Propagating acidity fronts in the iodate-arsenous acid reaction

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Propagating Acidity Fronts in the Iodate–Arsenous Acid Reaction

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Propagating fronts in unbuffered solutions containing iodate and arsenous acid give rise to large changes in hydrogen ion concentration within the narrow band of chemical activity. The pH-dependent propagation velocity decreases to extremely small values in basic solution where threshold behavior is exhibited.

The coupling of autocatalytic chemical reaction with diffusion in unstirred solution often gives rise to propagating fronts of chemical activity. A number of autocatalytic "clock reactions" are now known to exhibit fronts[1-7] which typically propagate into solution containing initial reactants undergoing very slow reaction and leave behind solution near the equilibrium composition. Autocatalytic reaction may also couple with mass transport from surface spreading and thermal convection, the extent of which depends upon the particular experimental configuration and reaction exothermicity.[7,8]

The iodate–arsenous acid reaction is autocatalytic in both iodide and hydrogen ion;[9] however, it is usually studied in acidic buffered solutions.[2,3] Figure 1 shows a chemical wave propagating in a thin film of solution containing iodate, arsenous acid, and sufficient sodium hydroxide to adjust the initial reaction mixture to pH 8.02. Starch and methyl orange indicators were also added for visualization of the wave. Ahead of the front the solution is yellow and behind red, corresponding to the basic and acidic forms of methyl orange indicator. Depending on the initial and final pH of the solution, other indicators may also be used to visualize the front. Phenolphthalein gives rise to a colorless region expanding into surrounding red solution and thymol blue-B generates a yellow wave expanding into blue for high initial pH and a red wave expanding into yellow for low initial pH. When starch indicator is also added, a thin blue band slightly behind the acidity front is exhibited, corresponding to the presence of the transient intermediate triiodide ion.[2-4,10]

The wave shown in Figure 1 was initiated at a Pt electrode in the center of the petri dish biased ca. +3.0 V against a second Pt electrode near the edge of the dish. At the first appearance of red coloration near the positive electrode the power was switched off and soon after the sharp front formed and began to propagate outward.

Front velocity as a function of initial solution pH is shown by the solid circles in Figure 2. Wave front position as a function of time (photographically measured) was linear at all values of initial solution pH and the front remained very sharp in even the slowest waves. The propagation velocity is almost insensitive to initial pH in the range 3.5 < pH < 7.5. For pH > 8.0, the velocity is strongly dependent on initial pH and in the most basic solutions the fronts propagate extremely slowly. The wave in Figure 1 required about 1 h to expand to the edges of the petri dish 12.5
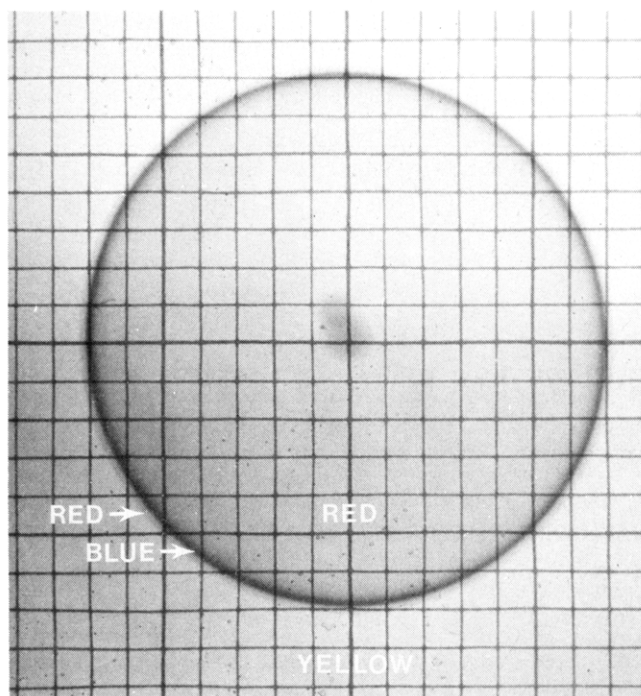

Figure 1. Front propagating into basic yellow solution (pH 8.02) and leaving behind acidic red solution (pH 2.28). Solution depth ca. 0.8 mm, solution temperature 25.0 ± 0.2 °C. Initial reaction mixture containing 6.43×10^{-3} M KIO_3, 1.99×10^{-2} M H_3AsO_3, 1.2×10^{-4} M methyl orange indicator, and 0.2% (wt) starch indicator adjusted with NaOH to pH 8.02. Field of view: 4.7 × 6.7 cm. Front velocity: 1.86×10^{-2} mm s^{-1}.
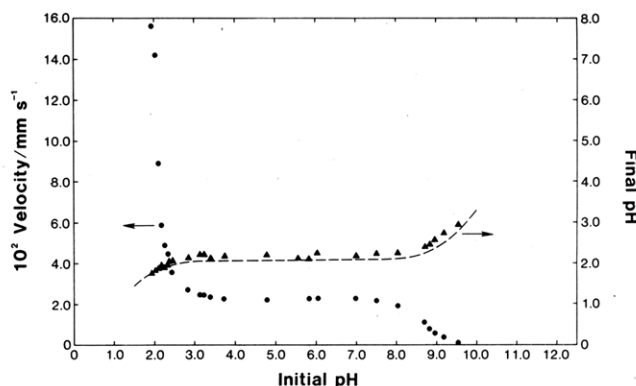

