

AIR/WATER INTERFACE

Two sides of the acid–base story

The ability of the water surface to donate or accept protons critically influences vital processes in chemistry and biology, but intense disagreement persists regarding this property. Researchers now show evidence that the air side of the air/water interface is more basic than the aqueous one.

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Many processes in chemistry and biology — such as atmospheric aerosol–gas exchanges, enzymatic catalysis or transmembrane proton transport — involve proton exchanges at the water surface, yet the unambiguous determination of the surface's acid–base character has remained elusive. In a study of the air/water interface that recently appeared in the *Proceedings of the National Academy of Sciences of the USA*, Augustín Colussi and co-workers conclude¹ that proton-transfer reactions confirm the presence of hydroxide ions on the surface of even very acidic water (bulk pH above 2). The researchers also suggest that the excess of hydroxide groups endows the surface of neat water (pH = 7) with negative charges. Both of these properties — the intrinsic acidity of the liquid water surface and its charge (and associated electrostatic potential) — have profound consequences in a wide variety of contexts and have been vigorously debated in the recent literature^{2–4}.

To probe the acid–base chemistry of both sides of the water surface, Colussi and co-workers monitored the deprotonation of a carboxylic acid (RCOOH, with $R = C_5H_{11}$; Fig. 1a): the aqueous solution was nebulized and the surface of the resulting droplets analysed by electrospray ionization mass spectrometry (ESI–MS). In one case, the aqueous solution contained dissolved carboxylic acid (RCOOH(aq.)); in the other, the aqueous droplets were briefly exposed to an effusive beam of the reactant gas (RCOOH(g)). The charged carboxylates (RCOO[−]) formed from deprotonation of the carboxylic acid, either in solution or as a gaseous reagent, were expelled by electrostatic interactions from the surface of the droplets into the gas phase, and detected. The measurements indicate that the gaseous acid species is deprotonated at much lower pHs than the dissolved counterpart (Fig. 1b). As the researchers note, it is reassuring that the deprotonation of the dissolved RCOOH(aq.) in solution occurs as expected from conventional solution studies.

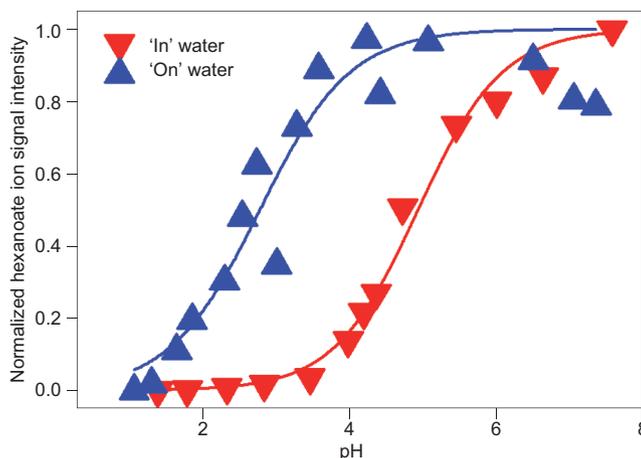
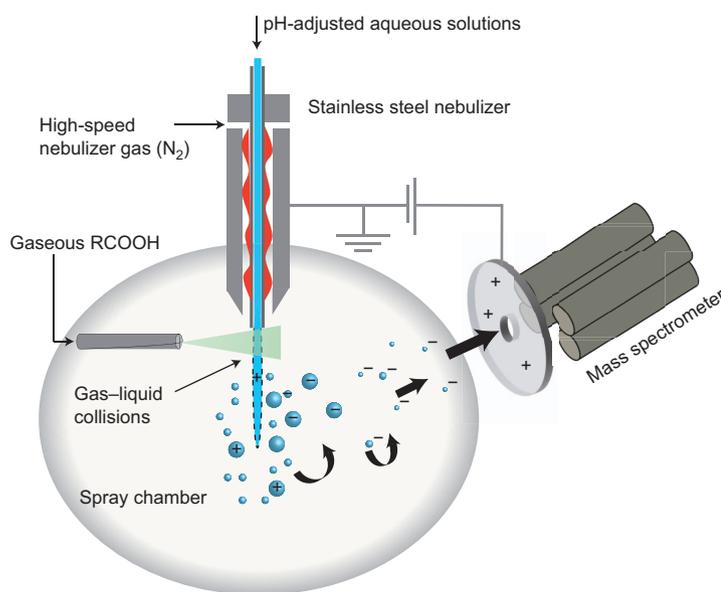


Figure 1 Basicity of the water interface probed by ESI–MS. **a**, Schematic diagram of the experimental set-up. Aqueous solutions (blue) are nebulized, and can interact with gaseous carboxylic acid (green beam). The resulting carboxylate species are then detected by ESI–MS. **b**, Normalized signal intensities of RCOO[−] detected on the surface of water (i) containing dissolved RCOOH(aq.) (red triangles); (ii) briefly exposed to gaseous RCOOH(g) (blue triangles). Figure reproduced with permission from ref. 1, © 2012 NAS.

