 339.033 | 1.0736 | 1.1013 |
| 339.045 | 1.0742 | 1.1008 |
| 339.070 | 1.0743 | 1.1002 |
| 339.097 | 1.0753 | 1.0996 |
| 339.115 | 1.0758 | 1.0991 |
| 339.140 | 1.0765 | 1.0984 |
| 339.159 | 1.0773 | 1.0976 |
| 339.181 | 1.0782 | 1.0967 |
| 339.203 | 1.0793 | 1.0957 |

**Table V.** Experimental Results of Refractive Index of HFC-152a at Saturated States

| Temperature (K) | Refractive index | |
|---|---|---|
| | Vapor | Liquid |
| 313.802 | 1.0083 | 1.2336 |
| 323.975 | 1.0106 | 1.2254 |
| 334.106 | 1.0136 | 1.2164 |
| 343.763 | 1.0173 | 1.2070 |
| 354.525 | 1.0228 | 1.1950 |
| 364.729 | 1.0302 | 1.1813 |
| 375.092 | 1.0426 | 1.1629 |
| 375.666 | 1.0429 | 1.1615 |
| 376.775 | 1.0448 | 1.1589 |
| 377.815 | 1.0466 | 1.1564 |
| 378.855 | 1.0487 | 1.1536 |
| 379.879 | 1.0510 | 1.1507 |
| 380.914 | 1.0536 | 1.1474 |
| 381.951 | 1.0565 | 1.1438 |
| 382.985 | 1.0600 | 1.1395 |
| 384.022 | 1.0643 | 1.1345 |
| 385.451 | 1.0742 | 1.1241 |
| 385.514 | 1.0746 | 1.1236 |
| 385.578 | 1.0752 | 1.1230 |
| 385.644 | 1.0757 | 1.1222 |
| 385.703 | 1.0763 | 1.1217 |
| 385.764 | 1.0770 | 1.1210 |
| 385.821 | 1.0776 | 1.1203 |
| 385.884 | 1.0784 | 1.1194 |
| 385.953 | 1.0794 | 1.1184 |
| 386.007 | 1.0802 | 1.1175 |
| 386.068 | 1.0811 | 1.1164 |
| 386.134 | 1.0824 | 1.1151 |
| 386.155 | 1.0829 | 1.1147 |
| 386.179 | 1.0833 | 1.1142 |

The refractive index of HCFC-22 has been measured by Rathjen et al. [6] with the wavelength $\lambda = 546.1$ nm, which is very close to the wavelength of 545 nm of the present study. Measurements for HFC-152a have been carried out by Chae et al. [7] with the wavelength $\lambda = 633$ nm. The present results for HCFC-22 quantify those by Rathjen et al. The refractive index is a function of wavelength and generally decreases with increase of wavelength. The present results for HFC-152a give slightly larger values than those by Chae et al., and it can be said that the two sets of data for the substance are consistent.

## 4. DISCUSSION

The main purpose of the present study is to make clear the behavior of the coexistence curve of the refractive index, namely, density near the critical temperature. By applying the experimental values of the refractive index of saturated vapor and liquid in the critical region to the following equation, the critical temperature $T_c$ is estimated,

$$T_c - T \propto (n_L - n_v)^{1/\beta} \tag{2}$$

where $n_L$ and $n_v$ are values of the refractive index at saturated liquid and vapor, respectively, and the critical exponent $\beta$ is assumed to be 0.325 [1]. The value of $T_c$ is determined from the analysis by means of Eq. (2) with the precision of $\pm 0.01$ K or better. However, the present apparatus has comparatively large windows, and it is difficult to keep the temperature of the cell uniform in the direction parallel to the light beam, and the uncertainty of $T_c$ is estimated to be $\pm 0.10$ K. The refraction angle can be measured by the uncertainty less than $\pm 0.01$ degree which corresponds to $\pm 0.0002$ of the uncertainty of the refractive index value.

In the coexistence curves the equation for $(n_L + n_v)/2$ proved to be a linear function of temperature. Thus, the critical refractive index $n_c$ for each substance is obtained by giving the value of the critical temperature. The values of the critical temperature and critical refractive index for the five refrigerants thus obtained are listed in Table VI. The values of the critical temperature of alternative refrigerants determined by direct observation have been reported. For most substances the reported value of $T_c$ from different references vary by 0.1–0.3 K. The values of the critical temperature in Table VI agree with the reported values within about 0.1 K and seem to be reasonable.

