

Surface Tension and Molar Surface Free Energy and Entropy of Water to  $-27.2\text{ }^{\circ}\text{C}$ M. A. Floriano<sup>†</sup> and C. A. Angell<sup>\*‡</sup>

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To remove a deficiency in the growing data base on supercooled water, the surface tension of water has been measured, using a small-sample capillary rise method, down to  $-27.2\text{ }^{\circ}\text{C}$ . The data do not accord with extrapolations of equations best fitting data above  $0\text{ }^{\circ}\text{C}$  but show a more rapid increase with decreasing temperature. This distinguishes water from other hydrogen-bonded fluids and focuses attention on weaknesses of classical interpretations of the temperature dependence of the surface tension. The observations are related to recent molecular dynamics studies of water surface tension. The possibility of an artifact in experimental studies, caused by anomalous gas solubility in the supercooled regime, is recognized.

## Introduction

Despite the large effort expended in the last decade exploring the frequently anomalous properties of water in its supercooled state,<sup>1,2</sup> the only measurements of the surface tension below zero ever published are two points at  $-5$  and  $-8\text{ }^{\circ}\text{C}$ <sup>3</sup>—and the point at  $-8\text{ }^{\circ}\text{C}$  is suspect. This is a serious deficiency since there is general agreement that the anomalies in the supercooled state are directly related to the fluctuations in volume and entropy associated with the buildup of the three-dimensional open network structure which minimizes the energy water molecule assemblages. A property determined at the surface, where the third dimension is necessarily diminished in influence, has the potential to show interesting and diagnostic differences from other properties.

In this paper we will describe a simple method for measuring the surface tension of supercooled water and will report and analyze data down to  $-27.2\text{ }^{\circ}\text{C}$ .

The tension to which liquids are subject at the interface with the vapor can be thought of as arising from the unbalanced attractions experienced by the molecules at the surface. The existence of a true mechanical tension at the surface of a liquid is demonstrated by many familiar phenomena, such as the drawing together of a small portion of liquid to a spherical drop, a shape that minimizes the surface area, hence also the surface energy for the given volume.<sup>4</sup> Another consequence is the formation of a curved meniscus at the surface of any liquid in a container. The difference in pressures acting at the convex and concave sides of the meniscus causes the well-known *capillary rise* effect.

This latter phenomenon provides a convenient and accurate method of measuring the surface tension of a liquid.<sup>5</sup> A glass-wetting liquid will rise in a glass capillary by an amount  $h$ , which is proportional directly to its surface tension  $\sigma$  and inversely to its density  $\rho$  and to the capillary radius  $r$ , according to the equation

$$h = 2\sigma/r\rho g \quad (1)$$

where  $g$  is the acceleration due to gravity.

We have adopted this "capillary rise" method for the present work because of its simplicity and relative accuracy and because the probability of heterogeneous nucleation leading to freezing can be kept small by using small-bore capillaries and cooling only the top  $\sim 10$  mm of the column, i.e. the small section containing the free surface. Since it is at the contact of the surface with the wall that the force producing the capillary rise is located, the temperature of the column away from this region is immaterial apart from a small effect of the density at the column temperature on the column height supported; see eq 1.

An account of the experimental procedure follows.

## Experimental Section

Borosilicate glass precision capillary tubings of nominal internal diameters of 100, 200, and 300  $\mu\text{m}$  were obtained from Fisher

and Porter. Still smaller diameters were obtained by heating a portion of a thick-walled Pyrex capillary tubing ( $\sim 0.5$  mm i.d.) until soft and then pulling at both ends until the desired diameter was obtained. The actual diameters of all capillaries were calibrated by measurements of the rise of distilled water at room temperature since the surface tension under these conditions ( $\gamma = 72.00\text{ mN m}^{-1}$  at  $T = 25\text{ }^{\circ}\text{C}$ ) is well-known (see for example ref 6). The correction was typically of the order of 0.1% but reached 2% in a few cases. The uniformity of the capillary bore was checked by changing the level of water in the reservoir and noting the change in  $h$ . In all cases the diameter was found to be constant within the precision of the measurements, estimated at about 0.5%.

