Analysis of Two Redox Couples in a Series: An Expanded Experiment To Introduce Undergraduate Students to Cyclic Voltammetry and Electrochemical Simulations

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Ⓢ *Supporting Information*

ABSTRACT: Cyclic voltammetry (CV) is a popular technique for the determination of electrochemical mechanisms because it can provide useful information on a redox couple. Computer simulations of CV data are sometimes used to study complex redox systems with interrelated processes. The following communication outlines an expanded version of an experiment developed to introduce undergraduate students to CV and electrochemical simulations. A new solvent/electrolyte system of dimethylformamide with 0.1 M tetrabutylammonium hexafluorophosphate increases analyte solubility, improves sample conductivity, and extends the electrochemical domain as compared to the original experiment. Simulation parameters determined by wave clipping the first redox couple of a series are used to simulate a more complex two-redox system of the same compound. Experiments designed to teach CV and electrochemical simulations to undergraduate students rarely use wave clipping as a technique to simplify experimental data for the analysis of a more complex system. The addition of wave clipping and the analysis of a two redox system increase the laboratory experience gained by the students as compared to the original experiment, which was limited to a single redox couple.

KEYWORDS: *Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, Hands-On Learning/Manipulatives, Electrochemistry*

■ INTRODUCTION

Cyclic voltammetry (CV) is often used to study electrochemical mechanisms because the method can provide useful information on a redox couple.[1−4] CV involves the application of a potential ramp on an unstirred solution while monitoring the current and then reversing the ramp for a return scan. The technique is sometimes taught in undergraduate chemistry laboratories.[5] The CV waveform depends on several processes including electron transfer, diffusion, and coupled homogeneous reactions. Electrochemical simulations are sometimes helpful in determining the various processes involved in the redox system.[1−4]

This communication outlines an expanded version of an experiment that was developed to introduce undergraduate students to CV and electrochemical simulations. Parameters obtained from wave clipping the first redox couple of a series are used to simulate a more complex two-redox system of the same compound.[2,4] Wave clipping involves adjusting the scan range of a CV experiment to isolate a redox couple of a series in order to simplify the subsequent analysis. The electrochemical domain of the original experiment was extended by using dimethylformamide (DMF) as the solvent and tetrabutylammonium hexafluorophosphate (TBAHFP) as the electrolyte. The extended electrochemical domain allows for the acquisition of the second redox couple.[6] Electrochemical experiments designed to teach CV to undergraduate students rarely use wave clipping as a technique to determine parameters for the analysis of a more complex redox system. The addition of wave clipping the first couple of a series to obtain parameters for the simulation of a more complex two redox system for the same compound increases the hands-on laboratory experience gained by the students as compared to the original procedure, which was limited to a single redox couple.

■ EXPERIMENTAL SECTION

Dimethylformamide (Sigma-Aldrich; ≥99.8%), benzophenone (Mallinckrodt; 99%), tetrabutylammonium hexafluorophosphate (Sigma-Aldrich; 98%), and mercury (Bethlehem; 99.9995%) were used without further purification. Samples were prepared containing 1×10^{-7} mol/cm^3 benzophenone in dimethylformamide with 0.1 M tetrabutylammonium hexafluorophosphate electrolyte. Oxygen was removed from the samples by bubbling with N$_2$ gas saturated with solvent with magnetic stirring at 600 rpm for 15 min. The voltammograms were acquired from unstirred solutions under N$_2$ blankets. Background scans of the solvent/electrolyte system were acquired using identical acquisition parameters as the samples (Table 1). Backgrounds were subtracted from sample voltammograms prior to simulation. The voltammograms were acquired using a BioAnalytical Systems, Inc. (BASi) Epsilon-2 potentiostat. A static drop mercury electrode (SDME) was the working electrode (surface area: 3.4×10^{-2} cm^2). The surface area was determined by weighing 10 mercury drops delivered into 20 mL of solvent/electrolyte, converting the mass of one drop into a volume using the density of mercury, and then applying equations for the volume and

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Table 1. Cyclic Voltammetry Acquisition Parameters for 1×10^{-7} mol/cm^3 Benzophenone in Dimethylformamide with 0.1 M Tetrabutylammonium Hexafluorophosphate Electrolyte