Accompanying theoretical calculations indicated that the surface deprotonation reaction was strongly impeded if hydroxide

ions (OH[−]) were not present. Measurement of the number of deprotonated acid (RCOO[−]) ions resulting from interaction of the liquid

jet with the impinging reactant gas is thus interpreted as quantifying the hydroxide concentration at the droplet surface. Carboxylate products, and by implication surface hydroxide ions, were detectable on the surface of aqueous solutions with bulk pH values as low as 2. In similar experiments¹ the researchers had observed H_3O^+ ions at the water interface for pH values up to 4 — combining the two results, they suggest that the water/air interface (on the air side) is neutral for bulk pH values around 3. By extrapolation, Colussi and co-workers also propose that the excess of hydroxide groups on the neat water surface (at pH = 7) produces a net negative surface charge. These results are in agreement with macroscopic electrophoresis experiments on air bubbles and oil droplets in water³, but conflict with those reported from recent surface spectroscopy experiments and computer simulations.

A classical molecular dynamics study by Jungwirth and co-workers⁵ predicted a greater tendency for hydrated protons than for hydroxide to accumulate at the water surface. This was further supported by both *ab initio* molecular dynamics simulations⁶ as well as quantum simulations⁷, yet more recent simulations⁸ find closer surface affinities for the two species. Second harmonic generation spectroscopy experiments³ supported a stronger surface propensity for protons, as did more recent phase-sensitive sum-frequency generation studies — although the latter were interpreted as demonstrating the presence of both hydronium and hydroxide ions at the water surface⁹. X-ray photoelectron spectroscopy experiments were also interpreted as indicating at most a very small interfacial hydroxide concentration, as expected from surface-tension data⁴.

A principal factor in rationalizing such disparate results from different experiments is their inherently different probing depths: second-order optical experiments are generally thought to probe

the outermost layers of liquid density, but this remains incompletely understood. And although photoelectron spectroscopy experiments probe deeper into the bulk — where the electron ‘escape length’, which determines the depth of the measurement, depends on its kinetic energy and the composition of the medium — but are still capable of sampling roughly 1-nm surface regions. In addition, theoretical calculations have revealed that the liquid/vapour interface is highly structured, with adjacent regions [Au: OK?] of enhancement and depletion of ions relative to their bulk concentrations^{2,4,5}, such that these differences in probing depth could lead to considerable variation in the measured results. Ostensibly, the surface reaction experiments of Colussi and co-workers probe the outermost layer or two, but again this is not certain.

Similarly conflicting results have been reported for the closely related surface electrostatic potential of water^{10,11}. Electrochemical results have supported a very small (<0.1 V) and negative potential. In contrast, several recent calculations predict a very large and positive value (roughly +3.0 V), in agreement with older electron holography experiments. Other calculations yield a large negative potential¹². Noting that the electric fields and forces resulting from the electrostatic potential across the approximately 10-nm liquid/vapour interface would be huge (up to 100 kT), such widely different values would imply very different behaviour for interfacial ions. The large predicted positive values would drive negative ions (such as hydroxide) to the surface while expelling protons. This effect could be crucial for explaining the function of voltage-gated proton channels, for example¹³. [Au: Refs 13 and 14 swapped so they are cited in order.]

Hence, as compelling as the results of the electrospray mass spectroscopy measurements are, they could be viewed as ‘just the latest salvo’ in this intense

controversy [Au:OK?]. Several crucial assumptions inherent to the analysis of Colussi and co-workers remain to be verified, such as the existence of sufficient time to establish autoionization and diffusional equilibrium¹⁴, the nature of charge distribution and dielectric properties inferred from the presence of the hydroxide groups, and the associated orientational distribution of water in the interfacial layers, which is intimately connected to the presence of interfacial ions.

Further advances in both theory and experiment are clearly needed to further elucidate both the basicity and the charge (and electrostatic potential) of the liquid water surface. The relevance of these issues extends well beyond the present context of the liquid/vapour interface, when one recognizes that water/protein interfaces behave similarly¹⁵. □

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