Before use the capillaries were cleaned with hot nitric acid followed by sulfuric acid and then thoroughly rinsed with distilled water. They were kept immersed in distilled water between measurements. The water used in the experiments was either triply distilled and filtered through a 0.45  $\mu\text{m}$  pore filter or doubly distilled and filtered in a 0.23  $\mu\text{m}$  pore filter.

For each set of measurements, the capillary rise tube was mounted in a reservoir, with the upper section in a controlled temperature zone, as shown in Figure 1. The temperature control device consisted of a copper tube 2.5 cm in diameter and approximately 10 cm long which could be raised and lowered perpendicularly over the capillary. At the two ends of the copper tubing,  $\text{N}_2$  gas, which was precooled or heated by passing it through a coil immersed in a bath at the desired temperature, was blown. For the subambient experiments the bath was ethanol and the temperature was set and controlled with a Flexi-Cool Refrigerator, FTS Systems, Inc. For above-ambient measurements the bath was water and the temperature was set and controlled by the same Flexicool unit in its heating mode.

The temperature was monitored with a type K thermocouple glued inside the copper tube in the vicinity of the capillary. The temperature inside the capillary was inferred in each experiment by a calibration chart obtained in a separate run where a second thermocouple was placed inside the capillary and the differences in the two (external and internal) temperatures were noted. This calibration experiment showed that the inside temperature was  $1.8^{\circ}$  lower than the outside at  $-30\text{ }^{\circ}\text{C}$  and  $1.4^{\circ}$  higher at  $60\text{ }^{\circ}\text{C}$ . This provided a graduated correction used in all temperature readings. The density of water to be used in calculating the surface tension via eq 1 is, however, not that at the temperature of the measurement because only the top 10 mm of the supported column departs from the ambient temperature. Accordingly we used, as

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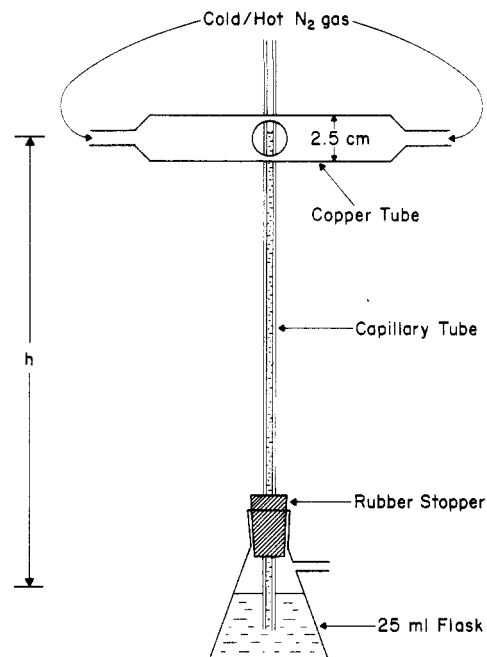
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**TABLE I: Surface Tension of Water,  $\sigma$ , at Different Temperatures**

