

pH-Dependent Redox Couple: Illustrating the Nernst Equation Using Cyclic Voltammetry

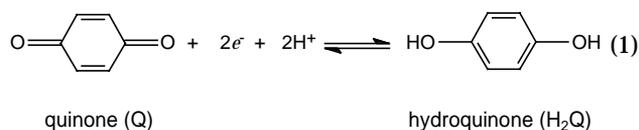
Mary M. Walczak,* Deborah A. Dryer, Dana D. Jacobson, Michele G. Foss, and Nolan T. Flynn

Department of Chemistry, St. Olaf College, Northfield, MN 55057

The Nernst equation relating potential to the activities of reactants and products is frequently discussed in chemistry classes, at both the advanced and introductory levels. At St. Olaf College, first-year students are introduced to electrochemistry and the Nernst equation during their second-semester Chemical Reactions course and they delve further into the subject when they take Analytical Chemistry, usually as juniors. The importance this topic receives in course work, however, is not usually paralleled in the laboratory. Many traditional electrochemistry experiments utilize toxic heavy metals, such as mercury and cadmium, as electrodes or electroactive species. Concern over the toxicity of these materials caused electrochemistry experiments to disappear from the curriculum and the Nernst equation became pencil-and-paper (or computer-and-printer) exercises.

Other nontoxic electrode materials, such as Pt, Au, and C, are available for use in laboratory experiments. Unfortunately, these electrodes sometimes require extensive preconditioning before use. These preconditioning procedures involve cleaning and polishing the electrode surface and cycling it in an acidic electrolyte. All of these steps are time consuming and require substantial technical competence. We have found that Au electrodes that are cleaned electrochemically and stored in 1 M H₂SO₄ remain sufficiently clean for use in the laboratory with minimal preconditioning. Occasional polishing with diamond paste followed by a short cycling period in acid is all the preconditioning required. In addition, the use of acid-cleaned glassware and high-purity water also minimizes electrode contamination and/or passivation.

Articles from an ACS symposium "Electrochemistry: State of the Art", published in this *Journal*, describe many interesting electrochemical processes and provide a useful teaching resource (1). Surprisingly, only a few experiments illustrating the effect of concentration on electrode potential have been published in this *Journal* (2). We wanted to add an experiment to our Analytical Chemistry curriculum that demonstrated the effect changing the concentration of the redox species had on half-wave potential. An excellent candidate for such an experiment is the hydroquinone/quinone redox couple (3). The half-reaction for this couple, illustrated in reaction 1, involves H⁺ ions. The standard reduction potential for this reaction in 1 M acid is 0.50 V vs. Ag|AgCl|sat'd KCl.



Changing the pH of the solution would alter the concentration of one of the species involved in the reaction and result in a shift in the redox potential. The equation for the electrode potential of this half-reaction can be rearranged

to illustrate the pH dependence,

$$E = E_{1/2} - \frac{0.0592}{2} \log \frac{[\text{H}_2\text{Q}]}{[\text{Q}]} - 0.0592\text{pH} \quad (2)$$

where $E_{1/2}$ includes corrections to the standard reduction potential for activity coefficients and diffusion coefficients—that is,

$$E_{1/2} = E^0 + \frac{RT}{nF} \left\{ \ln \frac{\gamma_{\text{O}}}{\gamma_{\text{R}}} + \ln \left(\frac{D_{\text{R}}}{D_{\text{O}}} \right)^{1/2} \right\}$$

From eq 2 it follows that increasing the pH of the solution will cause a decrease in the redox potential for the couple.

In cyclic voltammetry, the potential applied to the working electrode is swept linearly between two switching potentials ca. 0.2 V past the anodic and cathodic peak potentials. Just prior to a cathodic sweep the electroactive species exists primarily as Q. As the electrode potential is swept cathodically the Q is reduced to H₂Q and the ratio [Q]/[H₂Q] approaches zero. Thus, a cycle between entirely oxidized and entirely reduced species occurs as the working electrode potential is swept cathodically between the switching potentials.

