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Improvements of the experimental apparatus for measurement of the surface tension of supercooled liquids using horizontal capillary tube

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Abstract. An experimental apparatus with a horizontal capillary tube for measurement of the surface tension of supercooled liquids, i.e. liquids in a metastable state below the equilibrium freezing point, was designed and tested in the previous study [V. Vinš *et al.*, EPJ Web Conf. **92**, 02108 (2015)]. In this work, recent modifications of both the experimental setup and the measurement analysis are described. The main aim is to improve the accuracy and the reproducibility of measured surface tension and to achieve higher degrees of supercooling. Temperature probes measuring the temperature of cooling medium near the horizontal capillary tube were calibrated in the relevant temperature range from – 31 °C to + 45 °C. An additional pressure transducer was installed in the helium distribution setup at the position close to the capillary tube. The optical setup observing the liquid meniscus at the open end of the horizontal capillary tube together with the video analysis were thoroughly revised. The red laser illuminating the liquid meniscus, used at the original apparatus, was replaced by a fiber optic light source, which significantly improved the quality of the meniscus image. The modified apparatus was used for the measurement of surface tension of supercooled water at temperatures down to – 11 °C. The new data have a lower scatter compared to the previous horizontal measurements and show a good agreement with the other data obtained with a different measurement technique based on the modified capillary rise method.

1 Introduction

An experimental apparatus developed for the measurement of surface tension of supercooled liquids, i.e. metastable liquids at temperatures below the equilibrium freezing point, using a horizontal capillary tube was introduced in the previous study [1]. The apparatus is based on a measuring technique developed by Ferguson and Kennedy [2] in 1932. In this method, a short thread of liquid sample is placed inside a horizontal capillary tube. One end of the capillary tube is connected to the pressure setup which allows tuning of a small counterpressure of a gas. The other end is left open to the ambient. It is illuminated by the light source and observed by optics. The gas counterpressure compensates the surface forces at the two menisci of the liquid thread. At low counterpressure, the meniscus at the open end of the capillary tube is concave, i.e. inside the capillary tube. With increasing counterpressure, the outer meniscus changes its shape from concave to planar and subsequently to convex. In case of the planar shape of outer meniscus, the surface forces become equal to zero. Consequently, the counterpressure of gas is in equilibrium only with the surface forces at the second meniscus inside the capillary tube. In this case, the surface tension σ at the inner meniscus can be determined from the following equation

$$\sigma = \frac{\Delta p \cdot d}{4\cos\theta} , \qquad (1)$$

where Δp denotes the counterpressure of gas at the planar outer meniscus, d is the inner diameter of the capillary tube, and θ is the contact angle between the liquid and the capillary tube wall.

The horizontal technique by Ferguson and Kennedy [2] was later improved by Hacker and used for the measurement of surface tension of supercooled water in 1951 [3]. Hacker's data measured down to – 22 °C show a significant change in the temperature trend of the surface tension of supercooled water. This anomaly, called the second inflection point (SIP) in the surface tension of water [4], was trusted to be a real behavior of the supercooled water. The reason is also the fact that the data by Hacker have relatively low scattering and good internal consistency. However, recent experiments performed with another technique based on the modified capillary rise method show that the surface tension of water does not show any anomaly at temperatures down to – 26 °C [4-6]. The surface tension of supercooled water can be predicted by the IAPWS (International Association for Properties of Water and Steam) standard [6] extrapolated below 0.01 °C. The IAPWS standard has following form

$$\sigma = 235.8\,\tau^{1.256}\left(1 - 0.625\,\tau\right) , \qquad (2)$$

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where σ is the surface tension in mN m^{-1}, τ denotes a dimensionless temperature $1-T/T_c$ with the critical temperature of water $T_c = 647.096$ K. Equation (2) was developed by Vargaftik *et al.* [8] in 1970's and approved by IAPWS as an international standard [6]. The IAPWS standard is currently being revised with the use of recent experimental data in order to improve the estimates of its uncertainties and to extend the range of validity also to the supercooled region [8].

