International Tables of the Surface Tension of Water

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This paper presents a table for the surface tension of water from 0.01 to 374 °C and an interpolating equation which represents the values in the table to well within their estimated uncertainties. The table of values and the interpolating equation are those recommended by the International Association for the Properties of Steam (IAPS) in its recent official release. The experimental measurements of the surface tension of water and their uncertainties are discussed, as is the development of the IAPS tables.

Key words: critically evaluated data; internationally agreed-upon data; surface tension as a function of temperature; surface tension of water.

1. Introduction

The International Association for the Properties of Steam (IAPS) has approved an international table of values for the surface tension (σ) of water in equilibrium with its vapor over the entire liquid range. Given below is an analysis of the most important experimental studies of the surface tension of water, the results of which have served as the basis for the recommended values.

2. Experiments on Water Surface Tension

The total number of experimental studies of σ for water is large. They have been carried out to different levels of accuracy, and the majority of them cover the region of temperatures below the normal boiling point. A survey of the early low-temperature investigations is given in Ref. 1. Some experiments at high temperature are also considered in Ref. 2, however, the most important of these were carried out after Ref. 2 was written. We shall deal with the most carefully carried out works on σ for water.

The work of Richards and Coombs[3] was of great importance in the development of the capillary-rise technique. It gives a thorough analysis of the factors affecting the accuracy with which σ can be measured using the capillary-rise technique. The following factors were investigated:

(a) the sensitivity of the results to the accuracy with which the radius of the capillary was measured;

(b) the diameter which was necessary for the vessel into which the capillary was dipped in order that the surface of the water in the vessel could be considered plane;

(c) the influence of the size of the contact angle;

(d) the estimations of the weight of liquid in the meniscus; and

(e) the arrangement of lighting to permit the most accurate measurement of the height of the meniscus above the plane surface of the water in the containing vessel.

As a result of their measurements, Richards and Coombs recommend the value for water: $\sigma_{20\,^\circ\mathrm{C}} = 72.62\times10^{-3}$N/m.

The work of Richards and Carver[4] is a continuation of that of Richards and Coombs. These investigators observed that the contact angle (θ) of water on glass at room temperature is zero, derived a more accurate method for estimating the weight of liquid in the meniscus, and studied the influence of air and the ellipticity of the capillary section on the measurement of σ.

They obtained the value $\sigma_{20\,^\circ\mathrm{C}} = 72.73\times10^{-3}$N/m. They also re-evaluated the data of Richards and Coombs[3] and obtained $\sigma_{20\,^\circ\mathrm{C}} = 72.72\times10^{-3}$N/m.

Harkins and Brown,[5] using the capillary-rise method, made careful measurements of the surface tension of water in equilibrium with its vapor and with saturated air. In both cases, they obtained the value $\sigma_{20\,^\circ\mathrm{C}} = 72.80\times10^{-3}$N/m. In these experiments they used several different samples of water and several different capillaries. The uncertainty in the results obtained can be estimated to be about 0.1%.

As a result of investigations[3–5] the capillary-rise method was considerably improved and is, at present, one of the most reliable methods available for determining the surface tension of fluids over a range of temperatures. Moreover, a sound mathematical basis has been developed for determining σ from the capillary rise.

Gross[6] used a capillary method to measure σ for water over the temperature interval 0–60 °C. He obtained six values for σ which are of sufficient accuracy for consideration here.

Warren[7] has investigated the surface tension of water over the temperature range 0–90 °C using the maximum-bubble-pressure method. The author estimates the uncertainty of his measurements to be 0.01%. The measurements, however, were relative values based on $\sigma_{15\,^\circ\mathrm{C}} = 73.65\times10^{-3}$N/m. If these values are recalculated using $\sigma_{15\,^\circ\mathrm{C}} = 73.50\times10^{-3}$N/m which is accepted in this paper, they appear to be acceptable for use.

Moser[8] made three series of quite accurate measurements of the surface tension of water in the range of temperatures 0–100 °C using a ring-detachment method. The dependence of σ on temperature found in this work agrees with that obtained by Warren.

