Teze disertace

k získání vědeckého titulu "doktor věd"

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Experimental Investigation of Surface Tension of Aqueous Systems at Low Temperatures

název disertace

Komise pro obhajoby doktorských disertací v oboru Aplikovaná a teoretická mechanika

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Résumé of the Dissertation

The DSc. dissertation *Experimental Investigation of Surface Tension of Aqueous Systems at Low Temperatures* summarizes approximately 14 years of research carried out at the Thermodynamics department of the Institute of Thermomechanics of the Czech Academy of Sciences (IT CAS) in the field of experimental investigation of surface properties of aqueous mixtures at low temperatures. The main motivation of the research was to contribute to the ongoing scientific discussions on the anomalies of liquid water, especially in the low-temperature region. Compared to common liquids, the thermophysical properties of water exhibit several anomalies out of which the density maximum at 4 °C is most commonly known. The anomalies of low-temperature water can be well described by the second critical point model, when two forms of liquid water with different densities are considered within the metastable supercooled state. Based on historical data and recent molecular simulations, the surface tension of water was also suspected to show an anomaly at temperatures below −8 °C in a form of sudden change of the temperature trend, referred as the SIP (second inflection point) anomaly. In order to clarify the SIP anomaly, our team has developed several experimental techniques for accurate measurement of surface tension of water and later on of aqueous mixtures. The in-house designed experiments employ small amount of liquid in fused silica capillary tubes when the sample properties can still be considered as macroscopic. The experimental methods include: modified capillary elevation, capillary rise with helium counterpressure or with container elevation, and the horizontal capillary tube technique. Using a special temperature control chamber with optical glasses allowed to carry out experiments under the metastable supercooled conditions. The original experiments from 2014 to 2017 refuted the SIP anomaly down to −25 °C. However, the final measurements down to −31 °C provide certain room for its existence at low temperatures. The developed experimental techniques have been used for measurements with aqueous mixtures of technical or environmental relevance such as seawater, binary systems with ethylene glycol or sodium chloride. This research is still ongoing. An important aspect of the presented research is its relevance to the activities of the International Association for the Properties of Water and Steam (IAPWS). Two IAPWS standards directly reflect the results achieved in this work and the IAPWS Helmholtz Award was granted in 2019.

1 Introduction

The DSc. dissertation submitted in a cumulative form describes experimental research on surface tension of aqueous systems at low temperatures carried out at IT CAS since 2011. The topic is motivated by the intention to contribute to an ongoing scientific discussion on water anomalies and by the membership of the IT CAS researchers in IAPWS[1].

1.1 Water and aqueous mixtures

Water and its mixtures are the most important fluids for the Earth's ecosystem and for a large variety of technical applications. The properties of water and aqueous mixtures play a crucial role in engineering areas such as power generation through steam turbines, heat management, marine technologies and seawater desalination or drinking and wastewater treatment. In thermal applications, which fall within the primer scope of the Thermodynamics department at IT CAS, aqueous mixtures with lower alcohols such as methanol and ethanol, or ethylene glycol, serve as key components of heat transfer liquids and antifreeze in the heat and cold distribution, including the combustion engine cooling, the battery cooling in electric vehicles or the heating of cabins of public transport vehicles [1]. Most of these liquids exhibit a considerable decrease of the freezing temperature in a binary aqueous mixture which is substantially lower than that of the individual components. For instance, binary system with 60 % ethylene glycol mass fraction has the freezing temperature of $-51\,^\circ\mathrm{C}$ compared to $0\,^\circ\mathrm{C}$ of pure water and $-13\,^\circ\mathrm{C}$ of pure ethylene glycol [2]. Other small-concentration admixtures include corrosion inhibitors or additional non-toxic bio-component such as glycerol [3]. Systems with salts such as sodium chloride (NaCl), potassium chloride (KCl) or calcium chloride ($CaCl_2$) represent another group of working liquids employed, e.g., in secondary refrigeration circuits [4] for larger systems such as supermarket cold storage rooms. Secondary refrigerants lower the demands on the charge of primer refrigerant. This improves the safety and environmental impact of such systems as the primer refrigerants are typically based either on flammable hydrocarbons (HC) such as propane R290 or isobutane R600a or environmentally unfavorable halogenated hydrocarbons (HFC, HCFC) such as R134a or R513A with high global warming potential (GWP) [5]. Aqueous mixtures with

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[1] International Association for the Properties of Water and Steam; https://iapws.org/

lithium bromide (LiBr) and lithium chloride (LiCl) find application potential also in absorption refrigeration [6] or absorption power cycles with low-temperature heat sources [7].

Without any doubt water is the best described fluid and as such is used as the reference in many scientific and engineering applications. In the field of thermophysical properties, water has a crucial importance as the calibration fluid of experimental instruments. IAPWS is one of the international organizations trying to address properties of water and its mixtures especially with regard to engineering applications. Of particular interest are thermophysical properties, cycle chemistry guidelines, and other aspects of high-temperature steam, water and aqueous mixtures relevant to thermal power cycles and other technical and scientific areas.

1.2 Water at low temperatures

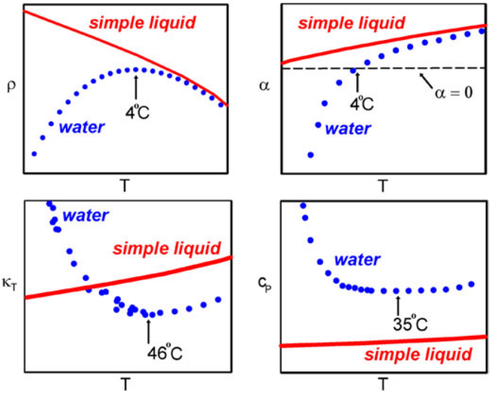

Figure 1: Anomalous properties of ordinary water at low temperatures compared to simple liquid (e.g., methane); ρ – liquid density, α – thermal expansion coefficient, κ_T – isothermal compressibility, c_p – isobaric heat capacity (taken from Debenedetti [8]).

Even though, aqueous systems have attracted attention of uncountable amount of scientists, there are still areas requiring further investigation, such as the anomalous properties below the room temperature. The best-known anomaly of liquid water compared to other simple liquids is the density maximum at 4 °C above the freezing temperature of 0 °C at 0.1 MPa. Other anomalies become pronounced in the supercooled region, i.e. in the thermodynamically metastable state below the equilibrium freezing temperature [9], [10]. Figure 1 taken from Debenedetti [8] shows the temperature trend of the selected thermodynamic properties of ordinary water at ambient pressure of 0.1 MPa. In the low-temperature region, isothermal compressibility and isobaric heat capacity show steep increases, while thermal expansion exhibits rapid drop with decreasing temperature. A serious obstacle to a definitive explanation of these anomalies is the difficulty of performing accurate experiments under the metastable supercooled conditions. Figure 2 taken from a comprehensive review article on supercooled

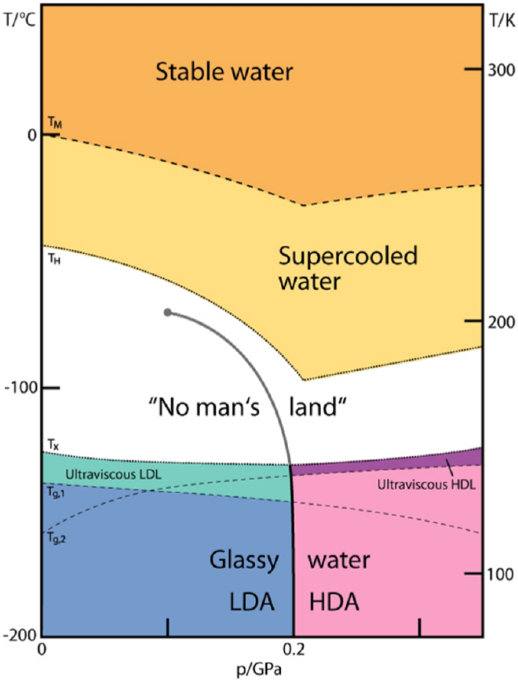

Figure 2: Temperature–pressure diagram of noncrystalline water (taken from Gallo et al. [11]); LDA – low-density amorphous ice, HDA – high-density amorphous ice, LDL – low-density liquid, HDL – high-density liquid.

water by Gallo et al. [11] shows the temperature–pressure phase diagram of noncrystalline water. The low-temperature anomalies of liquid water observed within the stable and supercooled regions seem to be quite well explained by the existence of the low-density liquid (LDL) and the high-density liquid (HDL) at temperatures below $-120\,^\circ\mathrm{C}$. The existence of such two liquid states with different densities would point on the liquid-liquid critical point (LLCP) referred also as the second critical point of water (gray dot at the end of a solid line in the white region). The associated critical fluctuations might be source of low-temperature anomalies observed in the supercooled liquid water and in the amorphous glassy water. The region below the homogeneous nucleation temperature T_H and above the crystallization line T_X is called the no-man's land. In this region, the crystalline ices have been observed experimentally so far. LDA and HDA denote the low- and high-density glassy solids (amorphous ices) observed experimentally by Mishima et al. [10]. LLCP would be located on an extended first-order LDA and HDA phase transition to the lower pressure and higher temperature region. Since the existence of LLCP cannot be verified experimentally, the molecular simulations are being used to investigate the low-temperature water. The second critical point is being assumed at $T_\mathrm{C2} \approx -70\,^\circ\mathrm{C}$ and $p_\mathrm{C2} \approx 140\,\mathrm{MPa}$, however with very large uncertainty.

