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# pH and the surface tension of water

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ABSTRACT

Despite the strong adsorption of hydroxide ions, the surface tension of water is almost independent of pH between pH 1 and 13 when the pH is adjusted by addition of HCl or NaOH. This is consistent with the Gibbs adsorption isotherm which measures the surface excess of all species in the double layer, if hydronium ions and hydroxide ions are adsorbed and sodium and chloride ions are not. The surface tension becomes pH dependent around pH 7 in millimolar NaCl or KCl solutions, for now sodium ions can replace hydronium ions as counterions to the adsorbed hydroxide ions.

## 1. Introduction

Surface tension is a fundamental property of water that affects many phenomena [1]. Textbooks ascribe the molecular origin of the surface tension to the difference in energy of molecules between the bulk and the pristine, surfactant-free surface. Yet it has been known for many years that air bubbles, as well as oil drops and inert polymer surfaces, acquire a negative charge in water [2]. This is attributed to the spontaneous adsorption of hydroxide ions at the interface. The pH dependence of the pristine surface tension of water now presents an apparent paradox. On the one hand is the compelling evidence, including the pH dependence of the $\zeta$ potential, that the interface is charged by the strong adsorption of hydroxide ions [2]. On the other hand there is indirect evidence that the surface tension is nearly pH independent around neutral pH. These two observations appear to be contradictory and have created an impression that the question of the charge at the interface is controversial [3]. The Gibbs adsorption isotherm provides an exact relationship between bulk concentrations, total surface coverage of adsorbed species, and the surface tension changes produced by adsorption [4,5]. Its careful application leads to the prediction that the surface tension around pH $\lesssim 7$ is independent of pH, despite the high surface concentration of the hydroxide ion [6]. Only in the presence of additional electrolyte is a pH dependence of the surface tension for expected pH < 7. An explanation of this phenomenon, the absence of a pH effect in the presence of hydroxide ion adsorption, and the report of new surface tension data, are the subjects of this Article. We present experimental results that resolve the apparent contradiction about the pH dependence of the surface tension, and that provide further evidence that the negative surface charge is created by adsorbed hydroxide ions. In fact, the appearance of pH dependence of the surface tension only in the presence of added salt rules out many mechanisms for the negative surface charge other than hydroxide adsorption [6].

There are surprisingly few data on the surface tension of water around neutral pH. The value for neat water is of course very well established (72.7 mN m$^{-1}$ at 293 K [7]) and recommended as a standard for surface tension measurements. It has generally been assumed that this is the surface tension of an uncharged, pristine interface, but two of us have recently described it as the surface tension of the hydroxide-adsorbed interface which forms from the pristine state in a few milliseconds [8]. The fact that this gives a reproducible constant value that can be used as a standard implies that the surface tension must be independent of pH around pH 5–7.

Similarly, there are few data available in the present literature for the surface tension of water over a wide pH range. Experimental data for surface or interfacial tensions were traditionally collected for the very extreme pH ranges and for neat water (*i.e.*

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pure water without added electrolyte) and with variable electrolyte concentrations. Classical examples are measurements of the surface tensions of electrolyte solutions of concentrations 0.1–1.0 M and studies on the Jones-Ray effect [9], a minimum in the surface tension at millimolar electrolyte concentrations in neutral water. The Jones-Ray effect has recently been confirmed spectroscopically [10]. The effect was originally, and again recently, interpreted in terms of electrolyte ion adsorption, but an alternative view is that it reflects salt effects on hydroxide ion adsorption [6,11,12]. Work by Lorenz is a rare example of the measurement of the pH dependence of surface tension from $[H^+] = 1$ mM to $[H^+] > 1$ M, but this study reported an inverse Jones-Ray effect, a maximum in the surface tension of water with HCl concentrations below about 30 mM HCl [13]. The purpose of the present work is to clarify the interpretation of the pH dependence of the surface tension, with additional experiments as required, and with particular attention to the surface adsorption of hydroxide.