Parameter	Single Redox Couple	Two Couples in Series
Initial potential, V	−1.50	−1.35
Switching potential, V	−2.00	−2.85
Final potential, V	−1.50	−1.35
Scan rates, V/s	0.1−0.6	0.1−0.6
Full scale, μA	1	1
Noise filter, Hz	1	1
Quiet time, s	2	2
Sample interval, V	1×10^{-3}	1×10^{-3}
Number of segments	2	2

surface area of a sphere.[1] Loss of area at the contact point with the SDME capillary was assumed to be negligible. Increasing the electrode area in the simulations was necessary to fit the experimental voltammograms. This could be the result of inaccurate area measurements, errors in benzophenone concentrations, or approximations that were made in the spreadsheet calculations.[1−3,7] While mercury thin-films or solid planar-disk electrodes would likely provide currents that were more consistent with the assumption of linear diffusion made in the spreadsheet, the SDME was chosen for this work because the renewable mercury surface requires no preparation (e.g., polishing) prior to use, which is useful for teaching numerous undergraduate students within a given laboratory period. The auxiliary electrode was a platinum wire (BASi, MW-1032; length, 7.5 cm; width, 0.5 mm). The reference electrode was Ag/AgCl/NaCl 3 M (BASi, MF-2052).

HAZARDS

Dimethylformamide (DMF) is a flammable liquid with acute toxicity that may cause reproductive harm. Avoid inhalation, skin, and eye contact. Use in a well-ventilated area, wear eye protection, avoid spark sources and flames, and wash skin thoroughly after handling. Tetrabutylammonium hexafluorophosphate (TBAHFP) causes skin, eye, and respiratory irritation. Avoid inhalation, wear eye protection, and wash skin thoroughly after handling. Benzophenone is an irritant and sensitizer. Avoid inhalation, wear eye protection, and wash skin thoroughly after handling. Mercury can be absorbed through skin, causes irritation, and can damage the central nervous system. Avoid skin contact and use in a well-ventilated area. Place trays underneath equipment and work areas to contain spills. Store mercury in approved containers and dispose of properly.

RESULTS

In the previous version of this experiment, undergraduate students analyzed acidified aqueous/ethanol solutions of benzophenone with 0.1 M sodium sulfate electrolyte using CV and an easy-to-use spreadsheet simulator written in Microsoft Excel.[7] Sample concentrations were limited to about 6×10^{-8} mol/cm^3 because of the low solubility of benzophenone. This resulted in small experimental peak currents that were roughly 2×10^{-7} A or less. Background scans contained distortions consistent with capacitance effects that increased with scan rate.[1,2] Simulations of the experimental data revealed peak broadening consistent with capacitance

effects, which increased with scan rate as well.[7] This limited the scan rate to 0.06 V/s or less.

Replacing the aqueous solutions of benzophenone with an organic system consisting of DMF as the solvent and 0.1 M TBAHFP as the electrolyte overcame the limited solubility and capacitance problems noted above. Background scans showed less distortion from capacitance effects using scan rates between 0.1 and 0.6 V/s. This suggested increased conductance as compared to the original solvent system.[1,2,6] The ability to use faster scan rates as compared to the original procedure helps to minimize mass transport via convection.[1,2] Benzophenone concentrations of about 1×10^{-7} mol/cm^3 provided improved CV waveforms with larger peak currents and fewer distortions (Figure 1). The reduction wave obtained during the forward
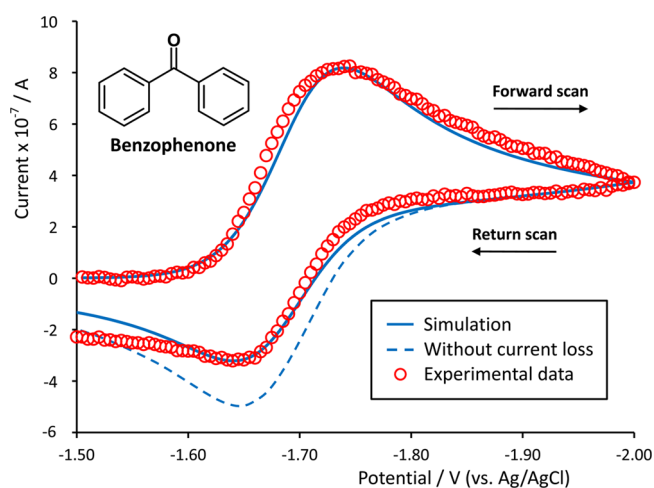