The debate on the existence of two liquid states with different densities and the second critical point is still ongoing. Therefore any new experiments supporting or refuting this hypothesis are of high importance.

1.3 Surface tension of liquid water

The surface tension can be in a simplified way described as the tendency of a liquid to shrink its free surface, and eventually its volume, e.g., in case of droplets, to a minimum level. It is caused by molecular forces acting on the liquid surface, where molecules in the liquid phase have stronger attraction to each other than with the molecules in the gas (vapor) phase. The surface tension plays an important role in many natural, biological and technical processes.

The temperature dependence of the surface tension of water can be described by the correlation of Vargaftik et al. [12] from 1983, which was later approved by IAPWS as the international standard [13]. The current standard is given as

$$\sigma(T) = B\tau^{\mu}\left(1 + b\tau\right), \tag{1}$$

where $\tau = 1 - T/T_\mathrm{C}$ is the relative distance from the critical point ($T_\mathrm{C} = 647.096\,\mathrm{K}$) and the critical exponent μ has value of 1.256. The coefficients B and b were correlated to the available experimental data and have values of $B = 235.8\,\mathrm{mN/m}$ and $b = -0.625$. Recently, several new correlations for the surface tension of ordinary water were developed, e.g. by Pátek et al. [14], Kalová and Mareš [15] or the correlations based on experimental data, including those presented in this dissertation, and molecular simulations by Rogers et al. [16] published in an article in the *Scientific Reports* journal.

Main motivation for the work of Rogers et al. [16] and other theoretical studies, based mostly on the molecular simulation approaches, such as by Lü and Wei [17], Wang et al. [18], or Malek et al. [19] focused on the surface tension of water is the possibility of another low-temperature anomaly of water. The surface tension is suspected to show a sudden increase in the temperature trend at low temperatures below approximately −8 °C. This anomaly has been supported primarily by the historical experimental data by Hacker [20] from 1951. The surface tension measured in a horizontal capillary tube followed the standard temperature trend at temperatures above 0 °C. However, in the subzero region, a substantial increase in surface tension was observed with decreasing temperature. This anomaly has been later referred as the second inflection point (SIP) in the temperature trend of the surface tension of water. The first (regular) inflection point appears within the stable region at temperature of 256 °C. **The SIP anomaly can be considered as another proof of the existence of two states of water at low temperatures**, i.e. the high-density liquid (HDL) and the low density liquid (LDL). For example, in 2005, Hrubý and Holten [21] developed a two-structure model of thermodynamic properties and surface tension of supercooled water, which fitted quite well the Hacker [20] data as shown in figure 3. It should be noted that other experimental data for the surface tension of water below 0 °C available till 2014 were limited to the works of Humphreys and Mohler from 1895 [22], Floriano and Angell from 1990 [23], and Trinh and Ohsaka from 1995 [24]. Unfortunately, these data suffer from considerable scattering or do not reach sufficiently low temperatures to adequately describe the surface tension of supercooled water.

In order to verify or refute the existence of SIP anomaly in the sur-

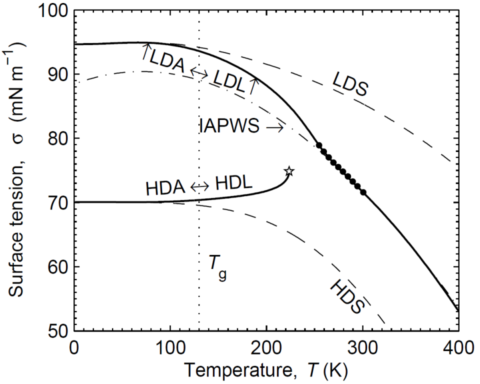

Figure 3: Surface tension of liquid and amorphous water; solid lines – model by Hrubý and Holten [21]; dots – data by Hacker [20] showing a sudden change of slope (figure taken from Hrubý and Holten [21]).

face tension of water, the research team from IT CAS led by Dr. Jan Hrubý (head of the Thermodynamics department) and Dr. Václav Vinš (head of the Laboratory of phase transition kinetics and later the Laboratory of thermophysical properties) initiated in 2011 a new research topic focused on the experimental investigation of surface tension of supercooled aqueous mixtures. As it will be further discussed, the initial experiments based on unique experimental techniques of own design did not follow the trend of historical data by Hacker [20] and did not confirm the existence of SIP anomaly down to −25 °C [25]–[27]. On the other hand, the final experiments carried out down to −31.4 °C with an improved apparatus [28] show an increasing deviation from the IAPWS standard [13] extrapolated to subzero temperatures. Consequently, the SIP anomaly in the temperature trend of water surface tension seems possible, however at much lower temperatures than originally expected.

2 Development of experimental techniques

Experimental techniques developed at IT CAS enable the measurement of surface tension of aqueous systems at low temperatures, with a special focus on metastable supercooled conditions. Experiments with systems under the thermodynamically metastable conditions set several additional requirements compared to *standard* equilibrium measurements, which can briefly be summarized as follows

1. **high purity of the sample**, i.e. avoid any impurities that may act as nucleation cores leading to a phase transition into a more thermodynamically stable phase/state,
2. **limited time scale of the experiment**, since the metastable system would transfer into the thermodynamic equilibrium after a sufficiently long time,
3. **small amount of the sample**, as in a larger system the probability of initiating a phase transition rises due to the higher risk of impurities.

In order to overcome these *obstacles* following approaches were selected in the design of the new experimental apparatuses.

- Fused silica capillary tubes with inner diameters of around 0.30 mm were used in the capillary–based experiments. In this case, relatively small liquid samples could be employed, while the properites of aqueous liquids can still be considered macroscopic, i.e. not influenced by the interactions with solid surfaces.
- The capillary tubes were placed in a special glass chamber equipped with optical glasses and connected to two thermostatic baths that allowed rapid change and, most of all, fast stabilization of temperature.
- Great attention was paid to the cleaning of the capillary tubes and sample containers as well as the sample purity.
- The ultrapure water was used for all experiments, except for the measurements with seawater when the IAPSO[2] standards from the OSIL company[3] were purchased. The ultrapure water was prepared from the Prague tap water purified in a stepwise manner with the reverse osmosis and the analytical purification system.

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[2] International Association for the Physical Sciences of the Oceans; https://iapso-ocean.org/

[3] Seawater Standards, https://osil.com/product-category/seawater-standards (OSIL, Hampshire PO9 1QN, United Kingdom).

- The capillary tubes were flushed and in later experiments also pressurized with high-purity helium, which shows low adsorption on the surface and solubility in aqueous liquids [29].

It should be noted that the experimental methods have been gradually improved in order to achieve deeper degrees of supercooling on the one hand and to obtain more accurate results on the other.

2.1 Modified capillary rise method

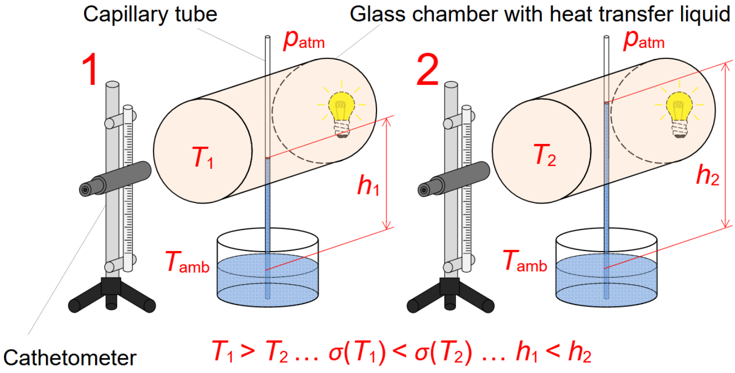

Figure 4: Measurement principle of the modified capillary rise technique.

Figure 4 shows a simplified scheme of the measurement principle of the modified capillary rise technique developed in the period 2011–2014 [25], [30]. A fused silica capillary tube in a vertical position is partly installed inside a temperature control chamber. The lower end of the capillary tube is submerged in the container with the liquid sample. Due to the surface forces acting on the vapor(gas)–liquid interface, the liquid column elevates to a certain height h given by the inner diameter of the capillary tube d, the surface tension σ and density ρ of the liquid

$$h = \frac{4\sigma\cos\theta}{\rho g d}\,. \tag{2}$$

g stands for the local gravity and θ for the contact angle of water on fused silica, which is close to 0° for a descending meniscus. Equation (2) describes the equilibrium between the surface forces on the liquid meniscus and the mass, or the hydrostatic pressure, of the liquid column elevated above the main liquid surface in the container. The surface tension, the liquid density, and consequently also the resulting height should be considered temperature dependent. The experiment is designed such that only the top part of the liquid column is placed inside the temperature control chamber. The change in temperature from T_1 to T_2 causes a change in surface tension resulting in a height change. In case $T_2 < T_1$, the surface tension increases and the height rises from h_1 to h_2, as depicted in figure 4. The increase in surface tension depending on a given temperature drop can therefore be determined from the height difference, which has been detected using a cathetometer and, in later experiments, a digital camera installed on a height gauge.