$T/^\circ\text{C}$	$\rho^a/\text{g cm}^{-3}$	capillary <sup>b</sup>	$(h)^c/\text{cm}$	$\sigma/\text{mN m}^{-1}$
-27.2	0.9968	1	42.425	79.86
-25.4	68	1	41.867	78.81
-23.6	65	3	15.886	77.57
-22.1	67	5	15.784	79.00
-20.1	68	1	41.548	78.21
-20.0	67	6	10.796	78.82
-18.8	65	7	10.737	78.64
-18.5	69	5	15.645	78.32
-17.5	69	6	10.718	78.27
-15.8	67	7	10.671	78.17
-15.3	68	7	10.656	78.07
-14.1	71	4	15.508	77.59
-13.5	71	5	15.540	77.81
-12.5	71	6	10.614	77.52
-11.1	69	3	15.736	76.87
-10.6	68	1	41.315	77.77
-10.6	68	2	42.872	76.51
-10.5	69	7	10.549	77.29
-9.8	69	7	10.560	77.37
-9.1	72	4	15.386	76.99
-8.0	73	6	10.574	77.24
-7.6	70	7	10.492	76.88
-5.7	70	3	15.635	76.39
-5.3	75	6	10.543	77.04
-5.0	68	1	40.884	76.96
-5.0	68	2	42.592	76.01
-3.6	73	4	15.150	75.82
-3.4	70	7	10.433	76.45
-3.2	71	7	10.387	76.12
-1.8	73	5	15.150	75.87
-1.0	70	3	15.453	75.50
0.3	71	7	10.352	75.86
0.5	73	4	15.064	75.44
1.5	74	6	10.358	75.67
1.6	70	3	15.453	75.50
2.3	73	4	15.001	75.07
3.7	68	1	39.785	74.89
3.7	68	2	42.475	75.80
4.3	74	6	10.324	75.43
4.8	71	7	10.291	75.42
5.6	73	5	14.946	74.85
7.3	73	6	10.273	75.05
7.4	73	4	14.827	74.20
9.6	71	7	10.159	74.45
12.1	73	5	14.768	73.96
14.0	71	7	10.090	73.94
16.2	70	7	10.018	73.41
24.8	71	5	14.380	72.00
24.9	71	6	9.858	72.00
24.9	71	4	14.390	72.00
25.0	70	3	14.737	72.00
25.4	68	7	9.828	72.00
29.7	67	7	9.768	71.55
33.3	69	6	9.648	70.45
37.2	68	4	13.994	70.00
40.9	66	6	9.478	69.19
43.0	62	7	9.487	69.46
48.0	63	6	9.333	68.11
48.4	60	7	9.340	68.37
53.0	61	6	9.274	67.67
55.4	63	4	13.401	67.00
60.0	54	7	8.975	65.66
60.0	57	6	9.030	65.86

<sup>a</sup>The density was calculated assuming that 1 cm of the total water column,  $h$ , was at temperature  $T$  while the rest was at room temperature, RT, using  $\rho = (1/h)\sigma_T + [(h-1)/h]\rho_{RT}$ , where the densities were taken from ref 11b. <sup>b</sup>The capillaries were (number, radius/ $\mu\text{m}$ ): 1, 38.5; 2, 36.5; 3, 99.91; 4, 102.30; 5, 102.38; 6, 149.34; 7, 149.04. <sup>c</sup>Difference between the level of water in the capillary,  $h$ , and in the reservoir, see Figure 1.

density, a value based on 1 cm at the measurement temperature and  $(h-1)$  cm at ambient. Both the meniscus height and the level of water in the reservoir (the differences between which establish  $h$ ) were measured to  $\pm 10 \mu\text{m}$  with a cathetometer (Precision Tools and Instruments Co., Ltd., England).



**Figure 1.** Schematic diagram of capillary rise apparatus used to determine surface tension of supercooled water. Only uppermost 1 cm of water column is cooled.

Measurements were always made with a descending meniscus. After temperature equilibration the column of water was pumped to a position a few millimeter higher than the equilibrium position of the reservoir flask (see Figure 1) and then allowing the meniscus fall back to the equilibrium position. This procedure was repeated several times and the equilibrium position was never observed to vary by more than  $\sim 10 \mu\text{m}$  except when an attempt was made to reduce the diameter of the capillary below approximately  $20 \mu\text{m}$  to increase the depth of supercooling attainable. The major source of error in these measurements was the reading of the reference level in different sets of measurements. Within any one series the scatter is less than the overall.