In the atmospheric research focused on nucleation processes, i.e. formation of droplets and ice crystals in the upper atmosphere, the correlation for the surface tension of supercooled water by Viisanen *et al.* [10] is often employed

$$\sigma = -2.75\cdot10^{-4}T^2 + 9.133\cdot10^{-3}T + 93.6635 \ , \qquad (3)$$

where σ is the surface tension in mN m^{-1} and T is the thermodynamic temperature. Equation (3) given as a simple quadratic fit of temperature provides similar results as the extrapolated IAPWS correlation in the temperature range down to – 25 °C. However at higher temperatures within the stable region, equation (3) shows significant deviation from the IAPWS standard.

In this study, the experimental apparatus with the horizontal capillary tube introduced in the previous work [1] was further modified in order to improve the reproducibility and the accuracy of measured surface tension of supercooled water. The improved setup will allow achieving higher degrees of supercooling of up to 20 °C. Main motivation for this work is to obtain new valuable data for supercooled water with an experimental method different from the recent measurements with the modified capillary rise technique [4-6]. Moreover, the new measurements with the horizontal capillary tube may clarify the SIP anomaly in the Hacker's data [3], as Hacker used also the horizontal technique. New data from the preliminary measurements on the improved apparatus at temperatures from – 11 °C to + 15 °C are also provided.

2 Experimental apparatus

The measurement principle is similar to that in the experiments by Ferguson and Kennedy [2] and Hacker [3]. A simplified scheme of the experimental setup is shown in Figure 1. The horizontal capillary tube is partly placed inside the temperature–controlled chamber with flowing ethanol. The liquid thread inside the capillary tube is long such that the inner meniscus is located inside the temperature–controlled chamber. The outer meniscus at the open end is kept at an ambient temperature. Knowing the inner diameter of capillary tube, the temperature of inner meniscus, and the counterpressure of gas corresponding to the planar meniscus at the open end, the surface tension can be determined from equation (1). A constant contact angle $\theta = 3°$ [11] can be considered for the water and the fused silica capillary tube at temperatures below 200 °C [12]. Helium with purity of 99.996% was used as a working gas due to its low solubility in water and negligible adsorption on the liquid surface of water.

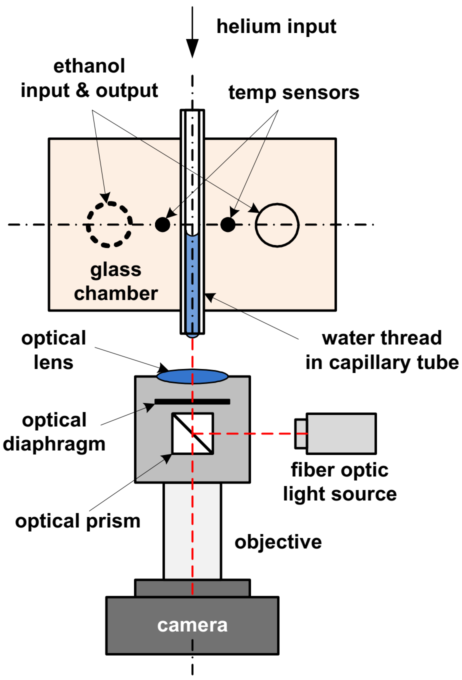


Figure 1. Scheme of experimental apparatus with the horizontal capillary tube; view from top

Similarly to our previous measurements with the modified capillary rise method [4-6], the horizontal measurement presented in this work is a relative measurement. The inner diameter of capillary tube d is evaluated as an average from the measurements at the reference temperature $T_{\mathrm{ref}} = 15$ °C and the surface tension calculated from the IAPWS correlation (2)

$$d = \frac{1}{N}\sum_{i=1}^{N}\frac{\Delta p\left(T_{\mathrm{ref},i}\right)\cdot\sigma_{\mathrm{IAPWS}}\left(T_{\mathrm{ref},i}\right)}{4\cos\theta} \ . \qquad (4)$$

The average inner diameter of capillary tube used in this study had value $d = 0.3353 \pm 0.0022$ mm.

