

# Can the pH at the air/water interface be different from the pH of bulk water?

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A recent article in PNAS (1) reports stable pH gradients in aqueous phosphate buffer microdroplets based on the pH dependence of surface-enhanced Raman spectroscopy (SERS) signals from 4-mercaptobenzoic acid-functionalized gold nanoparticle pH probes.

The probing SERS signals were a 1,470-cm<sup>-1</sup> shift assigned to a COO<sup>-</sup> stretching and a 1,710-cm<sup>-1</sup> shift from a CO stretching (1). Plots of signal intensities (relative to that of a pH-independent 1,080-cm<sup>-1</sup> signal from the aromatic ring) in bulk solutions as a function of pH (figure S1 of ref. 1) show a 1,710-cm<sup>-1</sup> signal that decreases with pH along a titration curve with an inflection point at pH = 6.91 and a 1,470-cm<sup>-1</sup> signal that increases quasiexponentially from pH 2–12. The pH dependence of the 1,470-cm<sup>-1</sup> signal (presumably associated with the COO<sup>-</sup> group of 4-mercaptobenzoate) is possible but puzzling because 4-mercaptobenzoic acid, with acidity constants pK<sub>a</sub>(COO-H) = 4.14 and pK<sub>a</sub>(S-H) = 6.62, should have been fully dissociated, and the COO<sup>-</sup> signal plateaued above pH ~9.

The pH across microdroplets was deduced from SERS signal intensities measured in situ and figure S1 of ref. 1. Figure 3 of ref. 1 shows pH values so

deduced as a function of the distance to the center of the microdroplets. The authors' interpretation of the results of figure 3 of ref. 1 is that pH drops 3.6 units from the centroids of the microdroplets to their air/water interfaces ~25 μm away.

This interpretation violates chemical thermodynamics. Since pH represents the chemical potential/activity of the proton, and the chemical potentials/activities of all species must be the same in all phases in equilibrium, the pH at the air/water interface cannot be different from the pH at the centroid of the microdroplets. The same rule applies to any body of water in thermal and mechanical equilibrium, large or small. Therefore, figure 3 of ref. 1 is not evidence of pH gradients or that protons accumulate at the air/water interface. The reason is that SERS signal intensities report concentrations rather than activities. Although activities are uniform throughout, the concentrations of the species that give rise to SERS signals, which depend inversely on activity coefficients, could vary with position within the microdroplets (2–4). In short, figure 3 of ref. 1 may reveal something interesting, but not a stable pH gradient.

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- 2 Mishra H, et al. (2012) Brønsted basicity of the air-water interface. *Proc Natl Acad Sci USA* 109:18679–18683.
- 3 Colussi AJ, Enami S (2014) Comment on "Surface acidity of water probed by free energy calculation for trimethylamine protonation." *J Phys Chem C* 118:2894.
- 4 Enami S, Hoffmann MR, Colussi AJ (2010) Proton availability at the air/water interface. *J Phys Chem Lett* 1:1599–1604.

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