The solution to the differential equations relating the current and potential in the cyclic voltammetry experiment for a reversible redox couple at a planar electrode has been developed by Nicholson and Shain (4). The result for the reduction of oxidized species O (i.e., O + $n\text{e}^- \rightarrow \text{R}$) is

$$i = nFAC_{\text{O}}^* \sqrt{\pi D_{\text{O}} a} \chi(at) \quad (3)$$

where i , n , F , and A , have their usual meanings; C_{O}^* and D_{O} are the concentration at the electrode surface and the diffusion coefficient, respectively, for the oxidized species; and $a = nFv/RT$. The function $\chi(at)$ holds the dependence on potential, and numerical tabulations of this function are found in the literature (4, 5). The function has the form $\chi(at) = \chi[(E - E_{1/2})n]$. Although most of the theoretical electrochemical literature seeks numerical solutions for generic redox reactions of the form O + $n\text{e}^- \rightarrow \text{R}$, the pH dependence of reaction 1 can be extracted from eq 3 when one realizes that the [H⁺] dependence is usually embedded in $E_{1/2}$ along with the activity coefficients and diffusion constants; that is,

$$E_{1/2} = E^0 + \frac{RT}{nF} \left\{ \ln \frac{\gamma_{\text{O}}}{\gamma_{\text{R}}} + \ln \left(\frac{D_{\text{R}}}{D_{\text{O}}} \right)^{1/2} + \ln [\text{H}^+]^m \right\}$$

where m is the number of H⁺ ions involved in the reaction (6).

In this experiment, students prepare buffer solutions of different pH containing hydroquinone and obtain cyclic voltammograms of the hydroquinone redox couple. A potential shift to more negative values occurs as the pH of the buffer solution increases as predicted by eq 2. This dramatic

*Corresponding author.

shift illustrates the applicability of the Nernst equation and gives students an appreciation of how potential depends on concentration.

Experimental Details

Instrumentation

The electrochemical cells are controlled with a computer-interfaced CV-27 voltammograph (Bioanalytical Systems, West Lafayette, IN). LabVIEW software (National Instruments, Austin, TX) and an AT-MIO-16DH A/D board (National Instruments) in an Epson 486 PC computer are used to interface the voltammograph to the computer. Collected data are saved as spreadsheet files and are manipulated using one of several commercially available spreadsheet programs.

Electrochemical Cells

The electrochemical cells and cell covers (which hold the 26-gauge wire Pt auxiliary electrode) were purchased from Bioanalytical Systems. The glass body of the cell was cleaned by soaking in a NoChromix (Godax Laboratories, New York) solution and rinsing with NanoPure water (Barnstead, Dubuque, IA). We found cleaning the cells in this manner imperative to remove small quantities of organic material that could subsequently contaminate the Au electrode.

The Ag|AgCl|sat'd KCl reference electrodes were prepared in house. Reliable, easily fabricated electrodes can be made by methods detailed in the literature (7-9). We stored the reference electrodes in a solution saturated in both KCl and AgCl when not in use.

The BAS Au electrodes have an area of 8 mm² and are encased in Kel-F. They are cleaned by polishing with diamond paste on a nylon polishing pad (Buehler, Lake Bluff, IL) and rinsing with NanoPure water. Polishing with fine grade alumina would also be appropriate. The Au electrode is then placed in the cell and cycled in 1 M H₂SO₄ between -0.20 V and 1.60 V until a steady-state voltammogram, shown in Figure 1, is obtained. A scan rate of 0.100 V/s was used for all recorded voltammograms. During the cleaning cycles the scan rate was sometimes increased to 0.200 V/s to expedite the electrode cleaning. The voltammogram in Figure 1 has an anodic wave between ca. 1.2 and 1.5 V, corresponding to oxidation of the gold surface. The cathodic wave at ca. 0.9 V is the subsequent reduction of the gold oxide. A region with low current flow at potentials more negative than these waves indicates that the Au surface is clean and there are no electrochemically active species in the solution. If other electrochemical waves are found, the cell is disassembled and both the Au and the cell are cleaned again. The Au electrode is stored in 1 M H₂SO₄ when not in use.