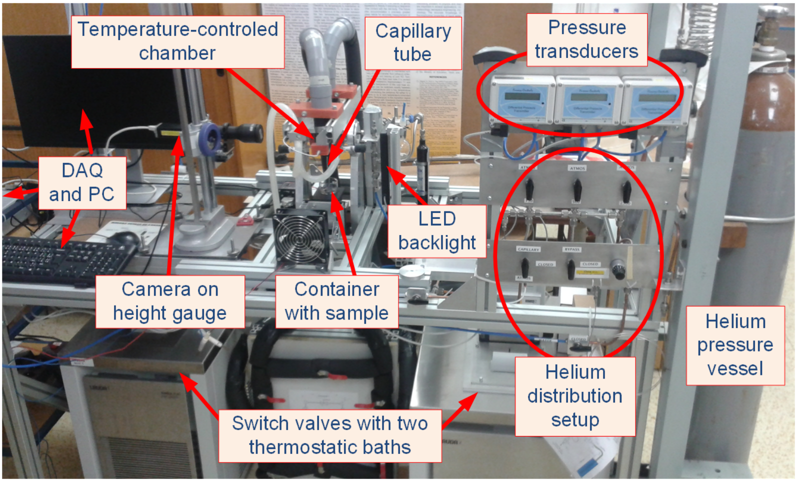

Figure 5: Photo of the experimental setup of the modified capillary rise technique in its present form in late 2024.

Photo of the experimental apparatus at the present state of late 2024 is shown in figure 5. The temperature control chamber with the capillary tube is installed on a aluminum support frame. The two thermostatic baths with liquid ethanol, maintaining temperature change with fast stabilization within approximately 7 minutes for a jump of 25 °C, are located under the support frame. On the right side, the helium distribution setup is installed. Left part of the apparatus contains height gauge with a digital camera and a measuring PC with data acquisition units.

The inner diameter of the chromatographic capillary tubes was inspected optically under a microscope. However, such analysis is only possible on a carefully treated cross-section and does not provide information on the actual diameter of the capillary tube with a total length of around 0.4 m. The inner diameters of the capillary tubes needed in equation (2) are therefore determined from the reference measurements with ultrapure water at a *stable* temperature above the freezing point, typically $T_{\mathrm{ref}} = 15\,^{\circ}\mathrm{C}$. The diameter is related to the surface tension of ordinary water given by the IAPWS standard [12], [13] at the reference temperature $\sigma_{\mathrm{w}}(T_{\mathrm{ref}})$. Consequently, the main output quantity of our experiments is the relative surface tension Y given as

$$Y(T,x) = \frac{\sigma(T,x)}{\sigma_{\mathrm{w}}(T_{\mathrm{ref}})}\,, \tag{3}$$

where σ is the surface tension of a given liquid at the target temperature T and x stands for the molar composition in case of aqueous mixtures.

2.2 Capillary rise with counterpressure

The capillary elevation described in figure 4 may suffer from hardly detectable error, when the capillary tube inner diameter can vary along the length. Inspection of the inner diameter of the fused silica capillary tubes along their length showed that the inner diameter of employed capillary tubes does not vary by more than 1.5 % along approximately 0.8 m of capillary tube length [31]. Even though such error may appear relatively low, it may still negatively influence the resulting surface tension data. A new experimental technique that overcomes the problem of possibly varying inner diameter of the capillary tube was therefore developed in the period between 2014 and 2015.

In the improved capillary rise method, a well-defined counterpressure of an inert gas (helium) is applied to the upper part of the capillary tube such that it compensates for the surface tension and subsequently the possible height changes. The counterpressure is tunned in a way that the liquid meniscus stays at a constant position within the capillary tube. The principle of the experiment is depicted in figure 6. In case, the temperature inside the glass chamber with the capillary tube is decreased from T_{ref} to the target temperature T_2, the surface tension increase is compensated by a slight counterpressure of helium in the range from several to a maximum

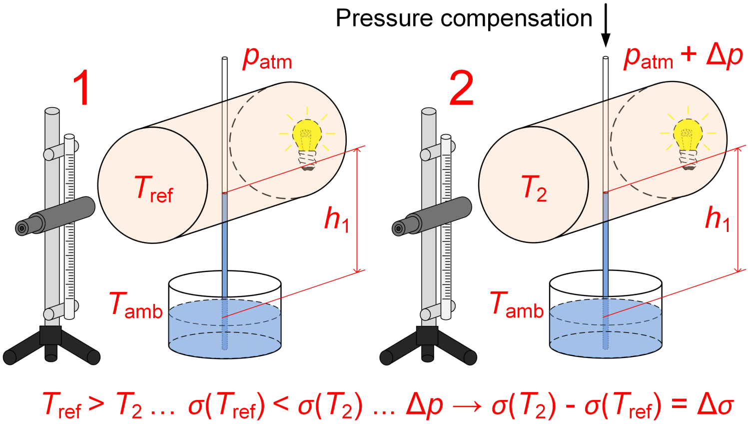

Figure 6: Measurement principle of the capillary rise with helium counterpressure.

of approximately 100 Pa. Flushing of the capillary tube with helium and tuning of counterpressure is performed with the helium distribution setup of own design.

2.3 Capillary rise with container elevation

As an alternative to the counterpressure technique, the apparatus was equipped with a lift table that enables variation of the vertical position of the liquid container under the capillary tube. The table position is varied using a servo actuator and detected by the digital indicator. The principle of surface tension measurement is similar to the counterpressure technique, where the intention to keep the upper liquid meniscus in a constant position inside the capillary tube remains the same. The change in surface tension caused by the different temperature is compensated by varying the height of the liquid surface inside the sample container.

2.4 Experiments with horizontal capillary tube

Inspired by the experiments on the surface tension of supercooled water carried out by Hacker [20] in 1951, our team has tried to develop a similar technique based on measurements inside a horizontal capillary tube [32], [33]. In the case of horizontal experiments, one end of the capillary tube

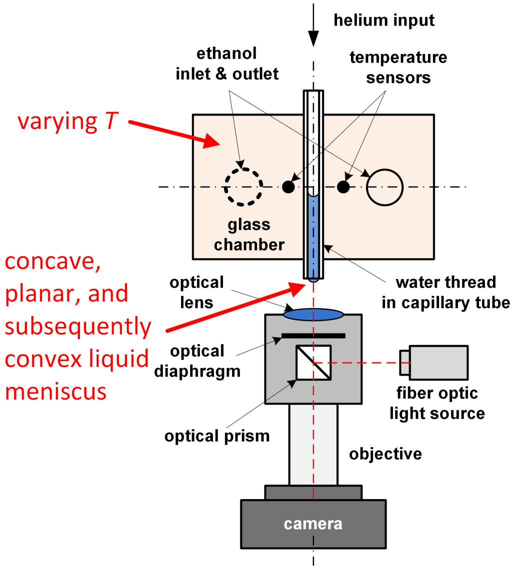

Figure 7: Scheme of the experimental apparatus with the horizontal capillary tube; view from the top.

is also connected to the helium distribution setup. However, the helium counterpressure is significantly higher in the range of 800 to 1100 Pa in case of pure water. The main reason for such *high* pressure is that it entirely compensates for the surface forces on the liquid meniscus, contrary to the capillary rise, where the surface forces act primarily against the hydrostatic forces of the elevated liquid column. In the case of horizontal technique, an approximately 2 cm long liquid thread is sucked inside the capillary tube. The liquid sample is held near the open end of the capillary tube by the helium counterpressure applied from the other side of the capillary tube. By increasing the helium counterpressure, the outer meniscus changes from concave to planar and subsequently convex shape. In case of a planar geometry, the meniscus does not exhibit any surface forces. Hence, the helium counterpressure is solely compensated by the surface forces acting on the second meniscus inside the capillary tube. The surface tension can therefore be determined as

$$\sigma = \frac{\Delta p}{4\cos\theta} d \,, \tag{4}$$

where Δp stands for the helium counterpressure. Simplified scheme of the horizontal experiment can be seen in figure 7.

The open end of the capillary tube requires special grinding and polishing to assure its flatness and perpendicularity to the main capillary tube axis [34]. The liquid meniscus at the open end is illuminated and observed by an in-house designed optical setup [35].

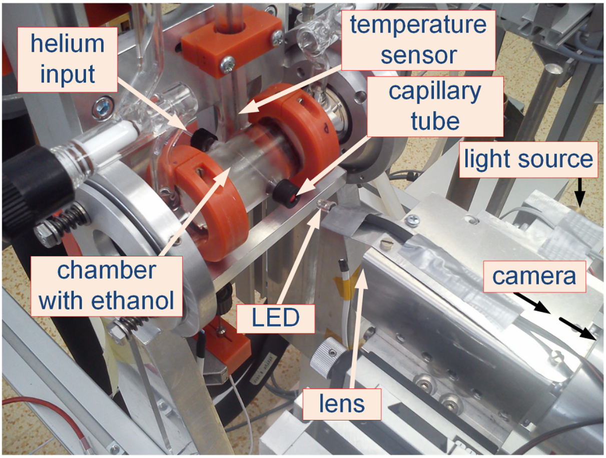

Figure 8: Photo of the horizontal capillary tube inside the temperature control chamber before the installation of thermal foam insulation.