All the experiments were performed with ultrapure water with a constant resistivity of 18.2 MΩ cm, total organic carbon content below 5 ppb, and free of particles larger than 0.2 μm.

3 Improvements of the setup

Preliminary measurements performed in the previous study [1] proved the functionality of main components of the new experimental apparatus with the horizontal capillary tube. However, only relatively low degree of supercooling of – 7 °C was achieved and the data for the surface tension of water were quite scattered. Consequently, several improvements of the entire apparatus were applied in this study. The temperature sensors were carefully calibrated in the relevant temperature range. An additional pressure transducer was installed in the helium distribution setup at a position closer to the capillary tube. Most importantly, the optical setup together with the subsequent analysis of recorded video were thoroughly revised, which markedly improved the accuracy and the consistency of measured data for the surface tension of water.

3.1 Measurement of temperature

Resistive temperature sensors Pt100 of Omega PR-11-3 series measuring the temperature of liquid ethanol inside the temperature–controlled chamber were carefully calibrated in the relevant temperature range from – 31 °C to + 45 °C. A secondary standard platinum resistance thermometer Isotech 909Q (25.5 ohm at 0 °C) was taken as the reference thermometer. All sensors were connected to the ASL F500 precision thermometer with accuracy better than ± 0.005 °C and ± 5 mK in the whole range from – 200 °C to + 962 °C. The calibrated sensors together with the reference thermometer were submerged in the Lauda Proline RP855 thermostatic bath with liquid ethanol. The accuracy of the thermostatic bath stated by the manufacturer is better than ± 0.01 °C. The standard deviation of the reference temperature did not exceed 0.0061 °C during the calibration.

Calibration curves were correlated with the Callendar–van Dusen (CvD) equation

$$R_t = R_0\left[1 + At + Bt^2 + C(t-100)t^3\right] , \qquad (5)$$

where t denotes temperature in degrees of Celsius, R_t is resistance in ohm at temperature t, R_0 is the reference resistance at 0 °C, and A, B, and C are correlated coefficients. Coefficient C is equal to zero for $t > 0$ °C. Calibration parameters for the two most important temperature sensors positioned near the capillary tube are given in Table 1. The value for C was taken from the norm DIN 90.

Table 1. CvD coefficients of the calibrated temperature probes.

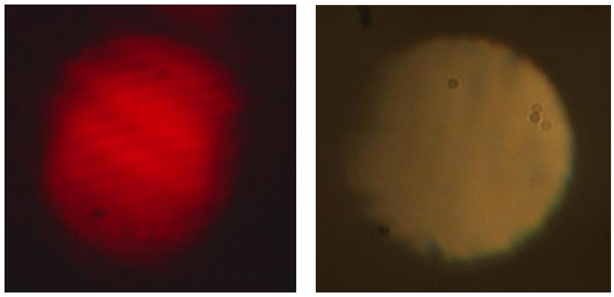
	Probe 22	**Probe 23**
R_0 / ohm	99.9862	99.9656
A / ohm °C^{-1}	$3.91442\cdot10^{-3}$	$3.91446\cdot10^{-3}$
B / ohm °C^{-2}	$-5.67342\cdot10^{-7}$	$-5.67737\cdot10^{-7}$
C / ohm °C^{-4}	$-4.1830\cdot10^{-12}$	$-4.1830\cdot10^{-12}$

