J. Chem. Eng. Data 1988, 33, 399–401

# Measurements of the Surface Tension of Three Refrigerants, R 22, R 115, and R 502

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**The surface tension was measured on three fluorocarbon refrigerants, R 22 (chlorodifluoromethane, $CHClF_2$), R 115 (chloropentafluoroethane, $CClF_2CF_3$), and R 502 (azeotropic mixture of 48.9 wt % R 22 and 51.1 wt % R 115), by using the capillary rise method. The results cover the range of temperatures from 273 K to a temperature close to the critical point of each substance. The uncertainty of surface tension measurements was estimated to be less than ±0.16 mN/m. For R 115 and R 502, van der Waals type correlations were developed based on the present results.**

## Introduction

In the present paper, measurements of the surface tension for R 502 (azeotropic mixture of 48.9 wt % R 22 and 51.1 wt % R 115) and of its component substances, R 22 and R 115, are presented. Although surface tension data were enough for R 22, only a single set of measurements for R 502 and R 115 has been reported up to the present by Heide (*1*) and Zheleznyi (*2*), respectively. Since our previous critical survey with the aid of correlational analyses for 17 fluorocarbon refrigerants (*3*) showed that surface tension data by Heide and by Zheleznyi had large discrepancies from other reliable measurements, the present results are the first contribution to reveal temperature dependence of surface tension for these two important refrigerants.

## Experimental Section

The experimental techniques employed for obtaining surface tension data are similar to those of our earlier work (*4*) for four fluorocarbon refrigerants, namely, R 11 ($CCl_3F$), R 12 ($CCl_2F_2$), R 113 ($C_2Cl_3F_3$), and R 114 ($C_2Cl_2F_4$), except for certain refinements described later. The apparatus is based on the capillary rise method well-known as one of the most accurate methods. The surface tension $\sigma$ is determined by the well-known relation given by Rayleigh (*5*)

$$\sigma = r(h_0 + r/3 - 0.1288r^2/h_0 + 0.1312r^3/h_0^2)g(\rho' - \rho'')/2 \cos \theta \quad (1)$$

where $\sigma$ denotes surface tension (N/m), $\theta$ (rad) is contact angle of the liquid–vapor meniscus at the inner surface of capillary, $g$ is local gravitational acceleration at Niigata, Japan, i.e., 9.799 73 m/s$^2$, $\rho'$ and $\rho''$ are saturated liquid and vapor densities (kg/m$^3$), $r$ is the inner radius of the capillary (m), and $h_0$ denotes the capillary rise height observed (m) by liquid level at the bottom of the meniscus in the capillary, respectively.

Two Pyrex glass capillaries used in our earlier work (*4*) have been used in the present measurements also, because even a minute difference in inner radius variation along the capillary length has been already determined by means of mercury thread. The variations in radii corresponding to the utilized parts in the present measurements are within the range of 0.1521–0.1541 mm for capillary I and 0.1703–0.1722 mm for capillary II, respectively. The calculations of surface tension are carried out by using the exact inner radius corresponding to the location of sample liquid meniscus, so as to obtain the accurate results.

The contact angle $\theta$ is considered to be 0 rad, since the inner walls of Pyrex glass capillaries have been carefully cleaned and measurements of the capillary rise height have been performed under the condition of a receding contact angle.

The saturated vapor density values $\rho''$ of three fluorocarbon refrigerants are calculated from the available thermodynamic correlations (*6–8*), whereas the saturated liquid density values $\rho'$ are based on the measurements and correlations we have already reported (*9*, *10*).

By using two capillaries installed in the cell, two independent sets of data have been obtained at the same experimental condition of sample liquid in equilibrium with its saturated vapor. The consistency between two sets of independent data confirms the reliability of the present measurements.

In our previous work, the platinum resistance thermometer has been installed in the thermostated bath and the bath fluid temperature near the sample cell has been measured for representing the sample liquid temperature. In the present study, however, a 25-Ω platinum resistance thermometer (Chino, Model R800-0) is installed into the sample cell so as to measure the sample liquid temperature directly. The bath fluid temperature is maintained constant for more than 1 h before respective surface tension measurements, and its fluctuation is kept within ±10 mK. Overall uncertainty of the temperature determined against the IPTS-68 is estimated less than ±10 mK.