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Ramsey and Shields[9] have investigated σ for water over the temperature range 0–130 °C by the capillary method. The glass tube containing the capillary had an inside diameter of ~ 10 mm. The surface of the water in the annular region between the capillary and the container has a considerable curvature for such a narrow container. The authors attempted to correct for this curvature but underestimated its effect. The values were recalculated later by Sugden.[10]

The results of a large number of investigations of σ for water at low temperatures were compiled and evaluated in Ref. 11; recommended values are given for the temperature range -9 to 140 °C. In Ref. 11 the surface is in equilibrium with air saturated with water vapor at atmospheric pressure for temperatures below 100 K and with saturated water vapor above it. Surface tensions measured under these two conditions using the capillary technique could be expected to differ because of the greater density of the saturated air and possible adsorption of components of the air at the interface. For water at pressures of about 1 atm, the differences are small (see Ref. 4) and fall within the overall reliability of the measurements, and can be neglected. Below 0 K the surface of the supercooled water is referred to. As will be shown later, these values for the surface tension of water can only be considered accurate below 100 °C.

Heyks and co-workers[12] investigated the region of temperatures higher than the normal boiling point. The measurements were made by the capillary-rise method over the temperature range 101–224 °C. The authors estimate the uncertainty in their data to range from 0.3% to 0.7%, however, they did not take the incomplete wetting of the capillary into account in their calculations. If these results were to be recalculated using the currently accepted values for the contact angle of water on quartz, the results could be used in preparing critically evaluated data for water.

Watanabe and co-workers[13] have measured σ for water by a capillary-rise method over the temperature range 20–200 °C. Unfortunately the data are only shown in a diagram.

More detailed investigations of the surface tension for water in the temperature range above the normal boiling point have been carried out at the Physics Chair of the Moscow Aviation Institute (MAI). Voljak[14] has used a differential capillary method. The apparatus consisted of two quartz capillaries sealed into a thick-walled quartz ampule. The method suggested by the author for selecting capillaries with a uniform inner cross section permitted selection of capillaries with a uniformity within $\pm 0.5\%$. Both uniformity of radius along a capillary and ellipticity of cross section were considered. Measurements were made over the temperature range 20–354 °C, and the uncertainty was estimated to be 0.4% at 150 °C and 5% at 340 °C.[15] There was a systematic error resulting from the temperature-measurement technique and the scatter of the experimental points was relatively large—up to 1% at temperatures below 250 °C and 3% at 350 °C.

The same method was used for succeeding experiments carried out at MAI,[16,17] but the experimental apparatus was improved. The control of the thermostat was more accurate and temperature was measured with a platinum-resistance thermometer with an uncertainty of ± 0.05 K. Capillaries with a uniformity of inner section of 0.05% were used, their radii were determined with an uncertainty of 0.1%. The results of the first set of measurements[16] on this apparatus were processed assuming the contact angle of water on quartz to be zero. Soon investigation[18] showed that the contact angle of water on quartz increases with temperature from a value of $\sim 4°$ at 0 °C to a value of $\sim 28°$ near the critical point. The succeeding measurements of σ for water[17] were processed using the results of the measurements of θ. The results published in Ref. 16 were recalculated to take into account the temperature dependence of the contact angle and also published in Ref. 17.

The ranges of temperature investigated in Refs. 16 and 17 are mutually overlapping, the results obtained are in agreement within 0.2×10^{-3} N/m at low temperatures and 0.1×10^{-3} N/m at high ones. The calculated uncertainty of these experiments varies from 0.3% at 20 °C to 1.7% at 360 °C, the greatest contribution coming from the uncertainty in the values of the contact angles. In the range of temperatures greater than 360 °C, the uncertainty was not greater than 0.07×10^{-3} N/m.

The results of Refs. 16 and 17 in the range of temperatures up to 100 °C agree well with the most reliable measurements in this range of temperature. It should also be noted that the value for the surface tension at 20 °C, 72.74×10^{-3} N/m practically coincides with the values from the very precise measurements at this temperature.[3–6]

The values obtained from Refs. 16 and 17 also agree with those from the high-temperature measurements[12–14] within their uncertainties.