3.2 Measurement of pressure

The analysis of uncertainties of measurements performed in the previous study [1] showed that the measurement of counterpressure Δp had the major influence on the uncertainty budget of measured surface tension. Therefore, new pressure transducer Omega PX 653 with a pressure range of 1245 Pa and accuracy 0.25% FS was additionally installed inside the helium distribution setup described in section 2.2 in the previous work [1]. The additional pressure transducer was placed after the mechanical filter shown in Figure 3 in the previous study [1]. Its position is markedly closer to the horizontal capillary tube than the original pressure transducer Furness Controls FCO 332 installed behind the high-precision needle valve on the pressure manifold. The additional transducer should help to detect possible differences between the pressure measured by the Furness Controls transducer on the manifold and the pressure near the capillary tube. Nevertheless, no significant differences or time delays, when varying the flow rate of helium through the distribution setup, were observed between the pressures measured at the manifold and near the capillary tube. The output signals of both pressure transducers were logged with a constant time step of 125 ms using the data acquisition (DAQ) unit Agilent 34970A with fast multiplexer 34902A.

3.3 Optical setup

The modifications of the optical setup and the subsequent analysis of recorded video represent the most important improvements compared to the previous study [1]. The original design of optical setup was described by Hošek *et al.* [13] in detail. In the current study, the red laser light source used for the illumination of liquid meniscus was replaced with a fiber optic light source Zeiss KL 200. An additional optical diaphragm was placed behind the optical prism shown in Figure 1 in order to exclude nonparallel beams which negatively influenced the final image of liquid meniscus. We note that the diaphragm was not used in the original setup with the red laser even though it was shown in Figure 1 in the previous study [1].



a) b)

Figure 2. Planar liquid meniscus illuminated by the red laser (a) and the fiber optic light source with diaphragm (b)

Figure 2 compares the pictures of planar liquid meniscus illuminated by the red laser and the fiber optic light source taken by the digital camera Thorlabs DCC1645C-HQ. As can be seen the picture taken with the fiber optic light source is more uniform compared to the picture obtained with the laser light source. The difference becomes more distinct when the meniscus has more convex or concave shape. In case of the laser light source, disturbing reflections appear in the image, which negatively affect the subsequent analysis of the recorded video.