Chemicals

Hydroquinone (99.99%, Aldrich), KCl (Fisher), NaClO₄ (Fisher), NaOH (99.9%, Aldrich), H₃PO₄ (Fisher), and CH₃COOH (Fisher) were used as received. All solutions were prepared with NanoPure water and were deoxygenated for 5-10 min with water-saturated N₂ before cycling.

The Experiment

The Au electrode was cleaned as described above. The amount of time students spent cleaning the Au was minimal. Typically, one student worked on preparing buffer solutions while another worked on cycling the Au electrode in 1 M H₂SO₄. If the electrode had not been used in several months, the instructor or lab assistant polished it with diamond paste and cycled it in 1 M H₂SO₄ before the start of the lab period. This was done primarily to insure that the experi-

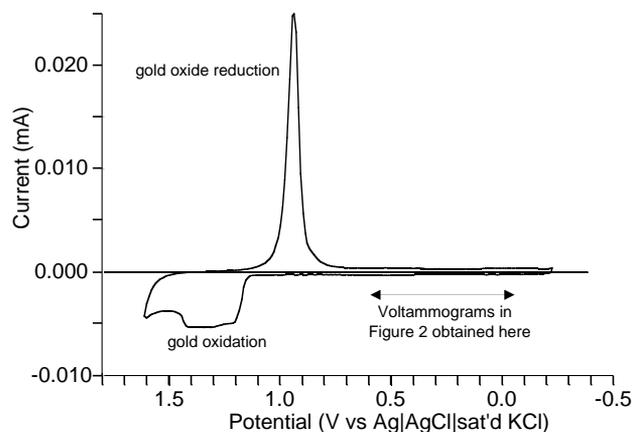


Figure 1. Cyclic voltammogram of Au working electrode in 1 M H₂SO₄.

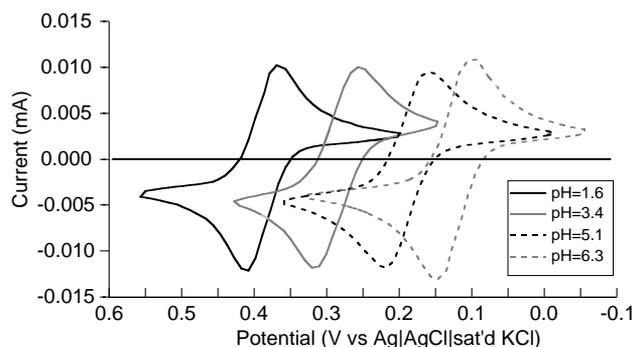


Figure 2. Cyclic voltammograms for 1 mM H₂Q solutions of varying pH. The pH was maintained with acetate/phosphate buffers. The ionic strength was not adjusted by addition of NaClO₄. For clarity, not all voltammograms recorded are displayed here.

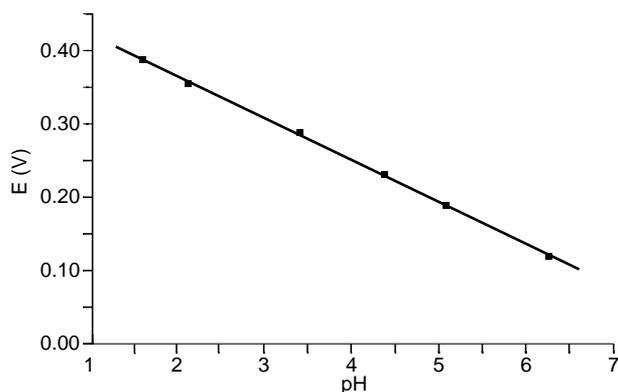


Figure 3. Average cathodic and anodic peak potential (E) vs. pH for 1 mM H₂Q in acetate/phosphate buffers of various pH. The ionic strength was not adjusted by addition of NaClO₄.

ment would be completed in the allotted four-hour time period. Cleaning by the instructor or lab assistant was not necessary for lab periods later the same week.

Students prepared four or five acetate/phosphate buffer solutions in the pH range 1–6. A mixed buffer system was used to span the entire pH range. Both acetate and phosphate were present at 0.1 M concentration. We limited ourselves to acidic pH's to avoid complications due to the dissociation of H₂Q above pH 6 (10). Buffers were adjusted to appropriate pH values with 0.1 M NaOH. The buffer solutions were 1 mM in hydroquinone.