3. Tables of Values for the Surface Tension of Water

As the results of an evaluation of the known investigations of the surface tension of water, Young and Harkins gave a table of values of σ for water over the temperature range -8 to 140 °C in Ref. 11. On the basis of Refs. 3, 4, 5, and 6, they recommended $\sigma = 72.75 \times 10^{-3}$ N/m, for the surface tension of water at 20 °C as a reference value, which since has found wide use in the calibration of instruments.

An analysis shows, however, that the selection of data made in preparing the tables[11] was not always justified. The values for σ at temperatures higher than 80 °C could only have been obtained by relying on the measurements on Ref. 9 as recalculated by Sugden.[10] However, as Sugden himself noted, the recalculated values are only reliable at moderate temperatures. Perhaps that is why one of the authors of Ref. 11, Harkins, only presented a table of recommended values for water covering the temperature range 0 to 60 °C in his monograph.[19] Also, in Ref. 20 recommended values for the surface tension of water are only given for the temperature range -10 to 100 °C; the values given are in close agreement with those in Ref. 11. Thus for many years relatively reliable values for the surface tension of water have only been available up to the normal boiling point.

Apparently, tables for the surface tension of water covering the entire liquid range were first given by Fritz.[21] The data on which these tables are based are not cited. For temperatures up to 100 °C these tables differ slightly from those given in Refs. 11 and 20. At higher temperatures, especially those approaching the critical, the values in Ref. 21 differ considerably from measured values obtained later.[16,17]

Values for the surface tension of water for the temperature range 0–374 °C, given in Vargaftik's reference book[22] and in Ref. 23 have been widely used in recent years. However, these tables are based on the values in Ref. 16 which were calculated without allowance for the incomplete wetting of quartz by water.

4. International Tables for the Surface Tension of Water

The General Meeting of the Eighth International Conference on the Properties of Steam held in Giens, France in 1974 instructed the International Association for the Properties of Steam to prepare international tables on the surface tension of water. Two papers presenting titles on surface tension were presented during the Conference,[24] and three drafts of tables were considered by Working Group 3, Other Properties, Especially Surface and Electrical Properties, during the meeting. The tables submitted by the Japanese Delegation were based on Refs. 11 and 21 for temperatures up to 100 °C and on the experimental data of Watanabe[13] and Vargaftik *et al.*[16,17] with allowance made for the temperature dependence of the contact angle of water on quartz. The tables were approximated by a nine-term polynomial in $(T_c - T)$ where T_c represents the critical temperature.

The tables submitted by the delegation from the FRG were based on Refs. 11 and 21 as well as the experimental data in Refs. 16 and 17. Three different interpolating equations were investigated: a seven-term polynomial in $T_c - T$, a polynomial in $T_c - T$ containing a term with a fractional exponent, and a binomial equation in $T_c - T$ with nonintegral exponents.

The tables submitted by the Soviet delegation were based on the mean values of the most accurate low-temperature experimental data[3–9] and the high-temperature data[12,13,16,17] corrected for the effect of temperature on the contact angle. The tables were approximated by a seven-term polynomial in $T_c - T$ with the first term having a fractional exponent.

These three submissions were considered by Working Group 3. Since the values of the surface tension recommended by the different submissions did not differ greatly, the decision was made to use the arithmetic means of the values given in the different submissions in the international tables. In 1976 this table was adopted by the International Association for the Properties of Steam and promulgated in an official release.[25]

