LETTER

REPLY TO COLUSSI:

Microdroplet interfacial pH, the ongoing discussion

Peter J. Vikesland[a,b,c,1], Haoran Wei[a,b,c], Qishen Huang[a,b,c], Huiyuan Guo[a,b], and Linsey C. Marr[a,b,c]

We thank Colussi for his interest (1) in our article "Aerosol microdroplets exhibit a stable pH gradient" (2). Over the course of many years, Colussi and his colleagues have made numerous contributions to our understanding of the complicated chemistry of the air/water interface, and one of the goals of our research was to further contribute to this discussion. In his letter, Colussi raises three points to which we want to respond:

i) Colussi notes that the pH-dependent change of the 1,410-cm^{-1} signal corresponding to COO^- should have plateaued for pH > 9, given that the $\text{p}K_a$ of the carboxylic acid group of 4-mercaptobenozoic acid (4-MBA) in solution is below 5. Missing from this analysis, however, is consideration of the effect of surface immobilization on the intrinsic $\text{p}K_a$ of 4-MBA. Both we (3) and others (4, 5) have shown that thiol-mediated binding of mercaptobenzoic acids to noble metal surfaces results in an increase in the measured $\text{p}K_a$ that can be attributed to the increased electron density of the benzoic acid that occurs following surface immobilization. This increase in $\text{p}K_a$ extends the range over which our pH probe produces reliable results.

ii) Colussi states that "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 statement is a simplification of our discussion. Instead, our interpretation is that the average pH at the centroid of 33 microdroplets was 3.6 pH units higher than the bulk solution from which the droplets were produced. In figure 3 of ref. 2, we report that pH decreases as one moves away from the centroid toward either the top or the bottom of the droplet. We then note that these reported pH values at least partially reflect the spatial averaging inherent to our optical surface-enhanced Raman spectroscopy (SERS) technique. A limitation of the probes used within our study is that they do not partition at the air/water interface (figure 2B of ref. 2), and thus we are not able to directly report the pH at the air/water interface.

iii) Colussi concludes by questioning our interpretation that a stable pH gradient exists within aerosol droplets. Inherent to his argument is the assumption that the system is at thermal and mechanical equilibrium. The validity of this assumption is unknown, given the lack of consensus regarding the dynamic nature of the interfacial structure of water and solutes at the air/water interface. Within the confined space of a microdroplet, concentration gradients may develop due to convective and interfacial forces (6). The temporal stability of such gradients is unknown, and equilibrium cannot necessarily be assumed (7, 8). Finally, the statement that "the pH at the air/water interface cannot be different from the pH at the centroid of the microdroplets" not only contradicts our results but also recent theoretical studies (9, 10).

Our study illustrates the capacity for SERS-based approaches to provide insight about droplet pH, and we welcome additional discussion of our findings.

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[a]Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA 24061; [b]Sustainable Nanotechnology Center, Virginia Tech Institute of Critical Technology and Applied Science, Blacksburg, VA 24061; and [c]Center for the Environmental Implications of Nanotechnology, Duke University, Durham, NC 27708

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[1]To whom correspondence should be addressed. Email: pvikes@vt.edu.

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