Surface Tension Measurement for a New Low-GWP Refrigerant HFO-1123 by a Differential Capillary Rise Method

Chieko KONDOU *†       Yukihiro HIGASHI **

* Graduate School, Engineering, Division of System Science, Nagasaki University (1-14 Bunkyo-machi, Nagasaki, 852-8521)
** NEXT-RP in WPI- International Institute for Carbon-Neutral Energy Research, Kyushu University (744 Motooka, Nishi-ku, Fukuoka, 819-0395)

Summary

By a differential capillary rise method, the surface tension was measured for a new candidate of low GWP refrigerant HFO-1123. 16 points of surface tension data with a propagated uncertainty of approximately ±0.22 mN m⁻¹ are presented in this paper. Based on the measured data, a Van der Waals type empirical correlation was proposed for HFO-1123: \( \sigma = 61.02 \left(1 - \frac{T}{T_{\text{crit}}} \right)^{1.30} \) [mN m⁻¹], where \( T_{\text{crit}} \) is a critical temperature of 331.7 K measured by Higashi and Akasaka. This empirical correlation agrees with the measured surface tension data at temperatures from 267 K to 304 K.

Keywords: Surface tension, Refrigerant, HFO-1123, Thermophysical property

1. Introduction

In the Kigali amendment to the Montreal protocol, a specific phase down schedule of production and consumption amount of HFCs (Hydro Fluoro Carbons) and HCFCs (Hydro Chloro Fluoro Carbons) is declared for the global warming mitigation. According to this schedule, until 2036, developed countries aim to reduce the CO₂ equivalent consumption amount 85% from the baseline of period 2011 to 2013[1]. In such circumstances, low GWP (global warming potential) refrigerants have been attracting the worldwide attention in air conditioning and refrigeration manufacturers. The current commercial focus is for HFOs (Hydro Fluoro Olefins) exhibiting GWP of less than one, with acceptance of the mild flammability. A binary mixture HFO-1123/HFC-32 is anticipated to be a new candidate of R410A (HFC-125/HFC-32 50/50 mass%) alternatives used in stationary air conditioning systems. Although the use of HFO-1123 alone causes the risk of disproportionate reaction, this substance potentially has a quite attractive thermophysical property[2-5] as the one of mixture components coupled with HFC-32. However, physical properties of HFO-1123 are not adequately clarified yet. The accurate measurement data are very important for the property calculation of HFO-1123/HFC-32. The one of properties, surface tension plays an important role in boiling and condensation heat transfer, which are essential in above devices. Surface tension data, precisely measured by a differential capillary-rise-height method, will be presented in this study. Then, based on the data, the empirical correlations expressing the temperature dependence will be proposed for HFO-1123.

2. Measurement

2.1 Apparatus

Fig. 1 shows an experimental apparatus designed for measuring the surface tension. This apparatus was originally developed by Okada et al. [6] based on a capillary rise height method. The surface tension is measured as the capillary elevation in a small
diameter tube immersed in a liquid. Two capillaries with inner radii of \( r_1 = 0.4222 \pm 0.0009 \) mm and \( r_2 = 0.7526 \pm 0.0009 \) mm are vertically set by a silicon supporting brace in a Pyrex glass tube that has 17 mm in inner diameter and 25 mm in outer diameter. The capillary radii were precisely measured with mercury slugs (Okada et al. 10). These capillaries and pressure vessel are carefully cleansed by using an alkaline aqueous solution and an ultrasound bath in the preparatory procedure. The liquid refrigerant is filled roughly to a half volume of the pressure vessels at a room temperature. Then, the pressure vessel is placed in a thermostatic bath (B), and the temperature in the thermostatic bath is kept constant with a fluctuation within ± 10 mK using a PID (K) controlled heater (F) and a chiller (G). The temperature is measured with a 100 Ω platinum resistance thermometer (M), ASL model F500, calibrated against ITS-90. The uncertainty of the temperature measurement is estimated to be within ± 5 mK. At a steady state, the capillary rise difference between the two capillary tubes is measured by using a digital traveling microscope (D) with a tolerance of 0.01 mm.