A constant frame rate of 8 frames per second, corresponding to the time step of 125 ms used also on DAQ for the pressure transducers, was set for the video record. Even though the digital camera and DAQ worked with the same time step, a difference in the lengths of the recorded video and the data logged by DAQ was observed. The video record was usually slightly shorter than the DAQ record. With the kind help of Thorlabs GmbH helpdesk, it was found that the reason for the shorter video record was caused by the failures in the video transmission between the camera and the measuring computer. Luckily, the Thorlabs software enables detection of such errors. An example of the log file containing the transmission errors is shown in Figure 3. Knowing the exact time of the missing frames allowed correcting the video in the subsequent analysis of the measurement such that the video record and the pressure record became fully consistent with each other.

```
24  -  15:05:32.291  -  Transfer failed: Capture Error (178).
25  -  15:05:51.858  -  Transfer failed: Capture Error (178).
26  -  15:06:57.758  -  Transfer failed: Capture Error (178).
27  -  15:07:33.334  -  Transfer failed: Capture Error (178).
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Figure 3. Example of the log file containing the flags for errors in the video transfer

4 Description of measurement

The principle of current measurement is similar to the previous study [1]. As it was discussed in section 3, the most important improvement lies in better analysis of the recorded video. An important fact that needs to be mentioned is that the open end of the horizontal capillary tube had to be precisely polished and grinded as described by Hošek and Studenovský [14]. The outer surface of the capillary tube has to be planar and perpendicular to the main capillary tube axis in order the well visible and reproducible planar meniscus can be achieved.

4.1 Methodology

The video record and the pressure record were synchronized using a white light-emitting diode (LED) illuminating the open end of the capillary tube. The power voltage of LED of 5 V was logged as an additional channel on DAQ for this purpose. The video record and the pressure record were synchronized by turning off and turning on the diode. No difference between the number of video frames and the number of data points logged by DAQ was detected after the video transfer analysis discussed in section 3.3. The measurements with only one missing frame were still taken as good points. All measurements with the difference higher than one frame were treated as bad points and excluded from the further analysis.

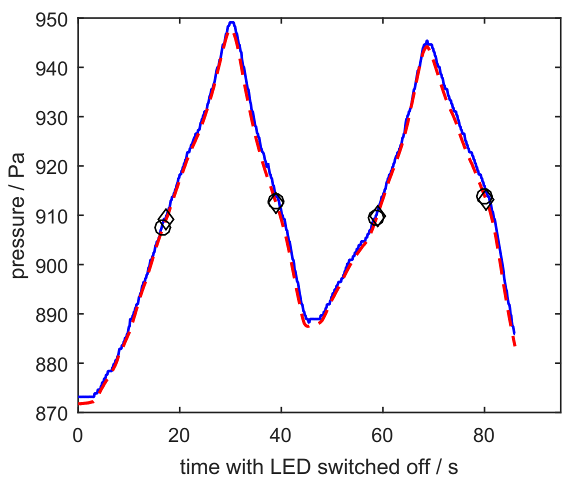

Figure 4. Two pressure loops measured over time with turned off LED for the measurement at – 6.9 °C. Red - -, pressure transducer Furness Controls FCO 332; blue –, pressure transducer Omega PX653. Pressures corresponding to the planar meniscus measured by, black ○, Furness Controls FCO 332 and, black ◊, Omega PX653.

Similarly as in the previous study [1], each measurement was taken as two subsequently increasing and decreasing pressure loops. The final value of counterpressure corresponding to the planar meniscus was taken as an overall average of two points at the increasing pressure and two points at the decreasing pressure. No systematic difference between the four values was observed in any of the current experiments. Figure 4 shows an example of the typical pressure course with two loops for the measurement at – 6.9 °C.