These values of σ are presented in Table 1 along with

TABLE 1. Surface tension of water as a function of temperature

t °C	$\sigma \cdot 10^{-3}$ N/m	$\Delta\sigma \cdot 10^{-3}$ N/m	$\delta\sigma \cdot 10^{-3}$ N/m	t °C	$\sigma \cdot 10^{-3}$ N/m	$\Delta\sigma \cdot 10^{-3}$ N/m	$\delta\sigma \cdot 10^{-3}$ N/m
0.01	75.64	0.38	0.01	190	39.95	0.22	0.00
5	74.95	0.37	0.00	195	38.82	0.22	0.00
10	74.23	0.37	−0.01	200	37.69	0.22	−0.01
15	73.50	0.37	−0.01	205	36.55	0.22	−0.01
20	72.75	0.36	−0.01	210	35.41	0.22	−0.02
25	71.99	0.36	−0.01	215	34.25	0.22	−0.01
30	71.20	0.36	0.00	220	33.10	0.22	−0.02
35	70.41	0.35	0.00	225	31.93	0.22	−0.02
40	69.60	0.35	0.00	230	30.77	0.22	−0.02
45	68.78	0.34	0.00	235	29.60	0.22	−0.02
50	67.94	0.34	0.01	240	28.42	0.22	−0.02
55	67.10	0.34	0.00	245	27.24	0.22	−0.01
60	66.24	0.33	0.00	250	26.06	0.22	−0.01
65	65.36	0.33	0.01	255	24.87	0.21	0.01
70	64.47	0.32	0.02	260	23.67	0.21	0.03
75	63.58	0.32	0.01	265	22.48	0.21	0.04
80	62.67	0.31	0.01	270	21.30	0.20	0.05
85	61.75	0.31	0.01	275	20.11	0.20	0.06
90	60.82	0.30	0.00	280	18.94	0.20	0.06
95	59.87	0.30	0.01	285	17.77	0.19	0.07
100	58.91	0.29	0.01	290	16.61	0.19	0.07
105	57.94	0.29	0.01	295	15.45	0.19	0.07
110	56.96	0.28	0.01	300	14.30	0.18	0.07
115	55.97	0.28	0.01	305	13.17	0.18	0.06
120	54.96	0.27	0.01	310	12.04	0.17	0.06
125	53.95	0.27	0.01	315	10.92	0.16	0.06
130	52.93	0.26	0.01	320	9.81	0.16	0.07
135	51.89	0.26	0.02	325	8.73	0.15	0.06
140	50.85	0.25	0.01	330	7.66	0.14	0.05
145	49.80	0.25	0.01	335	6.61	0.13	0.05
150	48.74	0.24	0.01	340	5.59	0.12	0.05
155	47.67	0.24	0.01	345	4.60	0.11	0.04
160	46.58	0.23	0.02	350	3.65	0.10	0.03
165	45.49	0.23	0.02	355	2.75	0.10	0.00
170	44.40	0.22	0.01	360	1.90	0.10	−0.10
175	43.30	0.22	0.01	365	1.13	0.10	−0.04
180	42.19	0.22	0.01	370	0.45	0.10	−0.06
185	41.07	0.22	0.01	374.00	0.00		0.00

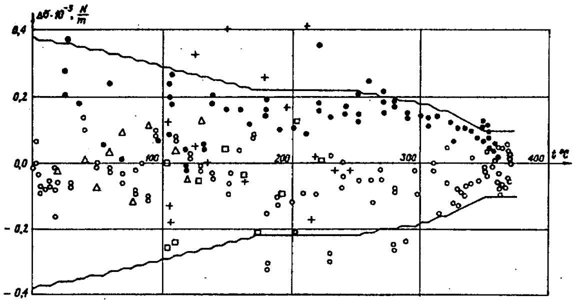

FIGURE 1. Deviation of experimental points from the international values of σ: ○ Vargaftik and others (Refs. 16 and 17); + Voljak (Ref. 14); □ Heyks and others (Ref. 12); △ Ramsey and Shields (Ref. 9).

their uncertainties estimated from the reliability of the experimental data.

As is evident from Fig. 1, most of the experimental points from the works used in evaluating the surface tension over a wide range of temperature fall within the estimated uncertainty of σ. The results of Refs. 3–8 fall well within these limits.

The values in the table are well represented by Eq. (1) with $T_c = 647.15$ K and this equation is recommended for use as an interpolating equation

$$\sigma = B\left[\frac{T_c - T}{T_c}\right]^{\mu}\left[1 + b\left(\frac{T_c - T}{T_c}\right)\right], \tag{1}$$

where $B = 235.8\times 10^{-3}$N/m, $b = -0.625$, and $\mu = 1.256$.