The observed capillary rise height has been corrected by considering the difference of refractive indexes between the liquid and vapor phase.

## Results

Research grade samples supplied by Du Pont-Mitsui Fluorochemicals Co. Ltd., Tokyo, Japan, are used in the present study. The purities of samples and the composition of R 502 were analyzed by gas chromatography at Du Pont-Mitsui Fluorochemicals Co. Ltd. The purities are better than 99.98 wt % for three refrigerants and the sample composition of R 502 is 48.9 wt % R 22 and 51.1 wt % R 115.

The experimental results obtained for three fluorocarbon refrigerants are given in Table I. The capillary constants $a^2$ calculated from following relation are given also in Table I

$$a^2 = r(h_0 + r/3 - 0.1288r^2/h_0 + 0.1312r^3/h_0^2)g/g_n = 2\sigma/[g_n(\rho' - \rho'')] \quad (2)$$

where $g_n$ denotes normal gravitational acceleration of 9.806 65 m/s$^2$. The temperature range covered is 273–353 K for R 22, 273–343 K for R 115, and 273–343 K for R 502. We obtained

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0021-9568/88/1733-0399$01.50/0

**Table I. Experimental Surface Tensions $\sigma$ of the Three Refrigerants at Temperature $T$**

| | | capillary I | | capillary II | |
|---|---|---|---|---|---|
| run | $T$, K | $\sigma$, mN/m | $a^2$, mm$^2$ | $\sigma$, mN/m | $a^2$, mm$^2$ |
| | | R 22 ($CHClF_2$) | | | |
| 1 | 273.18 | 11.67 | 1.889 | 11.70 | 1.893 |
| | 283.15 | 10.24 | 1.714 | 10.31 | 1.727 |
| | 293.15 | 8.79 | 1.531 | 8.87 | 1.544 |
| | 303.15 | 7.39 | 1.347 | 7.45 | 1.357 |
| | 313.15 | 6.03 | 1.158 | 6.11 | 1.173 |
| | 323.15 | 4.72 | 0.967 | 4.77 | 0.976 |
| | 333.16 | 3.47 | 0.771 | 3.50 | 0.777 |
| | 343.15 | 2.33 | 0.577 | 2.32 | 0.574 |
| | 353.16 | 1.28 | 0.374 | 1.27 | 0.371 |
| 2 | 273.18 | 11.62 | 1.881 | 11.78 | 1.906 |
| | 283.15 | 10.18 | 1.705 | 10.25 | 1.717 |
| | 293.14 | 8.74 | 1.522 | 8.84 | 1.540 |
| | 303.15 | 7.36 | 1.340 | 7.43 | 1.353 |
| | 313.15 | 5.99 | 1.151 | 6.08 | 1.167 |
| | 323.15 | 4.70 | 0.962 | 4.72 | 0.967 |
| | 333.15 | 3.47 | 0.771 | 3.47 | 0.771 |
| | 343.15 | 2.32 | 0.576 | 2.31 | 0.571 |
| | 353.15 | 1.25 | 0.366 | 1.25 | 0.366 |
| | | R 115 ($CClF_2CF_3$) | | | |
| 1 | 273.19 | 7.45 | 1.116 | 7.60 | 1.139 |
| | 283.15 | 6.29 | 0.982 | 6.30 | 0.984 |
| | 293.15 | 5.19 | 0.850 | 5.22 | 0.854 |
| | 303.15 | 4.14 | 0.717 | 4.17 | 0.723 |
| | 313.15 | 3.11 | 0.580 | 3.16 | 0.588 |
| | 323.15 | 2.18 | 0.446 | 2.19 | 0.448 |
| | 333.15 | 1.31 | 0.305 | 1.31 | 0.305 |
| | 343.15 | 0.54 | 0.159 | 0.53 | 0.156 |
| 2 | 273.17 | 7.52 | 1.126 | 7.48 | 1.120 |
| | 283.15 | 6.40 | 0.998 | 6.37 | 0.994 |
| | 293.14 | 5.28 | 0.865 | 5.27 | 0.863 |
| | 303.15 | 4.20 | 0.728 | 4.20 | 0.728 |
| | 313.15 | 3.20 | 0.595 | 3.18 | 0.593 |
| | 323.15 | 2.21 | 0.451 | 2.21 | 0.452 |
| | 333.15 | 1.34 | 0.313 | 1.32 | 0.307 |
| | 343.15 | 0.57 | 0.166 | 0.55 | 0.160 |
| | | R 502 (48.9 wt % R 22 + 51.1 wt % R 115) | | | |
| 1 | 273.19 | 8.41 | 1.331 | 8.49 | 1.344 |
| | 283.15 | 7.15 | 1.178 | 7.19 | 1.184 |
| | 293.14 | 5.96 | 1.029 | 5.99 | 1.034 |
| | 303.15 | 4.78 | 0.873 | 4.77 | 0.872 |
| | 313.15 | 3.64 | 0.712 | 3.65 | 0.714 |
| | 323.15 | 2.61 | 0.559 | 2.61 | 0.559 |
| | 333.15 | 1.60 | 0.389 | 1.63 | 0.395 |
| | 343.15 | 0.74 | 0.222 | 0.74 | 0.221 |
| 2 | 273.16 | 8.55 | 1.353 | 8.58 | 1.358 |
| | 283.15 | 7.26 | 1.196 | 7.34 | 1.208 |
| | 293.14 | 6.03 | 1.042 | 6.09 | 1.051 |
| | 303.15 | 4.84 | 0.884 | 4.90 | 0.895 |
| | 313.15 | 3.69 | 0.722 | 3.76 | 0.736 |
| | 323.15 | 2.60 | 0.557 | 2.65 | 0.567 |
| | 333.15 | 1.62 | 0.392 | 1.65 | 0.401 |
| | 343.16 | 0.74 | 0.221 | 0.77 | 0.231 |

