

Reply to “Comment on ‘Interfacial pH of an Isolated Silica–Water Interface’”

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We reported the measurement of interfacial pH by monitoring the optical absorbance change of a pH-sensitive probe molecule tethered to the silica–water interface.¹ The interpretations of the observations require a number of assumptions about the optical response of the chromophore at the surface and the formation of the interface structure as a function of the surface charge.

The pH-sensitive optical probe was a silyl derivative of Nile Blue, and we assumed that the optical properties of the Nile Blue derivative in solution are the same as the Nile Blue derivative on the surface: the λ_{max} of the chromophore on the surface is the same as the λ_{max} of the chromophore in solution. Using this assumption it is possible to make a quantitative estimate of the surface coverage as 5×10^{-5} of a monolayer. A surface coverage of $\sim 10^{-4}$ of a monolayer corresponds to $\sim 10^7$ probe molecules within the interface sampled by the evanescent field, or $\sim 10^{10} \text{ cm}^{-2}$. The molecular probe density may be compared with that used by Steel and Walker² of 10^{15} cm^{-2} . We also assume that lower probe concentrations will minimize the interface perturbations. These assumptions are the simplest possible to interpret the optical response of the probe to the charged interface structure but must be considered in the context that there are many sources of perturbation, as discussed in the original communication¹ and the comment.³

It is important to establish the nature of the chromophore on the surface, including a possible chromophore aggregation optical response. Tethering species to the silica surface to tune the hydrophilic/hydrophobic properties is well established using the silanol-siloxane tethering reactions,^{4–6} providing pure monolayers and mixed monolayers of molecules on the surfaces. We have made measurements⁷ on the pH-dependent adsorption of dye molecule to the silica surface, and the analysis reveals that the electrical properties of Schott glass used on our prism surface and fused silica are not significantly different. A surface with an aggregated molecular layer would not be stable to a change in solvent from water to IPA; however, the tethered probe surface shows a distinctive optical switching when the bulk solvent is changed (Figure 1): a clear switch is seen when the bulk solvent is switched from water pH 8 to IPA. The absorption in the presence of IPA is larger than that in water due to a solvato-chromic shift of the probe molecule in a medium with a different relative permittivity. The interface disruption kinetics are also observed during the switch from the bilayer structure at the silica–water interface to the silica–IPA interface: the switching is stable for many (<20) cycles. The surface switching shows no hysteresis as observed in other interfaces,⁸ principally due to the complete disruption of the charged interface structure

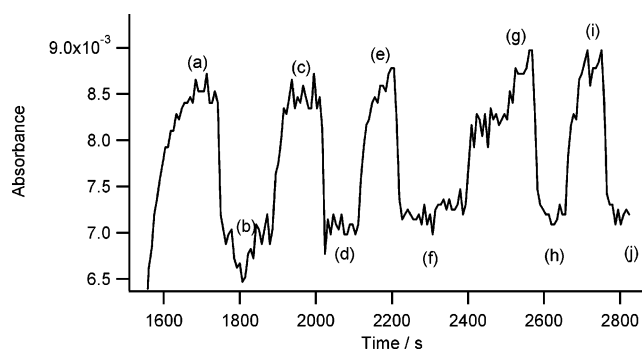


Figure 1. Switching the Nile Blue derivatized surface: (a), (c), (e), (g), and (i) are IPA solutions and (b), (d), (f), (h), and (j) are aqueous pH 8.2.

by the organic solvent. Aggregation of the chromophore on the surface is an unlikely interpretation of the data.

The structure of the charged interface changes during the titration in response to the increasing surface charge and hence surface potential. The bulk solution pH is changed for each pH step, but the surface is not washed or refreshed, which would disrupt the forming layer. The probe molecule is in an environment close to the surface and fully extended could be $\sim 1 \text{ nm}$ into the interface, but the positive charge on the molecule would suggest it is attracted closely to the surface, placing it within the inner Helmholtz plane. The optical response of the probe molecule is indeed sensitive to its local environment and, as discussed in the communication, and sensitive to many interfacial properties including a solvato-chromic response (demonstrated in Figure 1), the interfacial permittivity, the morphology of the surface, and the presence of the molecule in the electric field of the interface. These effects are averaged over the 10^7 probe molecules present in the evanescent field. A complete analysis will be required to model the precise shape of the optical response with bulk pH, including all of these factors.

The electrical properties of the interface are modeled using the Grahame and Boltzmann equations,⁷ to predict the Boltzmann enhancement of the surface proton concentration $[\text{H}^+]_s$ producing the interfacial pH. The response of the probe molecule can be understood by eqs 1 and 2 as the comment suggests, but corrections are needed for the interfacial structure and the effect of charge on the interfacial pH:

$$\log \frac{[A^-]_s}{HA} = \text{pH}_s - \text{p}K_a$$

All measurements of interfacial pH, A^- , and $\text{p}K_a$ at a charged interface require a model for the interfacial structure and the molecule within the interface. Generally, this is reported as a change in the $\text{p}K_a$ of the species at the interface.^{5,9,10} Konek et al.⁵ observed a change in the chemical bonding of the molecule due to interactions between adjacent molecules and the titratable proton in the nearly complete surface coverage of the derivative species. We have chosen to assume the $\text{p}K_a$ of the molecule tethered to the interface has remained the same as in solution and calculated the effects of the interfacial pH model on the color change of the chromophore. The counter assumption could be made assuming the interfacial pH is the same as the bulk and that the $\text{p}K_a$ of the species has changed significantly, but positive ions are clearly attracted to the negatively charged