Figure 8 shows photo of the final arrangement of the horizontal method before the installation of thermal foam insulation on the glass chamber and the ethanol tubing. LED installed at the top of the metal box, containing the optical prism with diaphragm and a lens, served for the synchronization of the video record with the data acquired for pressure and temperature. A typical measurement of surface tension consisted of a gradual two-loop change of helium counterpressure such that the outer liquid meniscus twice changed its shape from concave to planar and subsequently convex geometry and vise versa. In such case, the value of counterpressure corresponding to the planar meniscus was determined from four pressure values [27].

2.5 Additional measurements of surface tension and liquid density

In case of aqueous mixtures, the surface tension and also the liquid density at 0.1 MPa were investigated by using self-calibrated commercial instruments. Tensiometer Krüss K100 Mk2 in combination with a thermostatic liquid bath enables measurement of surface tension with the Wilhelmy plate and the du Noüy ring methods in the temperature range from −15 to 80 °C [36]. In addition, the tensiometer allows for the liquid density measurement based on the single-sinker buoyancy method [37], [38]. Recent experiments carried out in our Laboratory cover verification measurements of surface tension and density of binary aqueous systems such as those with methanol or ethylene glycol [39].

As mentioned in section 2.1, in the capillary rise techniques, the liquid density of the investigated sample needs to be known for the evaluation of the surface tension; see equation (2). In the introduced experiments, the temperature of the liquid column changes along the height. The lower part of the capillary tube submerged partially in the liquid container is kept at an ambient temperature of around 22 °C, while the upper part is located in the temperature control chamber, where the temperature can vary between 40 and −30 °C. Consequently, the temperature dependence of liquid density should be defined with high precision over the given range. In case of ordinary water and seawater, the multiparameter equations of state by Wagner and Pruß [40] and by Feistel [41] approved as international standards the IAPWS-95 EoS [42] and the IAPWS Formulation 2008 for the Thermodynamic Properties of Seawater [43] were used, respectively. For other binary aqueous systems such as with lower alcohols [44], ethylene glycol [39] or sodium chloride, the temperature-composition correlations for liquid density at 0.1 MPa are used.

Liquid density of weakly described aqueous systems has been measured by a highly-sensitive vibrating tube densimeter (VTD) Anton Paar DMA 5000 M with the resolution of down to $0.001\,\mathrm{kg\cdot m^{-3}}$. The densimeter determines the liquid density based on a shift in the oscillation period of a vibrating borosilicate glass U-tube filled either with dry air or the liquid sample. Our team has developed own calibration approach for the atmospheric VTD [45] providing more information on the repeatability of the measurements and the uncertainty of obtained data. The calibration is based on the following equation taken from the work by Fritz et al. [46]

$$\rho_{\text{fluid}}(T) = A(T)\left[1 + V_1 \Delta D_0(T) + V_2 \Delta D_0(T)^2\right] PQ(T)^2 - B(T), \qquad (5)$$

where $PQ = \tau/\tau_{\text{ref}}$ stands for the relative period of oscillation, ΔD_0 is the damping difference, and V_1 and V_2 are the damping calibration constants. A and B are the temperature dependent calibration constants. The relative period of oscillation PQ is a ratio between the oscillation period of the U-tube τ and the period of oscillation of a reference glass rod located close to the center of the U-tube τ_{ref}. The damping difference is given as $\Delta D_0 = \Delta D_{0,\text{sample}} - \Delta D_{0,\text{air}}$. Based on an extensive measurement campaign with pure water, dry air, and various liquids ranging from low-viscosity toluene to highly viscous glycerol, the standard combined uncertainty of fluid density was found to be $0.030\,\text{kg}\cdot\text{m}^{-3}$. However, for viscous liquids such as low-temperature glycerol, the standard combined uncertainty can increase up to $0.14\,\text{kg}\cdot\text{m}^{-3}$ [45].

The atmospheric VTD has been used to measure the liquid densities of aqueous systems with ethylene glycol, glycerol, or methanol over the entire composition range, seawater with a standard ocean salinity $35\,\text{g}\cdot\text{kg}^{-1}$, squalane and even fluorocarbon-based heat transfer liquids at temperatures typically from 0 to 90 °C [47]. With careful calibration, the high sensitivity of the instrument provides accurate density data that can be used for the development of temperature-density correlations needed to evaluate the surface tension measured with the capillary-rise techniques [39].

3 Results

This section contains a brief description of the achieved results described in the scientific articles published in the impacted journals and the conference proceedings indexed in the Web of Science[4] and Scopus[5] databases. Full references to the articles are listed in the second part of the Bibliography marked as *Own publications related to dissertation.*

3.1 Experiments with supercooled water

Preliminary information on the development of new experimental apparatus based on the modified capillary rise technique (section 2.1) together

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[4] Web of Science / Web of Knowledge; https://www.webofknowledge.com

[5] Scopus; https://www.scopus.com

with the results on surface tension collected down to −11 °C were presented in the conference article ***Design of an experimental apparatus for measurement of the surface tension of metastable fluids*** [30].

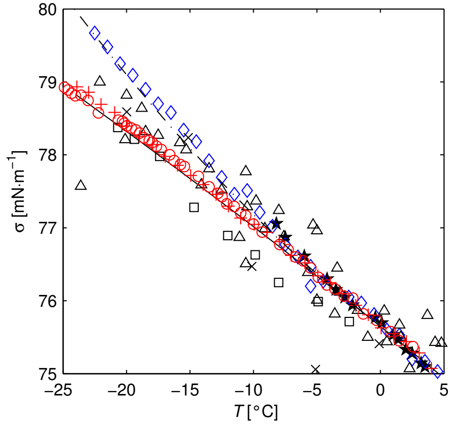

Figure 9: Surface tension of supercooled water. Experimental data: +, Prague setup; ○, Pilsen setup; ★, Humphreys and Mohler [22]; ◇, Hacker [20]; △, Floriano and Angell [23]; □, Trinh and Ohsaka [24]. ×, Lü and Wei molecular simulation [17]; −·, Dutcher et al. correlation [48]; −, IAPWS standard given by equation (1) [13]. Figure from Hrubý et al. [25].

The first successful experiments at high degrees of supercooling of up to 25 °C were presented in a prestigious journal in the field of physical chemistry the *Journal of Physical Chemistry Letters* issued by the American Chemical Society (ACS). The article entitled ***Surface tension of supercooled water: No inflection point down to −25 °C*** [25] describes experiments carried out with two similar capillary rise apparatuses: the one employing liquid ethanol for the temperature change and stabilization developed by our team at IT CAS in Prague and a similar apparatus, however with a gaseous cooling, designed by Prof. Radim Mareš in collaboration with Dr. Jan Hrubý, which was installed at the University of West Bohemia in Pilsen. As can be seen in figure 9, both data sets (red symbols) did not confirm the SIP anomaly as they did not follow the temperature trend of the historical data by Hacker [20] (blue diamonds).

Further experiments carried out with helium counterpressure (section

2.2) keeping the liquid meniscus at a fixed height inside the vertical capillary tube confirmed the previous findings [25]. The article ***Surface tension of supercooled water determined by using a counterpressure capillary rise method*** [26] provided more details on the experiment and showed that the surface tension of supercooled water can be well reproduced by the IAPWS standard [12], [13] extrapolated below 0 °C. The articles from 2014 [25] and 2015 [26] are referred in the revised release on the surface tension of ordinary water by IAPWS [13].

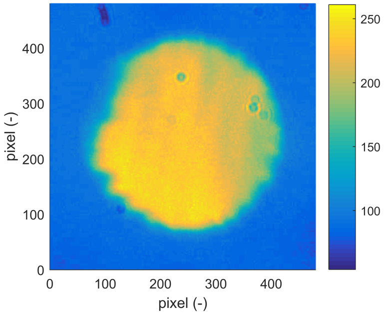

Figure 10: Contour plot showing the weighted sum over three channels of the RGB color model (RGB intensity) of the planar meniscus in a horizontal capillary tube. Example for the measurement at −10.33 °C. Figure from Vinš et al. [27].

Development of the horizontal technique is described in several conference articles. Initial design of the optical setup observing the liquid meniscus at the open end of the capillary tube together with the improvements of capillary tube grinding and polishing is presented in the article ***Influence of the light source on the liquid optical element planarity measurement*** [35]. Design of the entire apparatus with the horizontal capillary tube including preliminary experiments down to −7 °C and subsequently −11 °C is described in two other articles ***An apparatus with a horizontal capillary tube intended for measurement of the surface tension of supercooled liquids*** [32] and ***Improvements of the experimental apparatus for measurement of the surface tension of supercooled liquids using horizontal capillary tube*** [33]. The final results obtained with the horizontal method were published in the article entitled ***Surface tension of supercooled water: Inflection point-free course down to 250 K confirmed using a horizontal capillary tube*** in 2017 [27]. Although the article did not show any new findings in the field of water anomalies at low temperatures, the presented results are of high importance as they confirm previous findings achieved with the capillary rise based experiments [25], [26] employing different method.