Table 1 also gives the divergences ($\delta\sigma$) of the values (σ_c) calculated using Eq. (1) from the values recommended in the table. $\delta\sigma = \sigma_c - \sigma$. As is evident from the table, the divergence lies well within the estimated uncertainties.

5. References

[1]B. P. Weinberg, Zh. Russ. Fiz-Khim. O-va. **24**, 44 (1892).
[2]Gmelin's Handbuch der Anorganischen Chemie, 8 Aufl., System nummer 3, Berlin, 1963.
[3]T. W. Richards and L. Coombs, J. Am. Chem. Soc. **37**, 1656 (1915).
[4]T. W. Richards and E. K. Carver, J. Am. Chem. Soc. **43**, 827 (1921).
[5]W. D. Harkins and F. E. Brown, J. Am. Chem. Soc. **41**, 499 (1919).
[6]P. L. K. Gross, The Theory of Atomic Collisions, the Determination of a Standard for Surface Tension Measurements, Ph.D. thesis, University of Chicago, 1926. See also Ref. 19.
[7]E. L. Warren, Philos. Mag. **4**, 358 (1927).
[8]H. Moser, Ann. Phys. **82**, 993 (1927).
[9]W. R. Ramsey and J. Shields, J. Chem. Soc. **63–64**, 1–89 (1893).
[10]S. Sugden, J. Chem. Soc. **125**, 32 (1924).
[11]T. F. Young and W. D. Harkins, in *International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (McGraw–Hill, New York, 1928), Vol. 4.
[12]J. R. Heyks, M. K. Barnett, L. V. Jones, and E. Orban, J. Phys. Chem. **58**, 48 (1954).
[13]A. Watanabe, H. Watanabe, and K. Watanabe, Data Survey and Correlation of Surface Tension of Water with Saturation Temperature. Report to the meeting of Working Group III of The International Association for the Properties of Steam, Schleersee, FRG (1975). (Copies available from the Executive Secretary of the International Association for the Properties of Steam, Physics Bldg., A316, National Bureau of Standards, Washington, DC 20234.)
[14]L. D. Voljak, DAN USSR **74**, 307 (1950).
[15]L. D. Voljak, Teploenergetika **7**, 33 (1958).
[16]N. B. Vargaftik, L. D. Voljak, and B. N. Volkov, Temperature Dependence of the Surface Tension of Water in Tr. Vses. Nauch.-Tekh. Konf. Termodin, Sb. Dokl. Sekts. "Teplofiz. Svoistav Veshchestv," 3rd M. D. Vaisman, Ed. Leningrad, Leningrad. Tekhnol. Inst. Kholod. Prom. (1969).
[17]N. B. Varagaftik, L. D. Voljak, and B. N. Volkov, Teploenergetika **8**, 80 (1973).
[18]L. D. Voljak, V. G. Stepanov, and J. V. Tarlakov, Zh. Fiz-Khim. **46**, 1620 (1972).
[19]W. D. Harkins, in *Physical Methods of Organic Chemistry*, edited by A. Weissberger, 3rd completely revised and augmented edition, vol. 1, Technique of Organic Chemistry (Interscience, New York, 1959).
[20]*Landolt-Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik* (Springer, Berlin, 1956), 6 Aufl., B.2, Teil 3.
[21]W. Fritz, in *Die Grundgesetz der Wärmeübertragung*, 3rd ed., edited by H. Gröber, S. Erk, and U. Grigull (Springer, Berlin, 1969), 3 Aufl.
[22]N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd ed. (Hemisphere, Washington, 1975).
[23]M. P. Vukalovitch, S. L. Rivkin, and A. A. Alexandrov, *Tables of the Thermophysical Properties of Steam* (Publication of Standards, Moscow, 1969).
[24]Proceedings of the 8th International Conference on the Properties of Water and Steam, September, 1974, Giens (France), Editions Européennes Thermiques et Industries, Paris (1975).
[25]Release on Surface Tension of Water Substance issued by the International Association for the Properties of Steam, September (1975). Howard J. White, Jr., Executive Secretary, National Bureau of Standards, Washington, D.C.