## 2. Experimental methods

Surface tension measurements on the pH dependence of neat water solutions (Fig. 1) were done using the Cahn Radian 321 set-up with the plate method. Before each measurement, the platinum plate was cleaned by rinsing with water, rinsing with acetone, a final rinsing with ethanol, and then exposure of the side that was cleaned to UV-light for 5 min. Then the procedure was repeated for the other side of the plate. The initial surface tension value of neat water could slightly vary on a daily basis between 71.8 and 73.4 mN/m. For all measurements, a pH-series was only started when the result for the pure water was 72.8 mN/m as expected, and remained so for at least three consecutive measurements. In some of the series we also prepared multiple samples for analysis in parallel. These were (i) kept in the initial state for a final check after the measurement series to verify that the sample and the set-up still produced the initial value, (ii) treated in the same way as the measurement sample and measured at the end of the series, and (iii) treated in the same way as the measurement sample, but used exclusively for pH-measurement. The above precautions were taken to avoid variations in surface tension due to immersion of the pH electrode in a measurement solution [14]. The pH measurements were done using a combination electrode that was calibrated daily against commercial pH buffers (Merck, buffers in the range from pH 1 to 13). Error bars shown in Fig. 1 are the standard deviations of at least 5 independent experiments for each solution. The solution was prepared by filling a container that had been filled with argon by water. The solutions were kept always under an argon cushion, and the set-up was always flushed with argon. The argon was sent through a number of washing bottles that contained acid, base (to remove carbon dioxide), and water. Some long-term experiments with pure water were also conducted that showed that one solution could produce a constant value of the surface tension over 10 h. Surface tension measurements of the 10 mM salt solutions began with 10 mM NaCl or KBr solutions in Milli-Q water at pH 6–7 and were conducted under an atmosphere of argon with the pendant drop method on a CAM200 instrument (Fig. 2). Each data point is the average of 20 independent measurements with error bars given by twice the standard error in the mean, and represents an experiment with a single addition of HCl, HBr, NaOH or KOH to the measured pH; there was no incremental addition to obtain multiple pH values with the same sample. It should be noted that surface active impurities would generally lower the surface tension, not increase it as we observed in the acidic solutions. The surface tensions vary smoothly from pH less than 7 to pH greater than 7, where added salt lowers the surface tension. This smooth variation is consistent with similar surface composition above and below pH 7. We conclude then that amphiphilic impurities are not responsible for the observed surface tension behaviour.

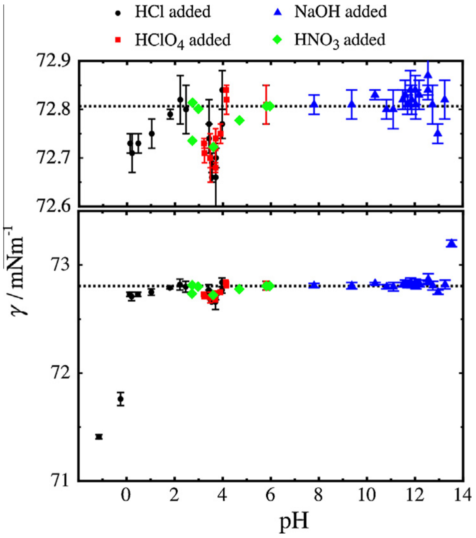

**Fig. 1.** pH dependence of surface tension of neat water at 298 K with added HCl, $HClO_4$, $HNO_3$, or NaOH. The error bars are the standard deviations of at least 5 independent measurements. Note that the upper panel of this plot is an expansion of the lower.

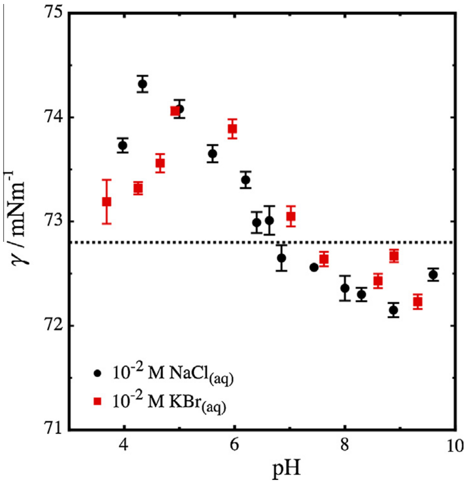

**Fig. 2.** The measured surface tension, $\gamma$, varying with pH in the presence of two monovalent salts at 10 mM concentration and 298 K. The error bars are twice the standard error in the mean calculated for the 20 independent measurements.

## 3. Results and discussion

The results of our new measurements of the surface tension of water at 298 K in the absence of added electrolyte are shown in Fig. 1. Only an acid (HCl, $HClO_4$, or $HNO_3$) or NaOH was added to adjust the pH. As described above, measures including work under argon were taken to exclude carbon dioxide in these experiments. The range of pH studied is enough to close the gap between the pH values of 1 and 13 for which data are already available [15].

Except for a small local minimum around pH 4, a probable manifestation of the Jones-Ray effect, the surface tension is essentially constant from pH 1 to pH 13. Langmuir [16] disputed the surface tension minimum seen by Jones and Ray, but it was later seen also by Dole and Swartout [17], and recently surface spectroscopic methods were used to verify the effect [10]. Nearly constant surface tension could be interpreted to indicate that none of the ions