Two to three independent measurements were carried out for each temperature. The uncertainty of measured temperature was better than ± 0.06 °C in all cases. The uncertainty of measured counterpressure of helium was better than ± 2.3 Pa, i.e. better than in the previous study [1] where $u(\Delta p)$ was better than ± 3.0 Pa.

4.2 Analysis of the video

Figure 5 shows a typical picture of capillary tube end taken by the digital camera. The capillary tube is illuminated by LED in this case. A small spot inside the capillary tube in the center of the figure is the concave meniscus illuminated by the fiber optic light source. The recorded video is analyzed inside the measuring rectangle containing the hole of capillary tube and its close surroundings. Yellow point on the right side of the figure is an arbitrary chosen point for the detection of light intensity of LED.

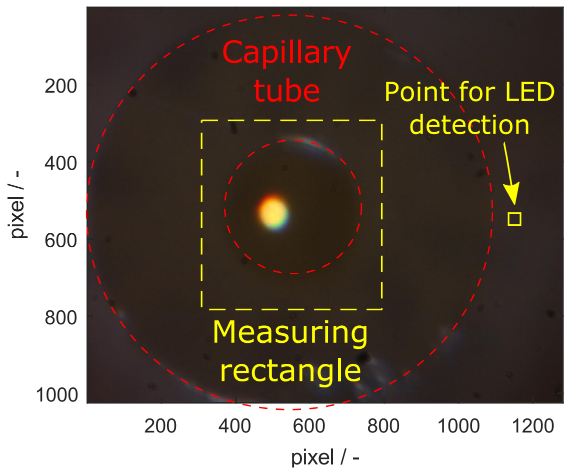

Figure 5. Photograph of the concave meniscus inside the capillary tube with the low counterpressure of helium at the beginning of measurement. LED is turned on.

The varying shape of liquid meniscus can be detected from the sum of light intensity inside the measuring rectangle. At the concave or convex shape, the meniscus behaves as a curved mirror. Consequently, only a small central part of the meniscus is visible in the camera and the sum of light intensity is relatively low. On the other hand, the planar meniscus behaves as a plane mirror. Most of the pixels inside the hole of capillary tube are illuminated in this case and the sum of light intensity within the measuring rectangle reaches its maximum.

Figure 6 shows an example of relative light intensity, i.e. the light intensity divided by its value at the start of measurement, over time for the measurement at – 6.9 °C. Clear four maxima in the light intensity were found, which correspond to the two pressure loops shown in Figure 4. The light intensity at the point for the detection of LED is also shown. Both the light intensity and the power voltage of LED change within one time step when turning LED on or off. Points for the synchronization of the recorded video and the recorded pressure are marked with purple circles.

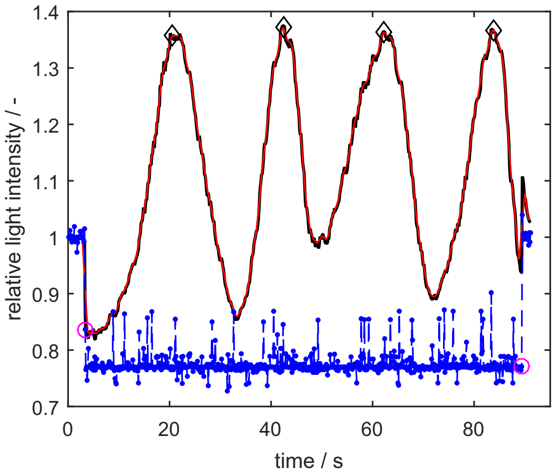

Figure 6. Relative light intensity I_i/I_1 over time for the measurement at – 6.9 °C. Blue -●-, light intensity at the point for detection of LED; purple ○, time of turning LED off/on; black –, sum of light intensity within the measuring rectangle; red –, moving average of light intensity within the rectangle; black ◊, maxima of sum of light intensity corresponding to the planar meniscus.

5 Results

The improved experimental apparatus with the horizontal capillary tube was successfully used for the measurement of surface tension of supercooled water. Preliminary measurements were performed at temperatures down to – 11 °C. Main reason for the presented measurements was to test the improved apparatus and to validate the video analysis. The relatively low degrees of supercooling were measured due to a potential risk of crystallization of the liquid sample. Unlike in the modified capillary rise method [4-6], the horizontal capillary tube is open to ambient, which increases the risk of abrupt solidification of the water sample.

Figure 7 shows the experimental data for the surface tension of supercooled water. The new measurements at temperatures between – 11 °C and + 15 °C (red diamonds) are in good agreement with both the capillary rise data [4-6] and the IAPWS correlation (2) extrapolated below 0.01 °C. The reference temperature T_{ref} for the evaluation of the inner diameter from equation (4) was + 15 °C.