Figure 1. Single redox couple of benzophenone and computer simulation. Parameters: $C_{bulk} = 1.0 \times 10^{-7}$ mol/cm^3, $E_1 = -1.50$ V, $E_2 = -2.00$ V, $\nu = 0.1$ V/s, $A = 3.7 \times 10^{-2}$ cm^2, $E^{o\prime}_1 = -1.69$ V, $n_1 = 1$, $k^o_1 = 0.01$ cm/s, $\alpha_1 = 0.5$, $D_1 = 1 \times 10^{-5}$ cm^2/s, $k_{2,1\ (dimer)} = 1.0 \times 10^6$ cm^3/(mol·s), $k_{1,1\ (anion)} = 0.04$ s^{-1}. See the Supporting Information (Table S1) for definitions of the simulation parameters.

scan was the result of electron transfer to benzophenone, which produced a radical anion reduction product in the vicinity of the working electrode (Figure 2, reaction 1).[8] The absolute value of the oxidation current peak obtained during the return scan was smaller than that of the current peak for reduction. This indicated that homogeneous reaction(s) occurred after the electron transfer that removed portion(s) of the reduction product from the vicinity of the working electrode during the return scan. One possible reaction involves the removal of the radical anion through a second-order dimerization process (Figure 2, reaction 2). Another possible reaction is the loss of the radical anion by reaction with trace water in the solvent (Figure 2, reaction 3).

To simulate the voltammogram in Figure 1, the bulk concentration (C_{bulk}) was set to the benzophenone sample concentration (see Experimental Section). The variables E_1, E_2, and ν (see the Supporting Information, Table S1) were set to their corresponding acquisition parameters (Table 1). The area of the electrode (A) was determined experimentally (see Experimental Section) and then adjusted in the simulations to compensate for variations in drop size, errors in sample concentration, and approximations that were made in the simulations.[1−3,7] The diffusion coefficient (D_1) was set to a literature value for benzophenone.[8] The remaining parameters
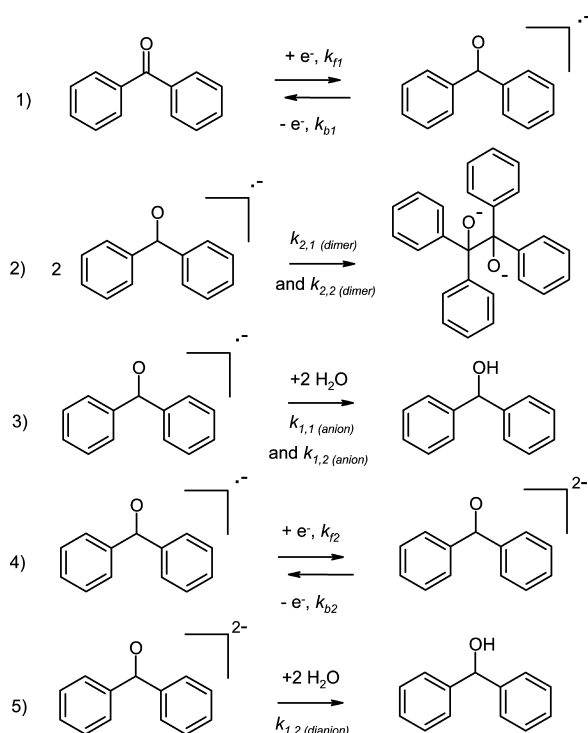
Figure 2. Reaction scheme for benzophenone: (1) First electron transfer; (2) dimerization; (3) hydrogen extraction from trace water in solvent by radical anion; (4) second electron transfer; (5) hydrogen extraction from trace water by dianion. Note: reactions 3 and 5 are not fully balanced.

