COMMENTS

Comment on "Interfacial pH at an Isolated Silica−Water Surface"

Poul B. Petersen and Richard J. Saykally*

Department of Chemistry, University of California, Berkeley, California 94720

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The recent Communication "Interfacial pH at an Isolated Silica−Water Surface" published in the *Journal of the American Chemical Society* (O'Reilly, J. P.; Butts, C. P.; I'Anson, I. A.; Shaw, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 1632) describes the use of evanescent wave cavity ringdown spectroscopy (e-CRDS) to measure the pH of the silica−water interface using a molecular probe tethered to the surface. The communication reports two major findings: The observation of a surface pH of two units lower than the bulk at high pH and the existence of a stable charged near-surface layer that is not disrupted upon lowering the pH to 1. Although the experiment constitutes a clever approach to the problem, the authors neglect several aspects of the experiment and overlook inherent problems with the indirect approach of using a molecular probe to detect the interfacial pH.

The authors wish to probe the pH at the neat water−silica interface and state that "the tethered chromophore is only sensitive to the pH in the local environment within 1 nm of the surface." More precisely, the dye molecule is only sensitive to the local environment around the chromophore itself (note that the probe molecule is larger than 1 nm). This implies that the probe actually will not measure the properties of the neat surface, but rather the properties of the interface perturbed by the chromophore. Since this is a local effect, the perturbation is independent of the surface concentration of the chromophore. Depending on the nature of the interface and the specific probe used, the degree of perturbation of the local interfacial structure will vary. Whereas Steel and Walker have successfully used small uncharged molecular probes to probe the structure of liquid−liquid interfaces,[1] the large and charged organic probe employed in the present study would probably have a significant perturbing effect on the water-silica interface and is thus probing the local region around the silica−dye−water interface.

The effect of the interface on the molecular probe itself is likewise important in these kinds of experiments and needs to be accounted for. Consider the generic acid−base equilibrium

$$\mathrm{HA} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+ \tag{1}$$

From the equilibrium constant expression, we obtain

$$\log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \mathrm{pH} - \mathrm{p}K_\mathrm{A} \tag{2}$$

An experiment of this kind measures the ratio of the protonated and unprotonated probe molecule, and will thus measure only the *difference* between the pH and pK_A. (This is not a problem in the bulk, where the pH can be measured independently using a pH electrode, after which the pK_A can be calculated. Once the pK_A is known, it can be used to determine the pH in other experiments.) However, at the interface, both the pH and the pK_A will change due to the altered environment. Since neither of these components can be measured directly, a model of the change in one of the quantities has to be invoked in order to calculate the desired quantity. In fact, several groups have successfully used the Gouy−Chapman model in connection with the Boltzmann equation to calculate the surface pH at the various interfaces in order to obtain interfacial pK_A values of several acids.[2,3] The surface pK_A values in these experiments differ significantly from the bulk values by several pK units. The chromophore at the surface cannot be assumed to exhibit the same properties as it does in the bulk.

In the present study, the surface pK_A of the modified probe was assumed identical to the bulk value estimated for a secondary iminium (around 9), without taking into account surface effects. The unmodified probe, a primary iminium, has a pK_A of ∼11 in the bulk. This is despite the fact that the UV-vis spectrum and thus the optical properties are significantly different. The modified Nile Blue is quoted to exhibit maxima at 592 and 470 nm, whereas unmodified Nile Blue exhibits maxima at 630 and 598 nm for the acid form and 500 nm for the base form. If the optical properties are different so would be the chemical and the pK_A. The obtained result relies directly on the chosen value of pK_A (eq 2).

Furthermore, it is unclear how the result of the observed shift of two pH units was obtained. It seem as though the surface pH was calculated using Grahame and Boltzmann equations, assuming a surface charge of the "silica" surface at the given bulk pH. The bulk pH dependence (of unmodified Nile blue?) was then shifted to the calculated surface pH (shifted by two units?), resulting in the dashed trace (c) in Figure 2. The observation of a shift of the surface pH by two pH units is then based on the comparison of the calculated surface pH dependence and the measured e-CRDS pH dependence with, at best, qualitative agreement (trace goes up, then down). One has to ask the question, what is the agreement with other shifts? or since the shift in surface pH is experimentally indistinguishable from a shift in surface pK_A, what significance can be attributed to the supposed agreement?

Other details need to be explained. The initial rise in both the bulk and surface absorbance, which would indicate a lowering of both the surface and bulk(!) pH with increasing bulk pH, is unexplained. The reported sensitivity of 0.001 pH units is completely unsubstantiated, and how the bulk absorbance of the chromophore was obtained and corrected for surface pH (trace c in Figure 2) is unclear. Furthermore, the authors reference the surface properties of silica, but the experiment was performed on Schott glass. This might not be a significant change, but it should at least be noted.

The notion of a stable surface layer that does not change with pH needs further justification. The layer obviously changes, in that upon lowering the bulk pH, the absorbance decreases. The

* Corresponding author: Richard J. Saykally, D31 Hildebrand Hall, University of California, Berkeley, CA 94720, Phone: +1 (510) 642−8269, Fax: +1 (510) 642−8369, e-mail adress: Saykally@berkeley.edu

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authors do not state whether this new curve is reproducible, i.e., if the absorbance curve is retraced would the bulk pH be increased again, making it a "permanent" structural change. Such a stable surface layer would be out of equilibrium with the bulk and seems unlikely for an acid−base reaction. The given justification due to changes in the Debye length needs further evaluation, although a Debye treatment of the problem seems futile considering the high potential of the deprotonated silica surface. It is not clear how the titration was performed. Were fresh solutions are made at each pH starting from a neutral solution or was the titration performed starting at low pH and adding base and then lowered again by adding acid? The method used will greatly change the counterion concentration and thus the Debye length.

Polyaromatic dye molecules are known to aggregate easily upon the addition of electrolytes.[4−6] To limit probe−probe interactions, the experiments are performed at a low coverage. However, this alone does not eliminate the possibility of aggregation. At submonolayer coverage, the dye molecules could still be located in local domains rather than being evenly distributed over the surface. Chromophores of this type are known to readily aggregate under the basic conditions wherein the tethering was performed.

Rather than evidencing the formation of a stable surface layer, the experiments probably indicate changes in the chromophore structure (i.e., aggregation or a phase or conformational change) at the surface that are known to occur when base or salts are added. Initially, the chromophore at the surface is in one structure that could also be due to contaminations. When the base is added, the structure is changed due to aggregation or removal of the contaminations. The original structure can be reproduced after washing with methanol, thereby reversing the aggregation or reintroducing the contaminations.

References and Notes

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