Students were given basic instructions on how to operate the instrument. They recorded voltammograms of hydroquinone in each pH solution. The positive and negative scan limits were changed for each solution so the scan was reversed 0.15 to 0.20 V past the peak of the cathodic and anodic waves. Positive scan limits ranged from 0.6 to 0.3 V; negative scan limits ranged from 0.2 to -0.05 V. We found that scanning into the gold oxidation region (i.e., potentials more positive than about 1 V) resulted in electrode contamination, which required polishing and cleaning before continuing. Voltammograms were saved as spreadsheet files by LabVIEW and imported into a spreadsheet program for graphical analysis. Students were asked to display all their voltammograms in a single plot, to plot the average of the cathodic and anodic peak potentials $E = (E_{p,a} + E_{p,c})/2$ vs. pH, and to determine the number of electrons involved in the redox process.

Some students prepared constant-ionic-strength buffers by making the acetate and phosphate concentrations ca. 0.05 M and adding NaClO₄ to keep the ionic strength constant at 0.1 M.¹ Voltammograms recorded in acetate/phosphate solution were indistinguishable from acetate/phosphate/NaClO₄ solutions of the same pH. We attribute this insensitivity toward ionic strength to the fairly high electrolyte concentrations used in our experiments. When the ionic strength was not held constant and the acetate and phosphate concentrations were both 0.1 M, the ionic strength varied between zero (pH 1.6) and 0.4 M (pH 6.3). Differences in the voltammograms may be observed if the buffering acid concentrations is dropped to 0.05 M in the solutions where the ionic strength is not held constant.

Results

A cyclic voltammogram for a 1 mM solution of hydroquinone in acetate/phosphate buffer of pH 1.6 is shown in Figure 2. From the anodic and cathodic peak potentials of 0.41 and 0.37 V, respectively, we find E is 0.39 V. The integrated peak currents² for the anodic and cathodic waves are 0.72 and 0.71 mC, respectively. Both these measurements indicate that the hydroquinone/quinone system behaves fairly reversibly, as expected at an Au working electrode (11).

According to eq 2, E should shift to more negative values as the solution pH increases. Voltammograms recorded by students for hydroquinone solutions in the pH range 1.6 to 6.3 are shown in Figure 2. As predicted, the entire voltammogram shifts to more negative potentials as the solution pH increases. Plotting voltammograms on the same graph provides an elegant illustration of the Nernst equation.

The pH dependence of potential can also be seen in Figure 3, where E is plotted against pH. The slope of the line is -57.3 (± 0.6) mV/pH unit. From eq 2, the slope of the plot of E vs. pH should be -59.2 mV/pH unit. Using the slope obtained experimentally to calculate the number of electrons involved in the half-reaction, we find reaction 1 to involve 2.07 ± 0.04 electrons. The value calculated is in

reasonable agreement with that predicted for reaction 1 (i.e., 2 electrons).

Conclusions

The hydroquinone redox couple is an excellent system for illustrating the Nernst equation. Changing the pH between 1 and 6 results in a total change in potential of 0.27 V. This large shift is easily discerned and follows the behavior expected from theory. The slope of the E vs. pH graph also correctly predicts the number of electrons involved in the hydroquinone/quinone half reaction.

Students had an opportunity to evaluate the semester's lab experiments at the end of the term. They were asked to state the most valuable skill they gained from each experiment. They considered three aspects of this experiment valuable: using a three-electrode cell, learning the basics of voltammetry, and seeing how pH affects potential. One student commented further that it was "great to have something visual and concrete to tie into abstract concepts like the Nernst equation and redox reactions."

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Notes

1. When the supporting electrolyte contained large concentrations of ClO₄⁻ the filling solution of the reference electrode was changed from saturated KCl to saturated NaCl to prevent formation of KClO₄(s) at the tip of the reference electrode.

2. The voltammetric waves were integrated using the method of Riemann Sums and the spreadsheet program. A straight line baseline was used.

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