36 measurements through two independent runs for R 22, 32 measurements through two runs for R 115, and 32 measurements through two runs for R 502.

As a result of error analysis, the estimated maximum uncertainty of the present results decreases with increasing temperature from ±0.16 mN/m at 270 K to ±0.06 mN/m at 350 K.

The results show that the surface tension decreases with increasing temperature and becomes zero at the critical point. The expression by van der Waals (*11*) is known to represent well the temperature dependence of surface tension

$$\sigma = \sigma_0(1 - T/T_c)^n \tag{3}$$

where $T$ and $T_c$ denote the temperature (K) and the critical temperature (K), respectively, and $\sigma_0$ and $n$ are numerical constants which depend only on the substance. In our previous paper (*3*) successful correlations have been proposed using this correlation for 17 different fluorocarbon refrigerants and we reported $\sigma_0$ and $n$ determined for respective substances. However, for 9 substances including R 115 and R 502, reliability of those correlations has been less than those for 8 other substances including R 22 simply due to the scarcity of reliable experimental data. Therefore $\sigma_0$ and $n$ for R 115 and R 502 have been newly determined based on the present results by least-squares fitting. The standard deviations of the present results from these correlations are 0.035 mN/m for R 115 and 0.053 mN/m for R 502. For R 22, however, new fitting is not developed because the present results agreed well with our previous correlation (*3*) satisfactorily. The values of constants $\sigma_0$ and $n$, and of critical temperature $T_c$ together with the literature sources for these three substances are given in Table II.

**Table II. Parameters $\sigma_0$ and $n$ of Eq 3, and the Critical Temperature $T_c$**

| substance | $\sigma_0$, mN/m | $n$ | $T_c$, K |
|---|---|---|---|
| R 22 | 61.23 (*3*) | 1.23 (*3*) | 369.32 (*21*) |
| R 115 | 48.52 | 1.255 | 353.1 (*7*) |
| R 502 | 54.23 | 1.263 | 355.37 (*22*) |