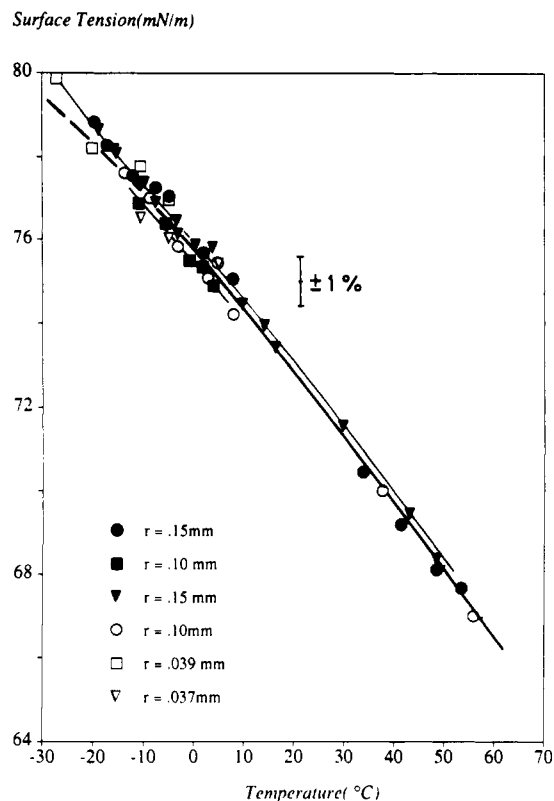
With the very small diameter tubing, results were irreproducible because the movement of the meniscus in the long columns supported in the case of small-diameter tubings was very sluggish (partly because of the  $r^{-4}$  dependence of the Poiseuille flow times and partly for reasons unknown). The reproducibility and the flow time problems were largely solved by replacing the long fine capillary by a composite of a short length of a fine capillary for the meniscus sealed into the end of a long wide-bore tube, for which the column of water supported was, of course, the same height. Unfortunately, the increase in supercooling expected with this column, in which only the fine bore part was really cold, was not obtained, and no refinement of the modification was attempted.

## Results

The experimental values of the surface tension of water under its own vapor pressure obtained between  $-27.2$  and  $60.0^\circ\text{C}$  are reported in Table I and displayed in Figure 2. In Table I are also listed other values used in the calculation of  $\sigma$ , including the density that was obtained as explained in the previous section, and the capillary diameters. In Figure 2 the thick solid line represents values obtained from an interpolation equation due to Vargaftik et al.<sup>6</sup>

$$\sigma = B \left[ \frac{T_c - T}{T_c} \right]^\mu \left[ 1 + b \left( \frac{T_c - T}{T_c} \right) \right] \quad (2)$$

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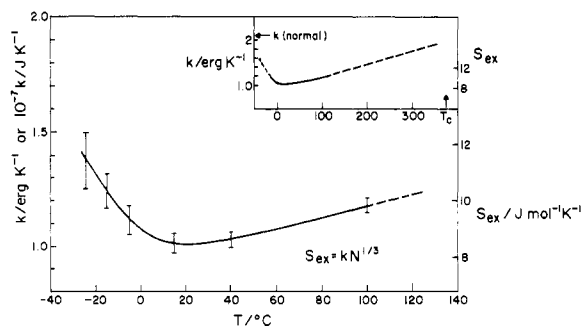
**Figure 2.** Surface tension vs temperature for six different series of experiments, each calibrated at room temperature. Scatter within individual series is smaller than overall scatter and is smallest for larger diameter capillaries. Thick solid line shows Vargaftig equation (eq 3), best fitting data for water above 0 °C; dashed continuation shows equation prediction for lower temperatures. Thin solid line shows temperature dependence indicated by present work ( $\blacktriangledown$  series). Note increasing slope at low temperatures after inflection around ambient temperature.

with  $T_c = 647.15$  K,  $B = 0.2358$  mN/m,  $\mu = 1.256$ , and  $b = -0.625$ . Equation 2 reproduced experimental data between 0.01 and 374 °C with an accuracy of approximately 0.02% in the temperature range overlapping with those of the present experiment. The dashed thick line at  $T < 0$  °C is an extrapolation of this equation. The thin solid line represents the best fit through our most scatter-free data set (solid triangles). This set, supported by the literature data to 0 °C, convinces us that below 0 °C the temperature dependence of the surface tensions ceases to diminish as eq 2 implies and in fact starts to increase again at about the temperature where the expansion coefficient becomes negative.

### Discussion

From an inspection of the data in Figure 2 it is clear that the surface tension of water in the temperature range that was investigated does not present major thermal anomalies. Concerning the question of whether a second inflection point in the surface tension–temperature curve exists around 10 °C,<sup>7</sup> our data indicate a positive departure of the experimental points from the line extrapolated from higher temperature data (eq 2) in the vicinity of 0 °C. However, the precision of our data is not such that this can be considered a real anomaly without further analysis; see below.