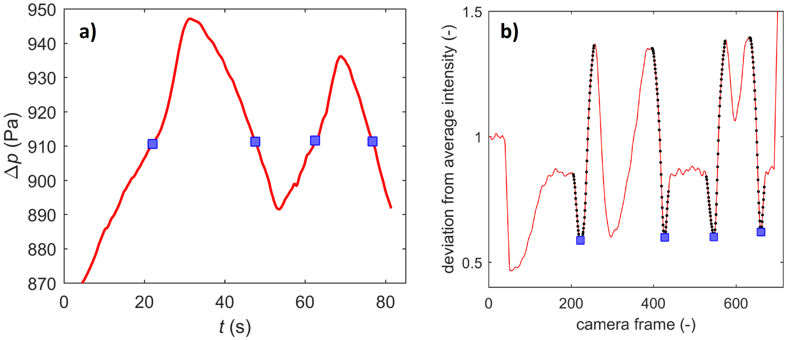

Figure 11: Data records for horizontal measurement at −10.33 °C. a) Pressure; –, recorded pressure; ■, pressure corresponding to the planar meniscus; Δp = 911.2 Pa. b) Deviation from the average RGB intensity of the illuminated area relative to the first video frame; –, deviation from the average RGB intensity; ■, minima in the deviation from the average RGB intensity. Figures from Vinš et al. [27].

Figure 10 shows a contour plot of the RGB color model corresponding to the picture of a planar liquid meniscus at the open end of the horizontal capillary tube taken by a digital camera. As mentioned in section 2.4, the helium pressure was gradually changed such that the liquid meniscus twice changed its shape from concave to planar and subsequently convex geometry and vise versa. Figure 11 shows an example of the recorded pressure loops (a) and corresponding changes in the RGB intensity of the illuminated liquid meniscus (b) for the measurement at −10.33 °C.

After 2017, the focus of our research changed from supercooled pure water to various aqueous mixtures, as described in the following section. Later, we have noticed that the experimental results started to attract the

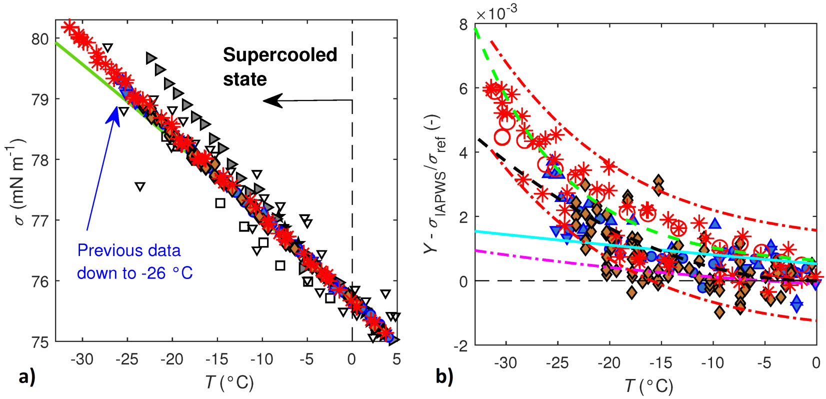

Figure 12: a) Final data for surface tension of supercooled water; b) Comparison of the extremely supercooled data with available correlations and previous measurements [25]–[27]. Difference of the relative surface tension Y, eq. (3), from the IAPWS standard extrapolated below the triple point. —, IAPWS standard [13] (eq. 1); ★, Humphreys and Mohler [22]; ▶, Hacker [20]; ▽, Floriano and Angell [23]; □, Trinh and Ohsaka [24]; —, correlation by Pátek et al. [14]; —·, correlation by Viisanen et al. [49]; – –, MD-based correlation by Rogers et al. [16]; – –, linear extrapolation of IAPWS standard [13] from 0.01 °C; ●, Hrubý et al. [25]; ▲, Vinš et al. p-data [26]; ▼, Vinš et al. h-data [26]; ♦, Vinš et al. [27]; ∗, this study *height* data; ○, this study *counterpressure* data; —·, uncertainty range of new data $U(Y)$. Figures taken from Vinš et al. [28].

attention of several research groups worldwide that are working on the theoretical description of low-temperature anomalies of water. In particular, our data were confronted with the predictions of molecular simulations using various molecular models of water, such as SPC/E, TIP4P/2005, or WAIL. Research groups like F. Wang et al., [16], [50], Malek et al. [19], or X. Wang et al. [18] tried to shed light on the existence of the SIP anomaly in the surface tension of water. We have therefore tried to improve the capillary rise techniques such that higher degrees of supercooling could be achieved still with good accuracy. The improvements covered, e.g., modifications of the temperature control unit enabling faster stabilization at lower temperatures, more accurate control of the height gauge and of the helium counterpressure, accurate calibration of temperature and pressure probes, careful preparation of water samples with regard to their purity, and cleaning of the capillary tubes. The article ***Possible anomaly in the surface tension of supercooled water: New experiments at extreme supercooling down to −31.4° C*** published again in the *Journal of Physical Chemistry Letters* in 2020 [28] represents our **final contribution to the experimental research of the surface tension of supercooled water**. Figure 12 shows final data for the temperature dependence of the surface tension of pure water (a) together with the deviation of the relative surface tension Y given in terms of eq. (3) from the extrapolated IAPWS standard [12], [13] (b). Contrary to previous works [25]–[27], the new measurements show a slight systematic deviation at temperatures below −20 °C from the IAPWS standard [12], [13] extrapolated below 0 °C. Therefore, the new data collected down to −31.4 °C provide room for an existence of the SIP anomaly in the deeply supercooled region. Unfortunately, further experiments at even lower supercooling are not possible with our equipment and with the 0.3 mm capillary tubes, where the water can still be considered macroscopic. It should be noted that the homogeneous freezing limit of water at 0.1 MPa is of around −38 °C.

3.2 Surface tension and density of aqueous mixtures

The aqueous systems investigated cover two groups of mixtures: the systems with alcohols such as methanol, ethanol, and ethylene glycol, which reduce the surface tension, and the mixtures with salts including sodium chloride or ammonium sulfate, which usually slightly increase the surface tension. The low-concentration systems are interesting in terms of the existence of SIP anomaly or other unexpected temperature and composition trends in the surface tension.

3.2.1 Density of aqueous mixtures

In order to evaluate the surface tension from the capillary rise techniques, the liquid density of a given mixture have to be known to determine the hydrostatic pressure of the elevated liquid column. As discussed in section 2.5, the vibrating tube densimeter Anton Paar DMA 5000 M enables accurate measurement of density with the expanded uncertainty of down to $0.060\,\mathrm{kg\cdot m^{-3}}$. Development of own calibration technique including assessment of the density uncertainties is described in article ***Comments on***

temperature calibration and uncertainty estimate of the vibrating tube densimeter operated at atmospheric pressure [45]. The results for water + ethylene glycol have been presented on couple of scientific conferences including the Annual IAPWS Meeting in Torino, 2023 and the 22nd Symposium on Thermophysical Properites in Boulder, 2024, and recently published in the article ***Density and surface tension of water + ethylene glycol mixtures as key components of heat transfer liquids*** [39]. Other investigated systems include methanol and glycerol.

Comparative measurements of density has been performed using the tensiometer Krüss K100 Mk2. The single sinker buoyancy measurements are not influenced by the sample viscosity and can be carried out at temperatures down to −15 °C. However, the expanded uncertainty of the buoyancy experiments is almost 15-times larger than in case of VTD.

3.2.2 Surface tension of aqueous mixtures

Experimental research on the surface tension of aqueous mixtures at low temperatures was initiated in 2017. The initial experiments carried out with the modified capillary rise method described in section 2.1 and marked as h involved measurements with lower alcohols, ethylene glycol and IAPSO standard seawater samples with various salinities. Recent experiments conducted since 2022 are based on the helium counterpressure method discussed in section 2.2 (marked as dp) as it was found to achieve better reproducibility of the measured data.

Seawater

With regard to the activities of our research team in IAPWS, we have decided to carry out an experimental campaign on the surface tension of seawater at low temperatures. A new standard for the surface tension of seawater has been prepared based on the correlation developed by Nayar et al. [51] in 2019. The modified capillary rise technique was used to collect new data for a series of IAPSO seawater standards with absolute salinities of 10, 30, 35, and 38 $\mathrm{g \cdot kg^{-1}}$. Figure 13 compares our results with the literature data available at temperatures above 1 °C. Our data published in the article ***Surface tension of seawater at low temperatures including supercooled region down to –25 °C***, [52] were found to be well reproduced by the correlation of Nayar et al. [51] extrapolated below

1 °C. The range of validity of the new IAPWS guideline for the surface tension of seawater could therefore be extended into the supercooled region at temperatures down to $-25\,^\circ$C for salinities up to $38\,\mathrm{g\cdot kg^{-1}}$ [53].