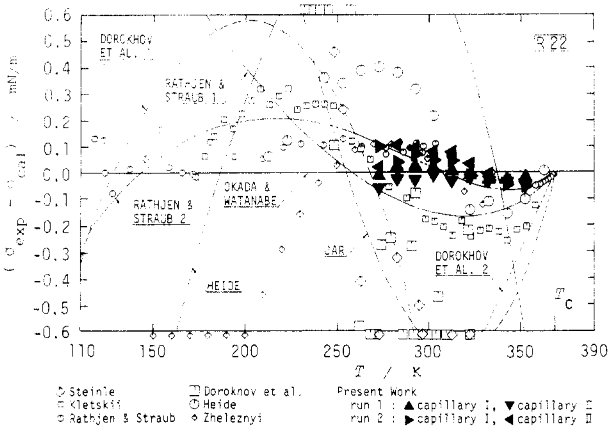

**Figure 1.** Comparison with respect to the surface tension of R 22.

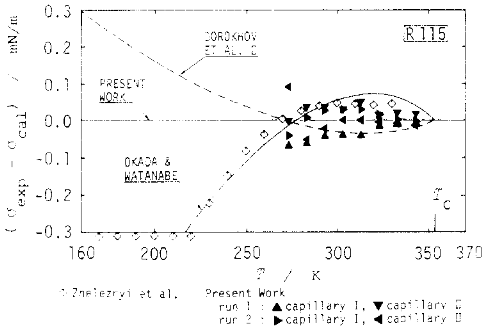

**Figure 2.** Comparison with respect to the surface tension of R 115.

## Discussion

For the purpose of comparing surface tension data and correlations and discussing their reliability, the deviation plots from the present correlations are shown in Figures 1-3. Off-scaled points are also plotted at the tops and bottoms of these figures.

First of all, good reproducibility of the present results is confirmed, since most of two sets of data observed with different capillaries agree well within ±0.1 mN/m, and, in addition, most of the results obtained in different experimental runs are also in good agreement each other within ±0.1 mN/m.

As for R 22 in Figure 1, rather sizable sets of experimental surface tension data have been reported (*1*, *12-20*). Among

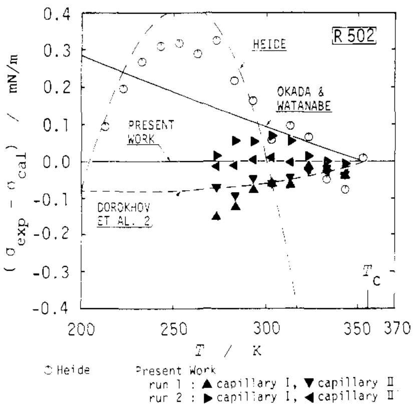

**Figure 3.** Comparison with respect to the surface tension of R 502.

these data, those of Rathjen and Straub (*17*–*19*) are evaluated to be the most reliable ones and therefore the correlation has been developed based on their data in our previous paper (*3*). Figure 1 reconfirms that the present results are in excellent agreement with the results by Rathjen and Straub and also with our previously proposed correlation. These agreements show the high reliability of our previous correlation and of measurements by Rathjen and Straub as well as by the present study. Surface tensions by Heide (*1*) and by Zheleznyi (*20*) have large discrepancies and obsolete temperature dependence from the correlation. A similar behavior has been found in comparison of their measured results for other refrigerants (*3*). Thus, we conclude that their measurements are less reliable.

For R 115 and R 502, only a single set of experimental data is available up to the present. As a result of comparison examined with respect to Figures 2 and 3, it is found that 17 measured values by Zheleznyi (*2*) for R 115 and 15 measurements by Heide (*1*) for R 502 show similar behavior as mentioned for R 22. Hence, we can summarize that the present correlations based on the present results are far more reliable than the values by Zheleznyi and by Heide, although the present results are not obtained at temperatures below 273 K.

## Glossary

| | |
|---|---|
| $a^2$ | capillary constant, m$^2$ |
| $g$ | local gravitational acceleration, m/s$^2$ |
| $g_n$ | normal gravitational acceleration = 9.80665 m/s$^2$ |
| $h_0$ | capillary rise height, m |
| $n$ | adjustable parameter in eq 3 |
| $r$ | inner radius of the capillary, m |
| $T$ | temperature, K |
| $T_c$ | critical temperature, K |
| $\theta$ | contact angle, rad |
| $\rho'$ | saturated liquid density, kg/m$^3$ |
| $\rho''$ | saturated vapor density, kg/m$^3$ |
| $\sigma$ | surface tension, mN/m |
| $\sigma_0$ | adjustable parameter in eq 3, mN/m |

**Registry No.** R22, 75-45-6; R115, 76-15-3; R502, 39432-81-0.

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Received for review October 27, 1986. Revised March 29, 1988. Accepted April 19, 1988. We are grateful to Du Pont-Mitsui Fluorochemicals Co. Ltd., Tokyo, for furnishing high-purity research grade samples and analyzing their purity. We are also indebted to the National Research Laboratory of Metrology, Ibaraki, Japan, for precise calibration of the platinum resistance thermometer against IPTS-68.