Fig. 2 illustrates the principle of differential capillary-rise-height method. More specifically, with the traveling microscope (D) and a CCD camera (I) shown in Fig.1, the height difference of the bottom of the meniscus in each capillary tube, \( \Delta h_\text{m} \) as shown in Fig. 2, is measured. Fig. 3 is the typical CCD image displayed on a monitor (J), shown in Fig. 1, to determine the position of the meniscus bottom. The differential height is read several times. The two standard deviations of the readings were approximately ±0.04 mm. This standard deviation is taken into account as the reading error in the differential height measurement. The contact angle \( \theta \), shown in Fig. 2, is approximated as zero assuming the semispherical meniscus. To obtain the actual differential capillary rise height, the measured differential height \( \Delta h_\text{m} \) at the bottom of the meniscus in each capillary tube is corrected by a methodology of Rayleigh7).

\[
\Delta h_\text{c} \approx \Delta h_\text{m} + \frac{(r_1 - r_2)}{3} \tag{1}
\]

where \( g \) and \( g_\text{n} \) are the local gravitational acceleration on third floor at Nagasaki-city Japan 9.79585 m s\(^{-2}\), and standard gravitational acceleration 9.80665 m s\(^{-2}\), respectively. The contact angle \( \theta \) of refrigerants in the capillary tube, which is well cleansed, is assumed zero. Thus, the surface tension \( \sigma \) is determined as,

\[
\sigma = \frac{g \Delta h_\text{m} (\rho' - \rho'')}{2(1/r_1 - 1/r_2)} \cos \theta \approx \frac{g \Delta h_\text{m} (\rho' - \rho'')}{2(1/r_1 - 1/r_2)} \tag{2}
\]

where \( \rho' \) and \( \rho'' \) are the orthobaric liquid and vapour densities.

2.1.1 Sample refrigerants

Table 1 specifies the sample refrigerant HFO-1123. The nominal purity of the sample, supplied by AGC Inc., is considered more than 99.5 mol%. The critical temperature, where the liquid-vapor interface vanishes, of HFO-1123 is 331.7 K, according to Higashi et al. 8). The density data are also very important factor to determine the surface tension in differential capillary rise height method, as described in Eq. (3). Fig. 4 plots the currently available density data in literatures for HFO-1123. In the figure, the lines show the calculated density with the EOS proposed by Akasaka et al.9. In this study, the densities \( \rho' \) and \( \rho'' \) in Eq. (3) are evaluated along this line at the measured temperature and the relative uncertainty in the densities are estimated as ± 0.4%.

![Fig. 1 Measurement apparatus](image)

![Fig. 2 Principle of the measurement method](image)

![Fig. 3 CCD image of the capillary rise height](image)
Table 1  Sample refrigerants

<table>
<thead>
<tr>
<th>Designation</th>
<th>Name</th>
<th>Structure</th>
<th>CAS number</th>
<th>Purity</th>
<th>Impurities</th>
<th>NBP</th>
<th>Critical temp.</th>
<th>ODP</th>
<th>GWP100</th>
<th>Safety class</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFO-1123</td>
<td>Trifluoroethylene</td>
<td>C(_2)F(_3) (=) C(_2)H</td>
<td>359-11-5</td>
<td>&gt; 99.5 mol%</td>
<td>acids &lt; 0.0001 mol%</td>
<td>214.2 K</td>
<td>331.7 K</td>
<td>0.3</td>
<td>0.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 4  Currently available data on measured and calculated orthobaric density

Table 2  Uncertainty in measurement parameters

<table>
<thead>
<tr>
<th>parameter</th>
<th>equipment</th>
<th>uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature (ITS-90)</td>
<td>ASL F500</td>
<td>±5 mK</td>
</tr>
<tr>
<td>differential capillary-rise-height, (\Delta h_m)</td>
<td>Nippon optical works, NRM-D-2XZ</td>
<td>±0.05 mm</td>
</tr>
<tr>
<td>inner radii of the capillaries, (r_1) and (r_2)</td>
<td>-</td>
<td>±0.0009 mm</td>
</tr>
<tr>
<td>orthobaric densities, (\rho') and (\rho'')</td>
<td>-</td>
<td>±0.4%</td>
</tr>
</tbody>
</table>

Table 2 lists the applied equipment/method and their uncertainties those affect surface tension measurement. From each uncertainty, the propagated measurement uncertainty (2k) in surface tension is estimated to be from ±0.2 mN m\(^{-1}\) to ±0.3 mN m\(^{-1}\).