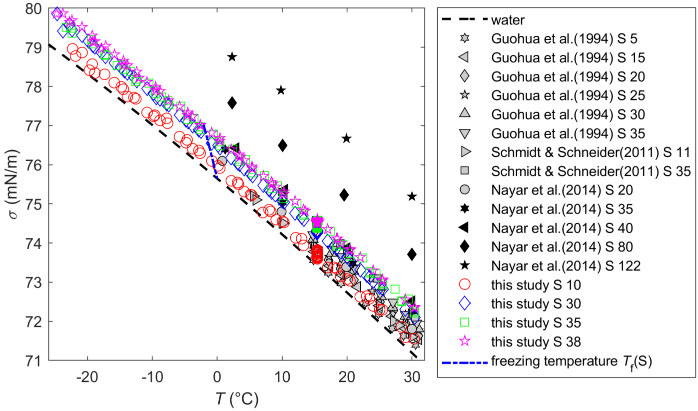

Figure 13: New data for the surface tension of seawater with absolute salinities $S = 10$ to $38\,\mathrm{g\cdot kg^{-1}}$ including the supercooled region compared to the literature data (Guohua et al. [54]; Schmidt and Schneider [55]; Nayar et al. [51]), and the IAPWS correlation (1) for pure water extrapolated below 0.01 °C. Freezing point temperature depending on salinity $T_\mathrm{f}(S)$ is taken from Feistel [41]. Figure modified from Vinš et al. [52].

Water + ethylene glycol

Water + ethylene glycol represents the first binary system thoroughly investigated by all the experimental methods described in section 2. The liquid samples with various mass fractions of ethylene glycol were prepared by a standard weighing method using the analytical balance XSE 205 DU (Mettler-Toledo AG, Switzerland) with a resolution of 0.1 mg. The liquid density of pure ethylene glycol and its aqueous mixtures were measured both with VTD and the single-sinker buoyancy methods. The data for surface tension were collected with the modified capillary rise technique (h – section 2.1), the capillary method with helium counterpressure (dp – sec. 2.2) and with the Wilhelmy plate method (sec. 2.5). New correlation for

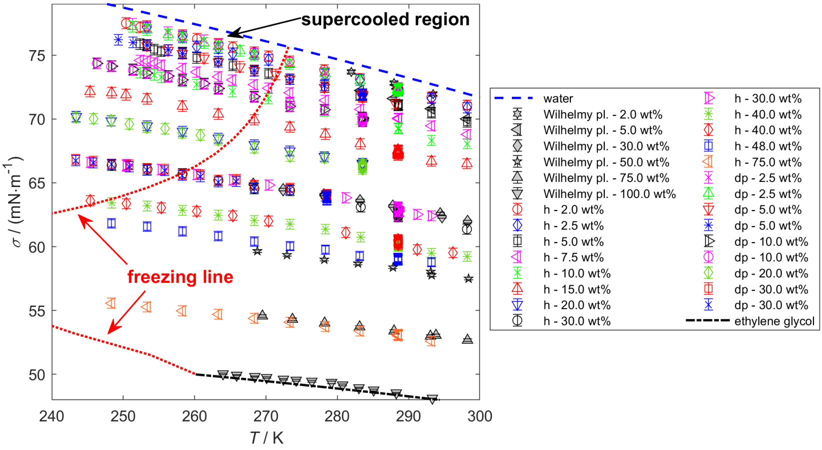

Figure 14: Low-temperature data for the surface tension of water + ethylene glycol binary system obtained in this work with the Wilhelmy plate and the capillary rise (both height h and counterpressure dp) methods compared with the IAPWS standard for pure water (1) and own correlation for ethylene glycol. Mass fraction of ethylene glycol marked as $wt\%$. Surface tension along the freezing line taken from ref. [2] was calculated from the readjusted model by Connors & Wright [56]. Figure modified from Vinš et al. [39].

the saturated liquid density of Rackett-type [57] was developed for pure ethylene glycol. The model for mixture density was developed based on the excess molar volume approach. The semi-empirical models for the surface tension of binary aqueous systems by Connors and Wright [56] and by Wang et al. [58] were readjusted to the new experimental data. The results are summarized in the article ***Density and surface tension of water + ethylene glycol mixtures as key components of heat transfer liquids*** [39]. Example of the new data for surface tension of water + ethylene glycol mixture are provided in figure 14.

Other binary mixtures

Preliminary data for **water + methanol** surface tension measured with the modified capillary rise method (h) were published in the conference article ***Surface tension of aqueous binary mixtures under the supercooled conditions – Development of the measuring technique and preliminary data for water + lower alcohols*** [44]. The final results obtained with the counterpressure technique (dp) are intended for publication in an impacted journal during 2025.

Figure 15 shows examples of the temperature dependence of surface tension of **water + ethanol** and **water + sodium chloride** (NaCl). The results obtained with both main modifications of the capillary elevation (i.e. capillary rise h and counterpressure dp) are compared with the additional measurements with the Wilhelmy plate method. The figures show a clear difference between the water + alcohol system and the water + salt mixture. Ethanol considerably decreases the surface tension, where $5\,wt\%$ causes a drop of approximately $10\,\mathrm{mN\cdot m^{-1}}$. On the other hand, sodium chloride slightly increases the surface tension. $5\,wt\%$ of NaCl results in an increase of around $1.5\,\mathrm{mN\cdot m^{-1}}$. It should be noted that such comparison is just illustrative, it would be appropriate to compare the influence of individual admixtures in terms of mole fraction, and actually of their concentrations on the liquid–vapor interface.

Other systems of our interest cover aqueous binaries with salts. Systems with **ammonium sulfate** ($(NH_4)_2SO_4$) and **ammonium nitrate** (NH_4NO_3) are of environmental importance as they act as the nucleation cores during the formation of water droplets and ice crystals in upper atmosphere. Accurate description of the surface tension of these mixtures at low temperatures including the supercooled state would be appreciated by the researchers focused on atmospheric research and nucleation of droplets and ice crystals. For instance, Goy et al. [59] showed that the water microdroplets can be supercooled down to $-42.6\,^\circ\mathrm{C}$ by evaporative cooling.

Multicomponent halide salts consisting of halide anions (e.g., Cl^-, Br^-, F^-) and alkali metal cations (e.g., Na^+, Li^+, K^+, Rb^+), or alkali earth metal cations (e.g., Ca^{2+}, Mg^{2+}) are of growing technical interest. Aqueous mixtures with halide salts can be used as working fluids in the absorption refrigeration and air-conditioning systems [4]. These applications based typically on a multi-stage circuit with different refrigerants in the high-pressure (e.g., $LiCl + H_2O$) and the low-pressure (e.g., $LiBr + H_2O$) loops,

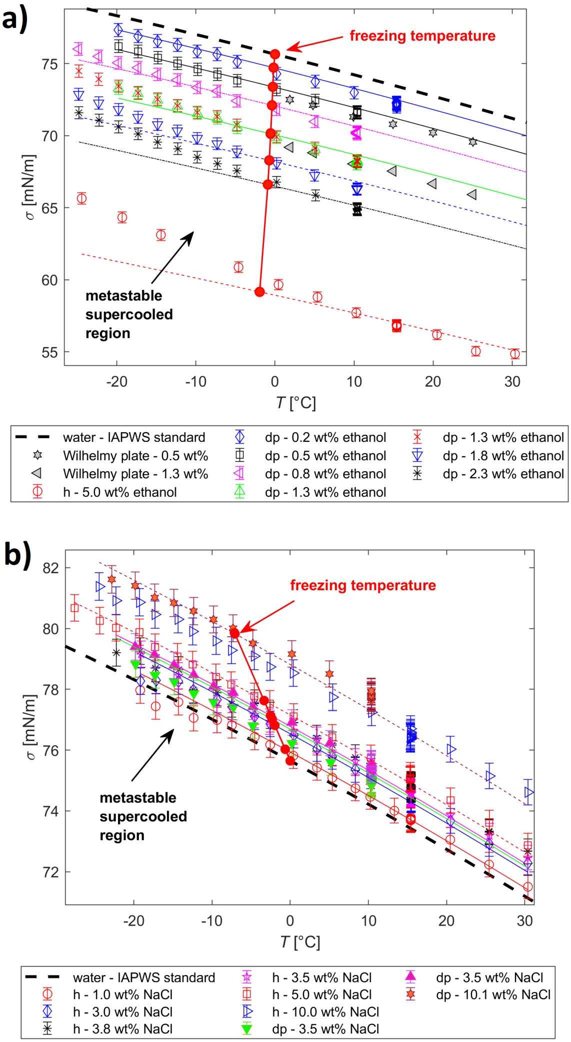

Figure 15: Surface tension of water + ethanol (a) and water + NaCl (b) depending on temperature. Comparison of the capillary rise (h), the helium counterpressure (dp), and the Wilhelmy plate methods. Composition given in terms of admixture mass fraction wt (%).

are of particular interest [6]. With regard to planed phase out of the traditional halogenated refrigerants with high GWP (global warming potential) or their PFAS (perfluoroalkyl and polyfluoroalkyl substances) nature, new alternative circuits and working fluids need to be sought for. For larger refrigeration units, brines, i.e. aqueous mixtures with NaCl or $CaCl_2$ are used as secondary refrigerants to distribute cold over larger areas. Mixtures with aqueous solution of LiBr, LiCl or $CaCl_2$ are being investigated also in the absorption power cycles with low-temperature heat source below 120 °C [7]. For all mentioned systems, the thermophysical properties such as density, heat capacity, thermal conductivity as well as surface tension need to be well known for the reliable and effective design of new heat transfer applications. The temperature region between −30 °C and 150 °C is of primary interest. Our team therefore intents to focus on these fluids in future research.

