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COMMENTARY

The pluses and minuses of microdroplet separation

Kathryn J. Vannoy[a] and Jeffrey E. Dick[a,b,1]

Anubhav Mahapatra

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Microdroplets traverse nature, suspending when waves crash on a beach, aggregating to create clouds, and condensing to form vesicles within our cells (1, 2). The chemistry in a cloud droplet versus the chemistry in the ocean occurs in volumes differing by nearly 40 orders of magnitude. However, only within the past decade have we started to seriously consider the question: Is chemistry different at the microdroplet scale compared to a bulk liquid phase? While there are plenty of reports indicating an emphatic "YES!" to this tantalizing question, mystery still surrounds the exact mechanism by which chemistry changes (3). In the past five years, the interfacial electric field at the microdroplet interface has been implicated as a driving force for curious chemistry, as many observations of spontaneous redox reactions, both oxidation and reduction, have been reported (4). We also note that redox reactions are not the only reactions that may be activated by an electric field. For example, Aragonès and coworkers have shown that the formation of carbon–carbon bonds can be accelerated depending on their orientation in an electric field (5).

Electric fields exist at the boundary of two or more phases; due to confinement, microdroplets present a perfect reactor to enhance the probability that the molecules they encapsulate will interact with electric fields. Importantly, in 2019, Zare's group proposed spontaneous generation of hydrogen peroxide in water microdroplets (6) through the oxidative power of the surface electric field, which was measured at 10 MV/cm (7). This is just enough energy to make possible the conversion of OH^- to $\cdot OH$ (8). These observations were confirmed by the detection of hydrogen peroxide, the relatively stable product of radical recombination, in microdroplets (6, 9). In all of these studies, bulk measurements are made on systems of microdroplets, and results are extrapolated down to implicate the individual microdroplet.