What is evident from Figure 2 is that the surface tension is not like other properties of water which display obvious anomalies as the temperature is lowered well into the supercooled region.<sup>2,8</sup> However, this is not unexpected. Another example of a property of water that varies unspectacularly with temperature even in the



**Figure 3.** Eotvos constant ( $k$  of eq 4) (left-hand axis) and molar excess surface entropy defined by Prigogine as  $N^{1/3}k$  (right-hand axis) as function of temperature for water. Note anomalous (unphysical in case of  $S_{ex}$ ) increases in supercooled regime (see text).

supercooled region is the vapor pressure.<sup>8</sup> In discussing the case it was pointed out<sup>8</sup> that the thermodynamic quantities showing interesting changes in behavior as the temperature was lowered, such as the heat capacity and expansivity, are all second derivatives of the liquid–free energy which is a logarithmic function of the vapor pressure. Consequently, to detect the much-discussed anomalies by vapor pressure measurements a very great precision in measurement would be needed. In the present instance the surface tension is numerically identical with the specific surface free energy; hence again anomalies comparable to those observed in direct  $C_p$  and  $\alpha$  measurements would only be detectable if the precision of the measurement could be greatly improved so that second derivative quantities could be examined.

On the other hand even with the data in hand we quickly find ourselves dealing with paradoxes particularly when we examine the more appropriate molar quantities. The surface free energy per mole,  $\sigma V_m^{2/3}$ , for instance, will eventually exhibit the same anomalies as the molar volume  $V_m$  exhibits, as the expansivity tends to diverge at  $-45$  °C.<sup>2</sup> Even in the range of the present measurements, however, anomalous behavior is apparent (in the temperature dependence of the surface tension) and is only accentuated by the volumetric anomalies. We return to these after an initial consideration of the new results from the classical viewpoint.

Observations of the supercooled liquid surface tension permit a critique of some classical concepts developed around the difference in temperature derivatives of the surface tension for water (and alcohols) and other molecular liquids. At the end of the last century following Eotvos<sup>9</sup> and Ramsay and Shields<sup>10</sup> it was believed that, by analogy with the gas law  $PV/nT = R$ , the temperature derivative of the molar surface free energy,  $d(\sigma V_m^{2/3})/dT$ , should be a constant. Incorporating the fact that surface tension vanishes at the critical temperature  $T_c$ , this analysis yielded

$$\sigma V_m^{2/3} = k(T_c - T) \quad (3)$$

with  $k = 2.1$  erg K<sup>-1</sup> for many liquids. Water and other hydrogen-bonded liquids, however, gave smaller values of  $k$ , which were also temperature dependent. This problem was disposed of by assuming that the low values were a result of molecular association which changed the effective molecular weight of the substance under study by an association factor  $x$ . Thus the temperature derivative of the molar surface free energy was written

$$-d(\sigma x V_m^{2/3})/dT = k = 2.1 \text{ erg K}^{-1} \quad (4)$$

so that the association factor could be obtained as

$$x = (2.1/k_{\text{obs}})^{3/2} \quad (5)$$

where  $k_{\text{obs}}$  is the experimentally observed slope. The inadequacy of this idea can be illustrated by using our low-temperature data and the molar volume data on supercooled water<sup>11</sup> to obtain the

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association factor  $x$  between 60 and  $-27.5$  °C.  $x$  of eq 15 will go inversely as  $k$  which is plotted in Figure 3. The low-temperature increases of  $k$  seen in Figure 3 suggests that the association in water, as opposed to other hydrogen bonded liquids, is decreasing with decreasing temperature in the supercooled regime where all other evidence suggests the contrary. Clearly the classical interpretation of deviations from the Eotvos rule is inadequate, as indeed has long been realized on other grounds.<sup>12</sup>