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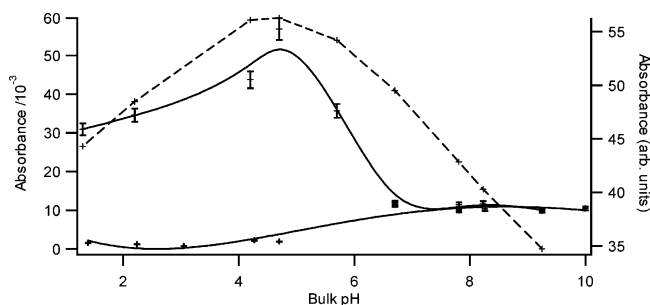


Figure 2. Variation of Interfacial pH with surface charge.

interface and the interfacial pH is different from bulk pH. The color change of the chromophore in solution is corrected for the interfacial pH given by

$$\text{pH}_s = \text{pH}_{\text{bulk}} \exp(-e\varphi/kt)$$

and produces a lower interfacial pH and an absorbance change for the chromophore as a function of the surface potential, φ , and charge on the proton, e . The correction for interfacial pH is made during the titration and compared with the absorbance of the tethered chromophore, Figure 2. The interfacial pH can be seen to be more acidic by approximately two pH units for the fully dissociated silica surface, although the detailed variation of the absorbance with pH is not well described for the reasons discussed above.

For the fully dissociated surface the surface potential is -125 mV, with respect to zero in the bulk, from a surface charge of $60 \mu\text{C cm}^{-2}$, corresponding to a surface silanol-site density of 2 nm^{-2} . The interfacial capacitance can then be determined as $500 \mu\text{C cm}^{-2}$ and points directly to the stability of the layer, the hysteresis in its formation, and the kinetics of disruption. The coulomb attraction between two charges reaches kT at 300 K when the separation is 56 nm (depending on the relative permittivity of the medium), suggesting that the layer structure near the charged surface has an intrinsic capacitance and will be thermally stable with respect to disruption. As seen in Figure 1, the charged layer is disrupted by organic solvent showing some disruption kinetics but re-forms on switching the surface. The inner Helmholtz plane is thought to have dimensions on the order of $2\text{--}5 \text{ \AA}$ and is associated with a tight binding layer of counterions that perhaps have lost their solvation shell.¹¹ Tight

binding between two oppositely charged ions with a solvent shell has an energy approximately $200 kT$ at 300 K and between desolvated ions should approach the lattice energy values. The tethered indicator is within 5 \AA of the surface, depending on its precise configuration, and must be sensitive to the solvent structure of the stable IHP.

Second harmonic generation (SHG) techniques dominate the study of interfaces, although the intense laser field may cause a perturbation to the native structure and the low signal intensity usually requires a large molecular probe density. Titration of the silica-water interface monitored by SHG¹² revealed a polarized water layer close to the surface perturbing the interfacial polarizability, suggesting a stable counterion layer but without an estimate of dimension. The absorption response of a molecular probe compares favorably with our result, and these experiments can be extended to complement SHG studies. Further, the interpretation of the interface structure may also require extension of the simple mean-field Poisson-Boltzmann model, perhaps including the ion-condensation ideas of strong coupling theories.¹³⁻¹⁵ A complete understanding of the optical response of the tethered indicator will reveal some unique observations of the structure of the inner Helmholtz plane.

References and Notes

- (1) O'Reilly, J. P.; Butts, C. P.; F'Anson, A. I.; Shaw, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 1632-1633.
- (2) Steel, W. H.; Walker, R. A. *Nature* **2003**, *424*, 296-299.
- (3) Petersen, P. B.; Saykally, R. J. *J. Phys. Chem. B* **2006**, *110*, 15037-15038.
- (4) Flink, S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Phys. Org. Chem.* **2004**, *14*, 407-415.
- (5) Knoek, C. T.; Mussoraffiti, M. J.; Al-Abadleh, H. A.; Bertin, P. A.; Nguyen, S. T.; Geiger, F. M. *J. Am. Chem. Soc.* **2004**, *126*, 11754-11755.
- (6) Silberzan, P.; Leger, L.; Ausserre, D.; Benattar, J. J. *Langmuir* **1991**, *7*, 1647.
- (7) Fisk, J. D.; Batten, R.; Jones, G.; O'Reilly, J. P.; Shaw, A. M. *J. Phys. Chem. B* **2005**, *109*, 14475-14480.
- (8) Lahann, J.; Mitragotri, S.; Tran, T.-N.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R. *Science* **2003**, *299*, 371-374.
- (9) Bryant, M. A.; Crooks, R. M. *Langmuir* **1993**, *9*, 385-387.
- (10) Shyue, J. J.; De Guire, M. R.; Nakanishi, T.; Masuda, Y.; Koumoto, K.; Sukemik, C. N. *Langmuir* **2004**, *20*, 8693-8698.
- (11) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley & Sons: New York, 2001.
- (12) Ong, S.; Zhao, X.; Eiseenthal, K. B. *Chem. Phys. Lett.* **1992**, *191*, 327-335.
- (13) Moreira, A. G.; Netz, R. R. *Europhys. Lett.* **2000**, *52*, 705-711.
- (14) Netz, R. R.; Orland, H. *Euro. Phys. J. E* **2000**, *1*, 203-214.
- (15) Attard, P. *J. Phys. Chem.* **1995**, *99*, 14174-14181.