Figure 2. Front propagation velocity (●) and final solution pH (▲) as a function of initial solution pH (adjusted by addition of NaOH or H_2SO_4). Dashed curve shows final pH calculated from initial pH and dissociation of H_3AsO_4 and H_3AsO_3. Conditions and reactant concentrations same as Figure 1 except initial pH.

cm in diameter. The slowest wave in Figure 2 (initial pH = 9.54; $v = 7.27 \times 10^{-4}$ mm s^{-1}) required nearly 24 hours to consume the reaction mixture in the petri dish. For values of initial pH > 9.6, fronts propagate a few millimeters outward from the initiation

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electrode, but then stop and slowly dissipate. These waves appeared only because the solution pH near the electrode was lowered by electrolytic oxidation of H_3AsO_3 and H_2O; the unaffected solution would not support the propagating front. At values of initial pH < 3.0, velocities increased sharply with decreasing pH; at pH < 1.9, the diminished lifetime of the bulk solution made velocity measurements impossible. Effects of pH on front propagation were reported in the early studies of this system by Epik and Shub[11] and Shub[12] reported a velocity dependence similar to that in Figure 2.

Shown in Figure 2 by solid triangles are values of final pH, corresponding to the solution behind the propagating front. In reaction mixtures with high initial pH, these values could be measured only after a front had completely consumed the film of solution in the petri dish. The solutions appeared to be indefinitely stable to significant reaction if a chemical wave was not deliberately initiated. The most basic solutions, monitored in a thermostated beaker, displayed no significant change in pH over the course of days. The values of final pH shown in Figure

2 are in good agreement with values calculated (dashed curve) by considering only the initial solution pH and the dissociation of H_3AsO_4 ($K_1 = 6.2 \times 10^{-3}$) and H_3AsO_3 ($K = 6.0 \times 10^{-10}$). We see that the front velocity is sensitive to initial pH only at the high and low values where the final pH deviates from the value established by the dissociation of H_3AsO_4.

Propagating fronts in the iodate–arsenous acid reaction have been studied in buffered solutions[2,3,8] and can be described with a simple reaction-diffusion model.[3,4,10] Fronts in unbuffered reaction mixtures exhibit a much wider range of velocities; propagation velocities for the highest and lowest pH in Figure 2 differ by a factor of 214. These fronts also exhibit threshold behavior in basic solution due to the neutralization of H^+ by OH^- ahead of the front that is not observed in acidic buffered medium. This threshold behavior gives rise to reaction mixtures that undergo significant chemical reaction only upon local initiation and subsequent front propagation. The unbuffered iodate–arsenous acid reaction also provides an opportunity to investigate reaction-diffusion behavior arising from two autocatalytic species, I^- and H^+, with very different diffusion coefficients.

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FEATURE ARTICLE

Molecular Forces in the Self-Organization of Amphiphiles

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Some good progress has been made in quantifying the mechanisms that drive the formation and set the structure of multimolecular aggregates like micelles, vesicles, bilayers, and microemulsions. Parallel advances have been made in understanding the nature of molecular forces between surfaces at distances below 100 Å. The interplay between these two areas provides new insights into the way that the physical chemistry of lipid self-assembly affects some biological processes.

Introduction

Over and over again in cell biology, precise recycling patterns occur that require transformations between aggregates like micelles, vesicles, and bilayer membranes. These aggregates are the subject of much interest in physical chemistry at this time. They are dynamic entities that provide a matrix to guide biochemical processes. A complex chain of chemical reactions in biochemistry at a molecular level is comprehensible in a bulk solution. But the containment of reactants and transport to another site effected through the self-organizing capacity of lipids is a more complicated issue. The lipids are physically associated, not chemically bound. Amphiphiles must have more than a passive role. It is known and understood that lipid membranes provide a matrix for enzymatic catalysis, for structural proteins, for photosynthesis, and for transport, and a protection to cells against the exterior environment. They mediate protein interactions. It is not known how.

Even in water, amphiphiles alone assemble into structures which mimic those in cell biology. With oil they form a diversity of much more complicated structures in microemulsions. Lipids and surfactants transform and reassemble into quite different structures in response to small changes in environment like temperature, concentration, and salt. The theme of this article is that this capacity for organization is beginning to be understood.

We can make these remarks explicit by considering the mechanism[1] of endocytosis as illustrated in Figure 1. In terms of specific biochemical processes, one focuses on the selectivity of the binding of ligand to the cell membrane proteins, the dissociation of the ligand complex induced by the decrease in pH within the endocytosome, the separation of the ligand and protein

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