Fig. 5 plots the surface tension measurement results of HFC-32 as a function of temperature. This fluid is selected because of the similar temperature range of the critical point and the normal boiling point to HFO-1123. Thus, the results in Fig. 5 can be used as a check to ensure that the measurement method is valid. The symbols in Fig. 5 show the present surface tension data and also various measurement data reported in literatures for comparison; meanwhile, the line shows the calculated surface tension by REFPROP 9.1\(^9\). Fig. 5(b) show the deviation of measurement data from the calculated surface tension of REFPROP. As shown in Fig. 5(a), the present data of series 1 highly overlap to that of series 2, which are measured with the other sample re-charged after months. Those data agree with the calculated and other measured surface tension within approximately ±0.2 mN m\(^{-1}\).
3. Results and Discussion

Fig. 6 plots the surface tension measurement results as a function of temperature for HFO-1123. The circled symbols show the present data of series from 1 to 3 those are measured on different days with re-charged sample. The vertical bars appended to the symbols show the measurement uncertainty in surface tension, which is estimated be typically ±0.2 mN m⁻¹.

![Graph showing surface tension measurement results](image)

As shown in Fig. 6, the data of series 1 to 3 overlap within ±0.2 mN m⁻¹. Comparing the data of HFO-1123 to HFC-32, surface tension of HFO-1123 is obviously lower than that of HFC-32. At a temperature of 270 K, the surface tension of HFO-1123 is 6.8 mN m⁻¹ that is 4.8 mN m⁻¹ lower than and 58% of HFC-32 surface tension. Table 3 lists the measured capillary constant \(a^2\) and the surface tension of series 1, 2, and 3. In temperature range from 266 K to 304 K, 16 points of measurement data are provided in total. The calculated densities and the measured capillary constant, which are used to determine the surface tension, are also listed in Table 3, so that the surface tension can be re-evaluated from Eq. (3) with the listed capillary constant and new density data when the equation of state or density data are updated in future.

On the basis of the above measurement data, an empirical correlation of Van der Waals type is here proposed.

\[
\sigma_{\text{HFO-1123}} = 61.02 \left(1 - \frac{T}{T_{\text{crit}}} \right)^{1.30} \text{[mN m⁻¹]}, \quad (4)
\]

\(T_{\text{crit}} = 331.7 \text{[K]}\)

The coefficient 61.02 and the exponent 1.30 in Eq. (4) are determined by least square mean method. The critical temperature \(T_{\text{crit}}\) is 331.7 K according to Higashi and Akasaka. The exponent of most non-polar organic fluids exhibit somewhat larger than 1.24, typically ranges from 1.26 to 1.28. The proposed exponent 1.30 appears to be reasonable for HFO-1123. The calculated surface tension by Eq. (4) is plotted as the line in Fig. 6(a). The deviation of measurement data from the calculated value is plotted in Fig. 6(b). As compared, the empirical correlation agrees with the measurement data within ±0.2 mN m⁻¹ in temperature range from 266 K to 304 K.

![Graph showing deviation from empirical correlation](image)

Table 3  Measured capillary constant and surface tension for HFO-1123

<table>
<thead>
<tr>
<th>Temp. (Vapor(^{5}) Liquid(^{3}))</th>
<th>Capillary constant (a^2)</th>
<th>Surface tension (\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T) [K]</td>
<td>(\rho_v) [kg m(^{-3})]</td>
<td>(\rho_l) [kg m(^{-3})]</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>269.72</td>
<td>43.71</td>
</tr>
<tr>
<td>272.95</td>
<td>48.34</td>
<td>1127.03</td>
</tr>
<tr>
<td>279.15</td>
<td>58.41</td>
<td>1099.94</td>
</tr>
<tr>
<td>283.57</td>
<td>66.71</td>
<td>1079.80</td>
</tr>
<tr>
<td>288.51</td>
<td>77.28</td>
<td>1056.28</td>
</tr>
<tr>
<td>293.22</td>
<td>88.89</td>
<td>1032.56</td>
</tr>
<tr>
<td>2</td>
<td>297.47</td>
<td>100.89</td>
</tr>
<tr>
<td>302.28</td>
<td>116.63</td>
<td>982.00</td>
</tr>
<tr>
<td>3</td>
<td>266.95</td>
<td>40.04</td>
</tr>
<tr>
<td>275.71</td>
<td>52.62</td>
<td>1115.10</td>
</tr>
<tr>
<td>281.19</td>
<td>62.13</td>
<td>1090.71</td>
</tr>
<tr>
<td>285.76</td>
<td>71.21</td>
<td>1069.53</td>
</tr>
<tr>
<td>290.50</td>
<td>81.99</td>
<td>1046.43</td>
</tr>
<tr>
<td>297.86</td>
<td>102.07</td>
<td>1007.63</td>
</tr>
<tr>
<td>301.49</td>
<td>113.84</td>
<td>986.78</td>
</tr>
<tr>
<td>303.55</td>
<td>121.21</td>
<td>974.27</td>
</tr>
</tbody>
</table>
The obtained surface tension data are compared with the predicting correlations proposed for other refrigerants. The four selected correlations are stated below.