An alternative and preferred interpretation of the anomalous temperature dependence of water and other H-bonded liquids has been suggested by Good.<sup>13</sup> Good calculated the molar surface entropy  $S_s$  defined from the specific surface entropy  $s_s = d\sigma/dT$  by

$$S_s = s_s A = 1.10 V^{2/3} N^{1/3} \frac{d\sigma}{dT} = 1.10 (M/\rho)^{2/3} N \frac{d\sigma}{dT} \quad (6)$$

for a large number of hydrogen bonded, polar, and nonpolar liquids and showed that the hydrogen bonded liquids fell into a separate group. This group had  $S_s$  values of  $\sim 10$ – $15$  J mol<sup>-1</sup> K<sup>-1</sup> ( $1.4$ – $2R$ ) compared to  $\sim 24$  J mol<sup>-1</sup> K<sup>-1</sup> ( $2.93R$ ) for nonpolar liquids. The deficiency of  $\sim 1.6R$  entropy units for water was attributed by Good to the hydrogen bonded ordering of a small number,  $1.6R/R \ln 2$  ( $\approx 2.3$ ), of outer layers of the water surface. The unusual (large positive) temperature dependence of the  $S_s$  for hydrogen-bonded liquids was then very reasonably interpreted in terms of the disordering of the inner layers with increasing thermal excitation.

Good's interpretation has been examined by Matsumoto and Kataoka<sup>14</sup> in the light of their detailed molecular dynamics simulation of the liquid–vapor interfaces of water (using the Caravetta–Clementi pair potential) and of the Lennard Jones system. Although they found  $S_s$  of eq 6 to be in quite good agreement with Good's compilation ( $2.5R$  for LJ at 100 K vs the  $2.93R$  independent of temperature for nonpolar liquids, compared with  $1.3R$  for water at 300 K increasing with increasing temperature) they were unable to support Good's dipole orientation interpretation. They found the entropy deficit due to orientation in the surface to be almost 1 order of magnitude less than that required to explain the observations. Matsumoto and Kataoka were unable to provide an alternative explanation but suggested that it might lie in "more complicated structure due to the hydrogen-bonded network, perhaps analogous to hydrophobic structure-making".

That  $d\sigma/dT$  is not a simple quantity to interpret is clear from its behavior in water below 0 °C (Figure 3) (and in any liquid near its critical temperature<sup>15</sup>). In these cases  $d\sigma/dT$  is increasing with decreasing temperature, so if one takes the "surface phase"

literally and calls  $d\sigma/dT$  its entropy, then the heat capacity per mole of the surface phase would be negative, which is impossible since a heat capacity is connected, in statistical thermodynamics, to the square of an entropy fluctuation.<sup>16</sup> Fortunately, as Widom has stressed<sup>15,17</sup> the identification of  $d\sigma/dT$  as an entropy depends on a special, and arbitrary, choice of the dividing surface (such that excess mass per unit area is zero). Furthermore,<sup>17</sup> to interpret the temperature dependence of  $d\sigma/dT$  as a heat capacity would require a more complicated, even temperature-dependent, choice of dividing surface. In any case the surface cannot be considered independently of the bulk and it is only the total heat capacity of the system (which is dominated by the bulk value) which must remain positive.<sup>17</sup>

These considerations should not lead us to dismiss the distinction between water and other hydrogen-bonded liquids at low temperatures. We suspect this difference is related to the fact that, at the surface of water, the open network structure, which is the source of rapid entropy decrease in supercooling bulk water, is missing. However there is another possibility to be considered. It is possible that the upturn in  $d\sigma/dT$  below 0 °C is an artifact peculiar to water, as follows. There is some suggestion, in the equations used to fit data on the solubility of gases in water,<sup>18</sup> that the solubility may increase anomalously in the supercooled regime and perhaps tend to infinity near the  $-45$  °C transition.<sup>19,20</sup> Since our interface is exposed to nitrogen, the surface gas concentration could increase anomalously and, by providing the guest molecules for a clathrate-like structuring in the surface layers, enhance the structure-related increase of the "pure" water surface tension. Indeed, Beaglehole<sup>21</sup> has recently reported anomalies in the surface structure of water when subjected to a temperature gradient in the presence of gases, which are not present in rigorously degassed water. The effect on the measured surface thermodynamic properties of surface concentrations of different gases will therefore have to be evaluated before the problems to which we have drawn attention can be fully assessed. The measurement of surface tension in the absence of any foreign vapor species would be more difficult but could in principle be performed on the surface of a degassed evacuated sample of high-purity water by light-scattering studies of the capillary waves.<sup>22</sup>

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