The refractive index $n$ is related to density $\rho$ by the Lorentz–Lorenz equation,

$$(n^2 - 1)/(n^2 + 2) = LL\rho \tag{3}$$

**Table VI.** Critical Temperature and Critical Refractive Index of Alternative Refrigerants

| Substance | Critical temperature (K) | Critical refractive index |
|---|---|---|
| HCFC-22 | $369.21 \pm 0.10$ | $1.1115 \pm 0.0005$ |
| HFC-23 | $299.06 \pm 0.10$ | $1.0806 \pm 0.0005$ |
| HFC-32 | $351.14 \pm 0.10$ | $1.0854 \pm 0.0005$ |
| HFC-125 | $339.22 \pm 0.10$ | $1.0873 \pm 0.0005$ |
| HFC-152a | $386.39 \pm 0.10$ | $1.0986 \pm 0.0005$ |

where $LL$ is called the LL function and is generally a function of temperature and density. In a very limited region of temperature and density, $LL$ is assumed to be constant. For alternative refrigerants, measured values of density in the critical region are not always available. As the experimental results of density for HFC-32 in the critical region are published by Higashi et al. [8], the case for HFC-32 is discussed. By using the value of density at a temperature approximately 5 K below $T_c$, the value of $LL$ in Eq. (3) is determined. With the value of $LL$ the values of density are calculated from the experimental results of the refractive index near the critical point in this work, and these are compared with the density values by Higashi et al. in Fig. 3. As $T_c = 351.26$ K in the work by Higashi et al. and $T_c = 351.14$ K in this study, $T - T_c$ for their values are calculated by using the value of $T_c$ proposed in their work. In the test cell where vapor and liquid coexist, the density of vapor increases downward in the vertical direction and becomes largest at the boundary, while the density of liquid increases in the same manner and is smallest at the boundary. Thus the calculated values of density at saturated states from refractive indices are the local ones and are given as the values at the boundary between vapor and liquid. On the contrary, the reported values of density by $PVT$ measurement are the average ones. If both calculated and directly measured values were correct, directly measured values of density of

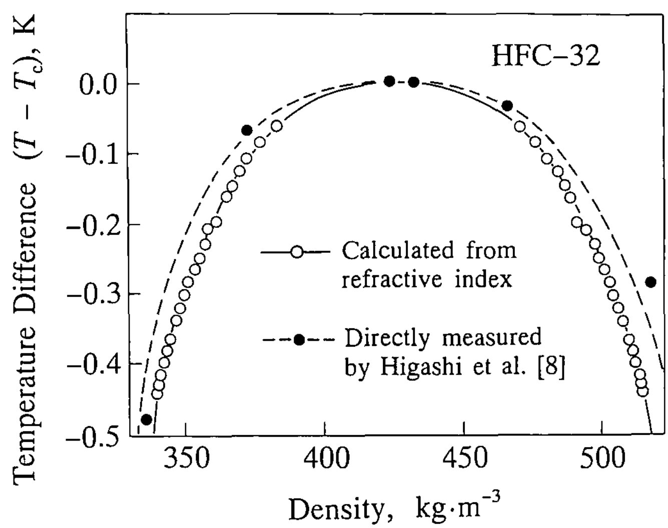


Fig. 3. Comparison between calculated values of density from refractive indices in this work and experimental values of density by Higashi et al. [8] for HFC-32.

saturated vapor should be smaller and those of saturated liquid should be larger than the calculated values. As shown in Fig. 3, the directly measured values somewhat scatter and the comparison in the figure is only qualitative. However, qualitively at least, the calculated and measured values do not contradict the consideration above, and it can be said that the calculated and measured values are consistent.

## 5. CONCLUSIONS

Measurements of the coexistence curves of the refractive index of five alternative refrigerants have been carried out in the range from the ambient to critical temperature. Near the critical temperature, the distribution of refractive index in the vertical direction has been considered. The values of the critical temperature and critical refractive index for each substance are estimated. In the case of HFC-32, the value of the LL function in the Lorentz–Lorenz equation are assumed to be constant in the limited region near the critical point, and the values of density of saturated vapor and liquid are calculated and are compared with the experimental values of density obtained by *PVT* measurement.

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