3.3 Molecular simulations of water surface tension

Next to the experimental research of the surface tension and density of aqueous systems, our team has carried out several molecular simulations of the water vapor–liquid phase interfaces. Two common molecular models of water the extended simple point charge (SPC/E) and the transferable intermolecular potential with 4 points (TIP4P/2005) were used for the modeling of so-called *SLAB* geometry, in which the liquid layer of molecules is located between two layers of vapor phase. The surface tension can be determined from the components of the pressure tensor and the size of the simulation box perpendicular to the liquid layer. The DL_POLY Classic [60] software was used for the molecular simulations performed on the IT CAS cluster. Own codes developed in Matlab were used for the definition of initial geometry and the post-processing of simulated data.

The conference articles indexed in Web of Science and Scopus databases by Planková et al. [61] (***Molecular simulation of water vapor–liquid phase interfaces using TIP4P/2005 model***) and Vinš et al. [62] (***Molecular simulations of the vapor-liquid phase interfaces of pure water modeled with the SPC/E and the TIP4P/2005 molecular models***) provide description of our results on the simulation of vapor-liquid phase interfaces of water at temperatures from 250 to 600 K.

4 Concluding remarks

The in-house developed experimental methods allowed for to obtain unique data for the surface tension of various aqueous systems at metastable supercooled state. The results for supercooled water did not confirm the SIP anomaly in the temperature trend of the surface tension down to $-20\,^{\circ}\mathrm{C}$ [25]–[27]. On the other hand, the final experiments carried out down to $-31.4\,^{\circ}\mathrm{C}$ provide some room for its existence, however at considerably lower temperatures than originally expected [28].

The results presented in this dissertation have direct link to two IAPWS issued documents describing the internationally recommended correlations for the surface tension of ordinary water [25], [26] and the surface tension of seawater [52]. Based on the experiments carried out by our team, the range of validity of both correlations could be extended to temperatures below the freezing point, i.e. into the supercooled region. The IAPWS standard R1-76(2014): Revised Release on the Surface Tension of Ordinary Water Substance [13] from 2014 and G14-19: Guideline on the Surface Tension of Seawater [53] issued in 2019 are provided in the dissertation appendix. The achievements described in the dissertation are directly linked to the IAPWS Helmholtz Award granted in 2019.

Recent experimental data for the surface tension and density of water + ethylene glycol [39] as the key components of many heat transfer liquids were used to develop accurate while easy-to-implement property models that can be employed in the scientific and engineering computations of heat transfer and fluid dynamics problems.

A number of students and young researchers participated in the presented research: Maurice Fransen from the Eindhoven University of Technology – three-month internship at IT CAS in 2013; students and later Ph.D. candidates Barbora Planková (supervisor J. Hrubý) and David Celný (co-supervisor V. Vinš) from the Czech Technical University in Prague (FNSPE); Josefine Gatter from the Dresden University of Technology – four-month internship between 2019 and 2020; Ph.D. candidate Jaroslav Pulec (supervisor V. Vinš) from the Technical University of Liberec (TUL).

The results of the presented research have so far been published in 10 impacted journal articles, 7 conference proceedings indexed in Web of Science and Scopus databases, and discussed at approximately 23 international scientific events. On December 28, 2024, the Web of Science citation record of the articles related to the DSc. dissertation reaches 207 citations with H-index of 8.

The presented work is still an ongoing research. Future activities should focus on the aqueous mixtures with halide salts exhibiting a promising technical potential as alternative environmental friendly heat transfer liquids and refrigerants. The thermophysical properties, including the surface tension need to be know particularly at low temperatures for the effective design of new technical applications.

References

[1] M. Kleiber and R. Joh, “VDI–Wärmeatlas, 11., bearbeitete und erweiterte Auflage,” in S. Kabelac, M. Kind, H. Martin, D. Mewes, K. Schaber, and P. Stephan, Eds. Springer–Verlag Berlin Heidelberg, 2013, ch. Stoffwerte von sonstigen reinen Fluiden, pp. 357–488.

[2] W. Haynes, D. Lide, and T. J. Bruno, Eds., *CRC Handbook of Chemistry and Physics, 97th Edition.* CRC Press - Taylor & Francis Group, 2016.

[3] T. Schütz, *Hucho – Aerodynamik des Automobils: Strömungsmechanik, Wärmetechnik, Fahr-dynamik, Komfort*, Six. Wiesbaden, Germany: Springer Vieweg, 2013.

[4] M. R. Conde, “Properties of aqueous solutions of lithium and calcium chlorides: Formulations for use in air conditioning equipment design,” *Int. J. Thermal. Sci.*, vol. 43, p. 367, 2004.

[5] K. Wang, M. Eisele, Y. Hwang, and R. Radermacher, “Review of secondary loop refrigeration systems,” *Int. J. Refrig.*, vol. 33, pp. 212–234, 2010.

[6] X. She, Y. Yin, M. Xu, and X. Zhang, “A novel low-grade heat-driven absorption refrigeration system with LiCl–H_2O and LiBr–H_2O working pairs,” *Int. J. Refrig.*, vol. 58, pp. 219–234, 2015.

[7] V. Novotný and M. Kolovratník, “Absorption power cycles for low-temperature heat sources using aqueous salt solutions as working fluids,” *Int. J. Energy Res.*, vol. 41, pp. 952–975, 2017.

[8] P. G. Debenedetti, “Supercooled and glassy water,” *J. Phys. Condens. Matter*, vol. 15, R1669, 2003.

[9] O. Mishima and H. E. Stanley, “The relationship between liquid, supercooled and glassy water,” *Nature*, vol. 396, pp. 329–335, 1998.

[10] M. O., C. L. D., and W. E., “An apparently first-order transition between two amorphous phases of ice induced by pressure,” *Nature*, vol. 314, pp. 76–78, 1985.

[11] P. Gallo *et al.*, “Water: A tale of two liquids,” *Chem. Rev.*, vol. 116, pp. 7463–7500, 2016.

[12] N. B. Vargaftik, B. N. Volkov, and L. D. Voljak, “International tables of the surface tension of water,” *J. Phys. Chem. Ref. Data*, vol. 12, pp. 817–820, 1983.

[13] *IAPWS R1-76: Revised release on surface tension of ordinary water substance*, 2014. [Online]. Available: `http://www.iapws.org/`.

[14] J. Pátek, J. Klomfar, and M. Součková, “Generation of recommendable values for the surface tension of water using a nonparametric regression,” *J. Chem. Eng. Data*, vol. 61, pp. 928–935, 2016.

[15] J. Kalová and R. Mareš, “Temperature dependence of the surface tension of water, including the supercooled region,” *Int. J. Thermophys.*, vol. 43, pp. 154-1–154-14, 2022.

[16] T. Rogers, K. Leong, and F. Wang, “Possible evidence for a new form of liquid buried in the surface tension of supercooled water,” *Sci. Rep.*, vol. 6, p. 33 284, 2016.

[17] Y. J. Lü and B. Wei, “Second inflection point of water surface tension,” *Appl. Phys. Lett.*, vol. 89, p. 164 106, 2006.

[18] X. Wang *et al.*, “Second inflection point of water surface tension in the deeply supercooled regime revealed by entropy anomaly and surface structure using molecular dynamics simulations,” *Phys. Chem. Chem. Phys.*, vol. 21, pp. 3360–3369, 2019.

[19] S. M. A. Malek, P. H. Poole, and I. Saika-Voivod, “Surface tension of supercooled water nanodroplets from computer simulations,” *J. Chem. Phys.*, vol. 150, p. 234 507, 2019.

[20] P. T. Hacker, “Experimental values of the surface tension of supercooled water, NACA TN 2510,” National Advisory Committee for Aeronautics, Tech. Rep., 1951.

[21] J. Hrubý and V. Holten, “A two-structure model of thermodynamic properties and surface tension of supercooled water. *Proceedings of the 14th International Conference on the Properties of Water and Steam*,” in *Water, Steam, and Aqueous Solutions for Electric Power. Advances in Science and Technology.*, Kyoto: Maruzen Co., 2005. [Online]. Available: `http://www.iapws.jp/proceedings.html`.

[22] W. J. Humphreys and J. F. Mohler, “Surface tension of water at temperatures below zero degree Centigrade,” *Phys. Rev.*, vol. 2, pp. 387–391, 1895.

[23] M. A. Floriano and C. A. Angell, “Surface tension and molar surface free energy and entropy of water to −27.2°C,” *J. Phys. Chem.*, vol. 94, pp. 4199–4202, 1990.

[24] E. Trinh and K. Ohsaka, “Measurement of density, sound velocity, surface tension, and viscosity of freely suspended supercooled liquids,” *Int. J. Thermophys.*, vol. 16, pp. 545–555, 1995.

[29] G. Wiegand and E. U. Franck, “Interfacial tension between water and non-polar fluids up to 473 K and 2800 bar,” *Ber. Bunseges. Phys. Chem.*, vol. 98, pp. 809–817, 1994.