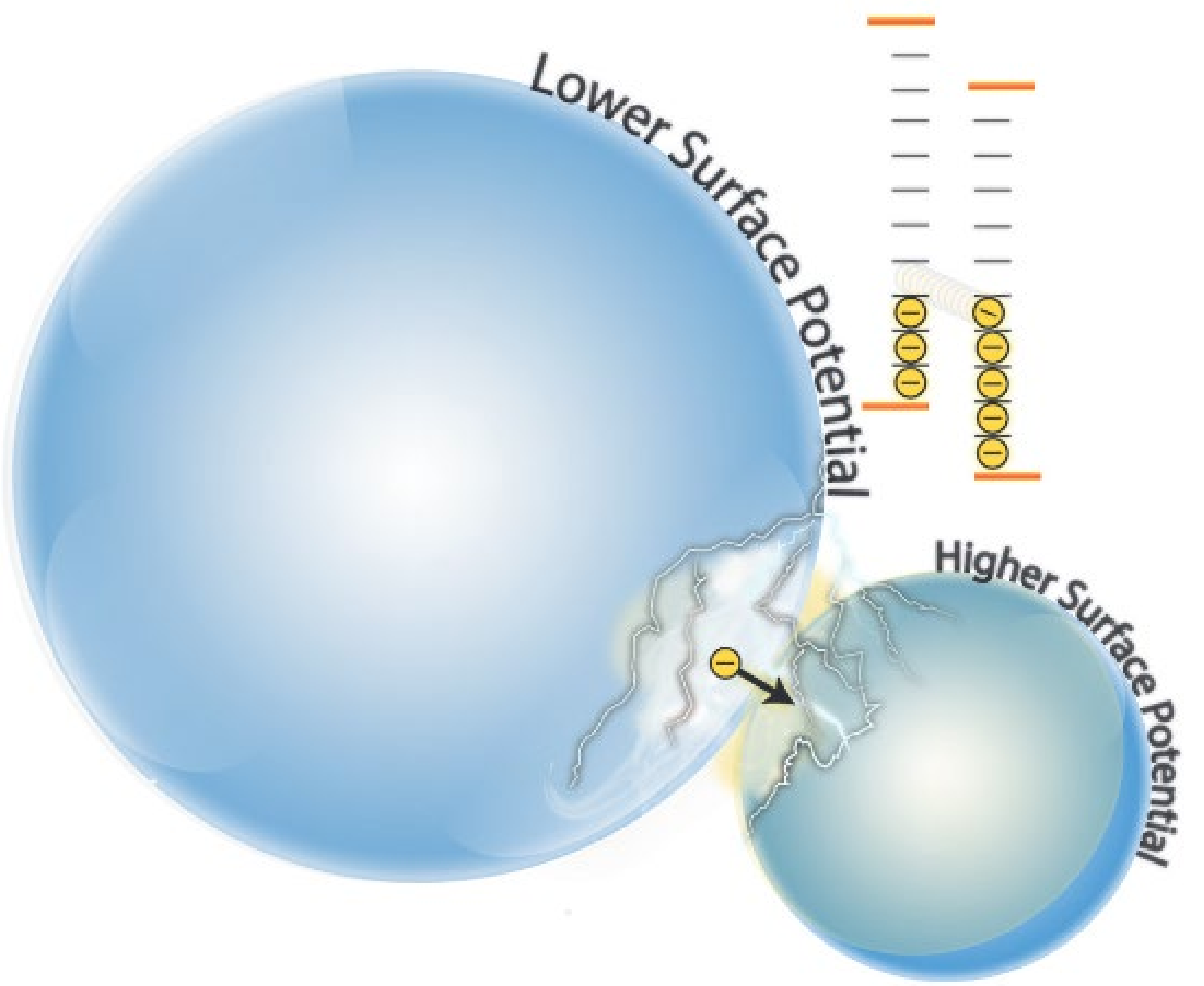

Fig. 1. Schematic of two microdroplets separating. The larger microdroplet has a lower relative surface potential and passes negative charge to the smaller microdroplet. Energy levels are shown that give the charge equilibration during the separation of two phases with differing electrochemical potentials.

In this *PNAS* article, Lin et al. present evidence that systems of microdroplets generated by ultrasonic atomization transfer charges between microdroplet surfaces during atomization through concepts surrounding contact electrification (10). This exciting study is a deep dive into the pluses and minuses of microdroplet formation, uncovering the striking observation that larger microdroplets house positive charges while smaller microdroplets house negative charges. The authors propose that microdroplets transfer their negative charges to the smaller droplets as they separate (Fig. 1). The charge of the "small" and "big" microdroplets was calculated by measuring their movement through varying electric field strengths. Powerful finite element modeling suggests that at the moment of droplet separation during the atomization process, microdroplet electric fields can reach 10^9 V/m, providing a reasonable pathway for energetically difficult processes, like the formation of hydroxyl radicals.

The presented experiment has similarities to the one performed by Millikan in 1909, where droplets of oil deflecting in an electric field were used to calculate the fundamental charge of the electron (an observation that won Millikan the Nobel Prize in Physics in 1923). Here, the authors performed a reminiscent technique to probe the charge on their system of microdroplets (a.k.a., fog) produced by ultrasonication. The fog was generated between two conductive plates of opposite polarity, parting in the electric field, with some moving toward the positive terminal and some moving toward the negative terminal. Their velocity, which was measured by a high-speed camera, can be related to the number of charges on a droplet of diameter *d*. Kelvin probe force microscopy was used to determine the average size of the split fog droplet systems (11, 12), demonstrating that the average size for the positive droplets ($d = 2.8$ μm) was about 2× larger than the negative droplets ($d = 1.2$ μm). The average charges were then determined to be $-2{,}384$ e^- for the large (positive owing to the negative number of electrons) droplets and +540 e$^-$ for the small (negative owing to the positive number of electrons) droplets. This dichotomy suggested that larger droplets were donating negative charges to the smaller droplets during microdroplet generation. This is an important implication as most of the studies demonstrating reactivity in microdroplets assume that the measured phenomenon occurs within single, isolated microdroplets, not considering that microdroplets within the system may be dynamically interacting with one another. Energy must be input in a bulk water to create a system of microdroplets (e.g., sound waves, voltage, solute flux across the boundary, mechanical vibrations, and so on), it is therefore an important consideration to understand how the energy is carried through, including droplet|droplet interactions, which must be at the core of dividing a bulk solution into isolated microcompartments. This rather elegant observation may have significant ramifications into how we imagine chemistry that occurs within droplets.