The difference between the experimental data and the IAPWS standard extrapolated below the triple point of water is shown in Figure 8. As can be seen, the new data obtained with the improved apparatus are more consistent than the previous measurements [1]. Moreover, the new data support the previous measurements of our group with the modified capillary rise method [4-6]. A linear extrapolation of the IAPWS correlation [6] from 0.01 °C and the correlation by Viisanen *et al.* [10] are also shown. The uncertainty of surface tension measured with the horizontal method is better than 0.62 mN m^{-1}. This value is 50% higher than the uncertainty of the capillary rise measurements [6], which have the uncertainty of 0.41 mN m^{-1} at temperatures around – 12 °C. Nevertheless, similarly to the capillary rise measurements, the main output quantity of the presented experiment shall be the relative surface tension $Y = \sigma/\sigma_{\text{corr}}(T_{\text{ref}})$. The relative surface tension together with its uncertainty will be determined in the next step.

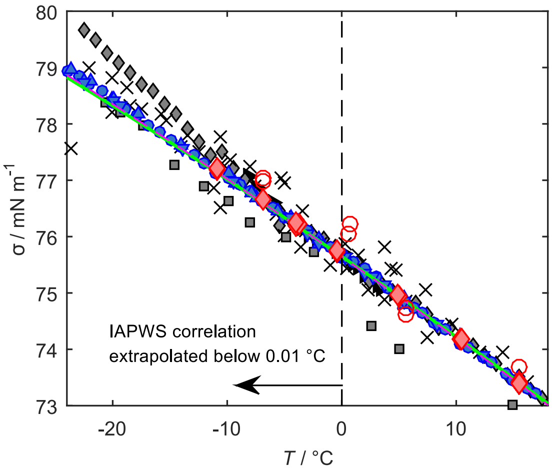

Figure 7. Experimental data for the surface tension of supercooled water. Green –, IAPWS correlation extrapolated below 0.01 °C [6]; purple - -, correlation by Viisanen *et al.* [10]; red ◊, this study; red ○, previous study [1]; black ►, Humphreys and Mohler [15]; black ♦, Hacker [3]; black x, Floriano and Angell [16]; black ■, Trinh and Ohsaka [17]; blue ●, Hrubý *et al.* [4]; blue ▲ and ▼, Vinš *et al.* [6] *p*-data and *h*-data, respectively.

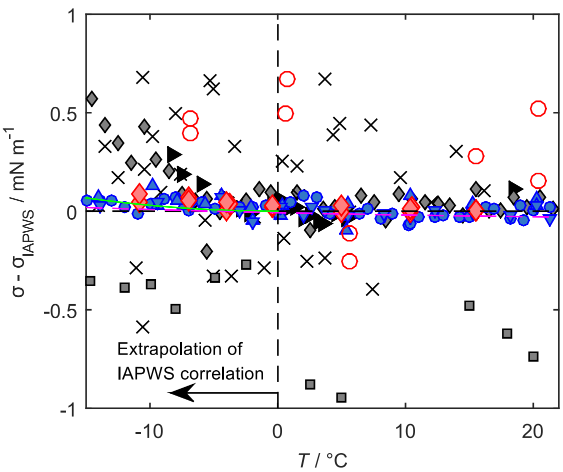

Figure 8. Difference between the experimental data for the surface tension of supercooled water and the IAPWS correlation extrapolated below 0.01 °C [6]. Green –, linear extrapolation of IAPWS correlation from the triple point; purple - -, correlation by Viisanen *et al.* [10]; red ◊, this study; red ○, previous study [1]; black ►, Humphreys and Mohler [15]; black ♦, Hacker [3]; black x, Floriano and Angell [16]; black ■, Trinh and Ohsaka [17]; blue ●, Hrubý *et al.* [4]; blue ▲ and ▼, Vinš *et al.* [6] *p*-data and *h*-data, respectively.

6 Conclusions

In this study, an experimental apparatus for measurement of the surface tension of supercooled liquids was improved compared to its original design introduced in the previous work [1]. Temperature sensors were calibrated in the range of temperatures relevant for the supercooled aqueous liquids. An additional pressure transducer was installed closer to the capillary tube and used for the control of the helium distribution setup. The optical setup and the analysis of recorded video was thoroughly revised. The new data for the surface tension of supercooled water measured down to – 11 °C are significantly less scattered than the previous measurements. Moreover, the data obtained with the horizontal technique agree with the capillary rise measurements [4-6], which represent a very important result of this study. The data for the surface tension of supercooled water obtained both with the capillary rise method and the horizontal technique will be used in the revision of the current IAPWS standard for the surface tension of water [6,8].

The SIP anomaly detected by Hacker [3], using also the horizontal capillary tube, was not observed in the new measurements in the temperature range from – 11 °C to + 15 °C. Nevertheless, further measurements at higher degrees of supercooling are planned in order to definitely clarify the SIP anomaly. The improved apparatus will allow achieving temperatures down to – 20 °C. A detailed analysis of the uncertainty budget and the evaluation of the relative surface tension are also under preparation.

Acknowledgement

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