[34] J. Hošek and K. Studenovský, “Reducing the edge chipping for capillary end face grinding and polishing,” *EPJ Web Conf.*, vol. 48, p. 00 005, 2013. DOI: `10.1051/epjconf/20134800005`.

[37] J. Klomfar, M. Součková, and J. Pátek, “Surface tension measurements for four 1-alkyl-3-methylimidazolium-based ionic liquids with hexafluorophosphate anion,” *J. Chem. Eng. Data*, vol. 54, no. 4, pp. 1389–1394, 2009.

[38] M. Součková, J. Klomfar, and Pátek, “Surface tension and 0.1 MPa density of 1-alkyl-3-methylimidazolium tetrafluoroborates in a homologous series perspective,” *J. Chem. Thermodyn.*, vol. 100, pp. 79–88, 2016.

[40] W. Wagner and A. Pruss, “The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use,” *J. Phys. Chem. Ref. Data*, vol. 31, pp. 387–535, 2002.

[41] R. Feistel, “A Gibbs function for seawater thermodynamics for –6 to 80 °C and salinity up to 120 g kg^{-1},” *Deep-Sea Res.*, vol. 55, pp. 1639–1671, 2008.

[42] *IAPWS R6-95(2018): Revised release on the IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use*, 2018. [Online]. Available: `http://www.iapws.org/`.

[43] *IAPWS R13-08: Release on the IAPWS formulation 2008 for the thermodynamic properties of seawater*, 2008. [Online]. Available: `http://www.iapws.org/`.

[46] G. Fritz, G. Scherf, and O. Glatter, “Applications of densiometry, ultrasonic speed measurements, and ultralow shear viscosimetry to aqueous fluids,” *J. Phys. Chem. B*, vol. 104, pp. 3463–3470, 2000.

[48] C. S. Dutcher, A. S. Wexler, and S. L. Clegg, “Surface tension of inorganic multicomponent aqueous electrolyte solutions and melts,” *J. Phys. Chem. A*, vol. 114, pp. 12 216–12 230, 2010.

[49] Y. Viisanen, R. Strey, and H. Reiss, “Homogeneous nucleation rates for water,” *J. Chem. Phys*, vol. 99, pp. 4680–4692, 1993.

[50] R. Weldon and F. Wang, “Water potential from adaptive force matching for ice and liquid with revised dispersion predicts supercooled liquid anomalies in good agreement with two independent experimental fits,” *J. Phys. Chem. B*, vol. 128, no. 14, pp. 3398–3407, 2024.

[51] K. G. Nayar, D. Panchanathan, G. H. McKinley, and J. H. Lienhard, “Surface tension of seawater,” *J. Phys. Chem. Ref. Data*, vol. 43, no. 4, p. 043 103, 2014.

[53] *IAPWS G14-19 : Guideline on the surface tension of seawater*, 2019. [Online]. Available: `http://www.iapws.org/`.

[54] C. Guohua, S. Jingzeng, G. Ling, and Z. Lijun, “Study on the surface tension of seawater,” *Oceanol. Limnol. Sin.*, vol. 25, pp. 306–311, 1994.

[55] R. Schmidt and B. Schneider, “The effect of surface films on the air-sea gas exchange in the Baltic Sea,” *Marine Chem.*, vol. 126, no. 1, pp. 56–62, 2011, ISSN: 0304-4203.

[56] K. A. Connors and J. L. Wright, “Dependence of surface tension on composition of binaryaqueous-organic solutions,” *Anal. Chem.*, vol. 61, no. 3, pp. 194–198, 1989.

[57] A. Vetere, “Again the Rackett equation,” *Chem. Eng. J.*, vol. 49, pp. 27–33, 1992.

[58] P. Wang, A. Anderko, and R. D. Young, “Modeling surface tension of concentrated and mixed-solvent electrolyte systems,” *Ind. Eng. Chem. Res.*, vol. 50, pp. 4086–4098, 2011.

[59] C. Goy *et al.*, “Shrinking of rapidly evaporating water microdroplets reveals their extreme supercooling,” *Phys. Rev. Lett.*, vol. 120, p. 015 501, 2018.

[60] I. T. Todorov, W. Smith, K. Trachenkob, and M. T. Dove, “DL_POLY_3: New dimensions in molecular dynamics simulations via massive parallelism,” *J. Mater. Chem.*, vol. 16, pp. 1911–1918, 2006.

Own publications related to dissertation

[25] J. Hrubý, V. Vinš, R. Mareš, J. Hykl, and J. Kalová, “Surface tension of supercooled water: No inflection point down to –25 °C,” *J. Phys. Chem. Lett.*, vol. 5, pp. 425–428, 2014.

[26] V. Vinš, M. Fransen, J. Hykl, and J. Hrubý, “Surface tension of supercooled water determined by using a counterpressure capillary rise method,” *J. Phys. Chem. B*, vol. 119, pp. 5567–5575, 2015.

[27] V. Vinš, J. Hošek, J. Hykl, and J. Hrubý, “Surface tension of supercooled water: Inflection point-free course down to 250 K confirmed using a horizontal capillary tube,” *J. Chem. Eng. Data*, vol. 62, pp. 3823–3832, 2017.

[28] V. Vinš *et al.*, “Possible anomaly in the surface tension of supercooled water: New experiments at extreme supercooling down to -31.4 °C,” *J. Phys. Chem. Lett.*, vol. 11, no. 11, pp. 4443–4447, 2020.

[30] V. Vinš, J. Hrubý, J. Hykl, J. Blaha, and B. Šmíd, “Design of an experimental apparatus for measurement of the surface tension of metastable fluids,” *EPJ Web Conf.*, vol. 45, p. 01 094, 2013. DOI: `10.1051/epjconf/20134501094`.

[31] A. Blahut, J. Hykl, P. Peukert, V. Vinš, and J. Hrubý, “Relative density and isobaric expansivity of cold and supercooled heavy water from 254 to 298 K and up to 100 MPa,” *J. Chem. Phys.*, vol. 151, p. 034 505, 2019.

[32] V. Vinš, J. Hošek, J. Hykl, and J. Hrubý, “An apparatus with a horizontal capillary tube intended for measurement of the surface tension of supercooled liquids,” *EPJ Web Conf.*, vol. 92, p. 02 108, 2015. DOI: `10.1051/epjconf/20159202108`.

[33] V. Vinš, J. Hošek, J. Hykl, and J. Hrubý, “Improvements of the experimental apparatus for measurement of the surface tension of supercooled liquids using horizontal capillary tube,” *EPJ Web Conf.*, vol. 114, p. 02 135, 2016. DOI: `10.1051/epjconf/201611402135`.

[35] J. Hošek, V. Vinš, and J. Hykl, “Influence of the light source on the liquid optical element planarity measurement,” *SPIE Proc. – Optics and Measurement Conf. 2014*, vol. 9442, 94420E-1 –94420E-8, 2015. DOI: `10.1117/12.2086494`.

[36] V. Vinš *et al.*, “Surface tension and density of dielectric heat transfer fluids of HFE type-experimental data at 0.1 MPa and modeling with PC-SAFT equation of state and density gradient theory,” *Int. J. Refrig.*, vol. 131, pp. 956–969, 2021.

[39] V. Vinš, M. Součková, O. Prokopová, M. Čenský, J. Hrubý, and A. Blahut, “Density and surface tension of water + ethylene glycol mixtures as key components of heat transfer liquids,” *Int. J. Refrig.*, vol. (accepted for publication 7.1.2025), 2025.

[44] V. Vinš, J. Hykl, Z. Nikl, M. Čenský, and J. Hrubý, “Surface tension of aqueous binary mixtures under the supercooled conditions: Development of the measuring technique and preliminary data for water + lower alcohols,” *EPJ Web Conf.*, vol. 180, p. 02 118, 2018. DOI: `10.1051/epjconf/201818002118`.

[45] O. Prokopová, A. Blahut, M. Čenský, M. Součková, and V. Vinš, “Comments on temperature calibration and uncertainty estimate of the vibrating tube densimeter operated at atmospheric pressure,” *J. Chem. Thermodyn.*, vol. 173, pp. 106855-1–106855-11, 2022.

[47] O. Prokopová *et al.*, “Influence of isomeric composition and sample handling on the liquid density of hydrofluorethers measured by vibrating tube densimeter at 0.1 MPa,” *Int. J. Thermophys.*, vol. 44, pp. 139-1 - 139–21, 2023.

[52] V. Vinš, J. Hykl, and J. Hrubý, “Surface tension of seawater at low temperatures including supercooled region down to –25 °C,” *Marine Chem.*, vol. 213, pp. 13–23, 2019.

[61] B. Planková, V. Vinš, J. Hrubý, M. Duška, T. Němec, and D. Celný, “Molecular simulation of water vapor-liquid phase interfaces using TIP4P/2005 model,” *EPJ Web Conf.*, vol. 92, p. 02 071, 2015. DOI: `10.1051/epjconf/20159202071`.

[62] V. Vinš, D. Celný, B. Planková, T. Němec, M. Duška, and J. Hrubý, “Molecular simulations of the vapor-liquid phase interfaces of pure water modeled with the SPC/E and the TIP4P/2005 molecular models,” *EPJ Web Conf.*, vol. 114, p. 02 136, 2016. DOI: `10.1051/epjconf/201611402136`.