DiNicola et al. (2013)\(^{15}\):
\[
\sigma = 0.658 \times 10^{-3} P_{\text{crit}}^{0.618} T_{\text{crit}}^{0.34} \times (1 + \omega)^{0.77} \left(1 - \frac{T}{T_{\text{crit}}}\right)^{1.262} \tag{5}
\]
where, \(\omega\) is the acentric factor.

Miqueu et al. (2000)\(^{16}\):
\[
\sigma = kT_{\text{crit}}^{2/3} \left(\frac{N_{\lambda}}{V}_{\text{crit}}\right)^{2/3} \times \left(4.35 + 4.14\omega\right) \left(\frac{T}{T_{\text{crit}}}\right)^{1.26} \times \left[1 + 0.19\left(\frac{T}{T_{\text{crit}}}\right)^{0.5} - 0.25\left(\frac{T}{T_{\text{crit}}}\right)\right] \tag{6}
\]
where, \(V_{\text{crit}}, k,\) and \(N_{\lambda}\) are the critical molar volume in cm\(^3\) mol\(^{-1}\), the Boltzmann constant in J K\(^{-1}\), and the Avogadro constant in mol\(^{-1}\).

Miller and Thodos (1963)\(^{17}\):
\[
\sigma = P_{\text{crit}}^{2/3} T_{\text{crit}}^{1/3} Q \left(1 - \frac{T}{T_{\text{crit}}}\right)^{1/3}. \tag{7}
\]
\(Q\) is typically called Reidel parameter expressed as,
\[
Q = 0.1196 \left[1 + \frac{\ln\left(P_{\text{crit}}/1.01325\right)}{1 - \frac{T_{\text{NBP}}}{T_{\text{crit}}} - 0.279}\right] \tag{8}
\]
where, \(T_{\text{NBP}}\) is the normal boiling temperature in K.

Gharagheizi et al. (2012)\(^{18}\):
\[
\sigma = 10^{-4} \left(\frac{T_{\text{crit}}}{T_{\text{crit}}}\right)^{11/9} P_{\text{crit}} \left(1 - \frac{T}{T_{\text{crit}}}\right)^{11/9} \times \left[\frac{7.728729 \left(\frac{T_{\text{NBP}}}{T_{\text{crit}}}\right)}{2.476318 \left(\frac{T_{\text{NBP}}}{T_{\text{crit}}}\right) + V_{\text{crit}}}\right] \tag{9}
\]

Fig. 7 compares the predicted surface tension to the measured. The solid and dashed lines show the above predictions and the empirical correlation Eq. (4). The prediction of Miller and Thodos\(^{17}\) over estimates the surface tension for HFO-1123. The prediction of DiNicola et al.\(^{15}\) and Gharagheizi et al.\(^{18}\) show the best agreement with the measurement results.

Table 4 evaluates the two standard deviation, \(2\sigma\), and the bias, \(\overline{\varepsilon}\), of the selected predictions from the measurement results. This deviation indicates the scattering in measurement data, which is approximately \(\pm 0.2\) mN m\(^{-1}\), and the degree of overlap in the surface tension curvature against the temperature. The curvature of DiNicola et al.\(^{15}\) appears to fit best to the measured. The bias indicates the agreement of the center value. Gharaghizi et al.\(^{18}\) appears to give the calculation line passes through the center of measured data, as shown in Fig. 7.

4. Conclusions

By a differential capillary rise method, liquid-vapor interface surface tension was measured for HFO-1123 at temperatures from 266 K to 304 K and from 266 K to 340 K, respectively. Based on the data, the following empirical correlations were proposed.
Those correlations agreed with the measured data within the measurement uncertainty. The predicting correlation of DiNicola et al. and Gharagheizi et al. proposed for other refrigerants showed reasonable agreement with the present data.

Acknowledgements

The sample refrigerants are kindly donated by AGC Inc. This study was financially supported by the JSPS KAKENHI Grant Number 17K14603 and AGC Inc. The authors are grateful for their support.

References

19) Raabe, G., Molecular simulation studies in hydrofluoroolefine (HFO) working fluids and their blends, Science and Technology for the Built Environment, 2016, 22(8), pp. 1077-1089.