Contact electrification, a conceptual framework put forth by the authors to help contextualize the results, has a long history (13). Even in 1898, Alessandro Volta contended that his Voltaic Pile worked through contact theory, where two different metals contacting together caused chemical reactions to occur at each end of the metal. Volta found that when two metals were in contact at one end, and the other two ends were placed in different liquids, electrochemical reactions were sustained. At the end of the day, Volta was not correct, but his hands were tied since the concepts of ions and electrons were still decades away, highlighting the importance of new measurement tools (vide infra) in gaining mechanistic insight. While we now know that chemical reactions are driven because of difference in the electrochemical potentials of two liquid phases, the idea of two phases coming into contact and driving charge transfer must be a consideration in microdroplet chemistry. Contact electrification is ubiquitous across all kinds of material interfaces (solid–solid, solid–liquid, liquid–liquid, solid–liquid–liquid, etc.), and the mechanisms for charge transfer vary (e.g., ion transfer, electron transfer, and material transfer) (13). Previously, Bard and coworkers demonstrated that electron transfer reactions could proceed even on insulators that are sufficiently charged, highlighting the importance of electrostatic electrochemistry (14). Therefore, the conceptually elegant advance put forward by the authors is that when two phases form from a single phase, sizes may be different, charge parity may be violated, and interesting and unexpected chemistry can occur.

This framework adds necessary details to fuel the ongoing discussion of mechanistic considerations in microdroplet reactivity. Previously, it was reported that a water droplet's surface potential may be dependent on the size, or more specifically, the curvature of the droplet (15). The authors present a theory where the discrepancy between the surface potential of a big droplet and a small droplet drives charge transfer. This mechanism is commonly discussed in solid-state physics. Here, negative charges are moved from the big droplet to the small droplet at the moment of microdroplet separation. As such, this paper suggests that the most potent electric field to consider is the one that forms between the surfaces of these droplets, as opposed to previous works that examine the electric field at an isolated microdroplet interface.

There are exciting opportunities for mechanistic insight in understanding the curious chemistry in microdroplets. The paper published by Lin et al. not only presents interesting observations but an innovative conceptual framework to help guide mechanistic considerations. The role of the electric field and electrostatic interactions, especially in environmentally relevant places like the atmosphere, must be considered to understand how chemistry changes in dynamic systems of tiny volumes. This is likely the most important question as we enter the next decade of microdroplet chemistry. As the community is crystallizing on the opinion that chemistry does change in microdroplets, how exactly those changes come about gives society the greatest opportunity to discover new knowledge. However, answering the question of "How?" is more difficult as it has no binary result but presents an exciting task for all flavors of chemists—from makers to modelers to measurers. Undoubtedly, microdroplet chemistry will be used to create new molecules and drive innovative transformations in making and—perhaps more importantly—breaking bonds. Modeling the electric fields at phase boundaries, droplet curvature, molecular solvation and adsorption to the interface, and double-layer arrangement require methods more precise than continuum theories. As such, density functional theory and molecular dynamics can augment our understanding of tiny interfaces.

Finally, the development of new measurement tools is of paramount importance. Almost every claim in scientific literature is backed by some type of measurement. New ways of measuring can yield claims that have never been claimable, uncovering new truths about Nature under unimaginable conditions. The paper by Lin et al. highlights the beauty of developing new measurement tools—or new ways of making a measurement—that can have broad implications for our understanding of the natural world. We must build upon measurement techniques that currently exist, such as fluorescence (17, 18), mass spectrochemistry (3), NMR (19), and electrochemistry (20) to paint a clear perspective of a model for microdroplet chemistry. We can further take a play from the authors' book and invoke previously known physical processes, like contact electrification, to test the model's framework and validity. This process, repeated over years, has the potential to unveil insight into how life formed on this planet (and perhaps a few others).

-Thank you