Figure 3. Two redox couples in series for benzophenone and simulation. Parameters: $C_{bulk} = 1.2 \times 10^{-7}$ mol/cm^3, $E_1 = -1.35$ V, $E_2 = -2.85$ V, $\nu = 0.1$ V/s, $A = 4.0 \times 10^{-2}$ cm^2, $E^{o\prime}_1 = -1.70$ V, $n_1 = 1$, $k^o_1 = 0.01$ cm/s, $\alpha_1 = 0.6$, $D_1 = 1.1 \times 10^{-5}$ cm^2/s, $k_{2,1\,(dimer)} = 1.0 \times 10^6$ cm^3/(mol·s), $k_{1,1\,(anion)} = 0.05$ s^{-1}, $E^{o\prime}_2 = -2.22$ V, $n_2 = 1$, $k^o_2 = 5 \times 10^{-4}$ cm/s, $\alpha_2 = 0.6$, $D_2 = 6.0 \times 10^{-6}$ cm^2/s, $k_{2,2\,(dimer)} = 1.0 \times 10^6$ cm^3/(mol·s), $k_{1,2\,(anion)} = 0.05$ s^{-1}, $k_{1,2\,(dianion)} = 0.09$ s^{-1}.

were determined by carefully fitting the experimental data using a combination of visual inspection and a least-squares-fit optimization macro provided in the CV spreadsheet.[2,7] Final adjustments to the simulation parameters were made by visual inspection to compensate for distortions in the experimental data (capacitance effects, adsorption peaks, etc.) which are not included in the simulations.[1−3,7]

The DMF solutions also provided an extended electrochemical domain as compared to the original samples because there was little hydrogen ion present to contribute to the current during reduction.[6] This allowed the determination of a second redox couple for benzophenone located at a more negative potential (Figure 3). An increase in the current from the reduction of solvent begins at about −2.75 V, after the second reduction wave of benzophenone at −2.34 V. The current peak for the second reduction wave at −2.34 V is smaller than the current peak of the first reduction wave at −1.76 V. Dimerization (Figure 2; reaction 2; $k_{2,1\,(dimer)}$) removes a portion of the radical anion from the electrode region prior to the second electron transfer resulting in a smaller current peak for the second reduction wave. Other contributions to the smaller current peak for the second reduction wave include diffusion of the radical anion away from the electrode prior to the second electron transfer and hydrogen extraction from trace water in the solvent by the radical anion (Figure 2; reaction 3; $k_{1,1\,(anion)}$). The two redox couples in a series were simulated using the fluxes of the product from the first reduction wave in the concentration calculations of the reactant for the second reduction wave in the sequence (see the Supporting Information, eqs 9−12).[1,7]

The simulation parameters from Figure 1 were used as initial values for the simulation of the first redox couple in Figure 3.
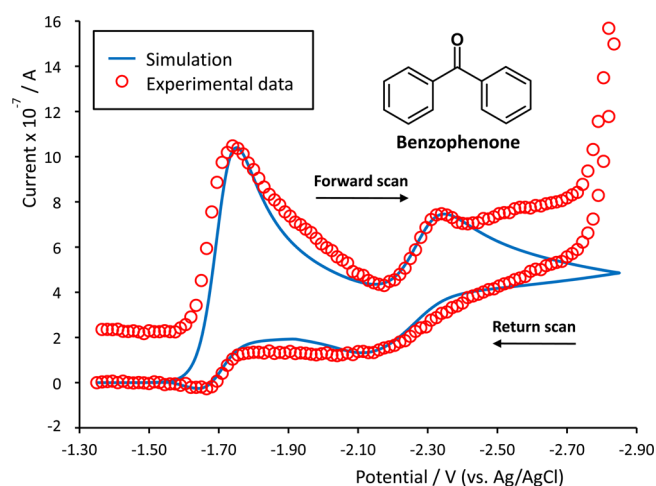
The experimental scan range (i.e., the difference between the initial and switching potentials noted in Table 1) used to acquire the voltammogram in Figure 1 (0.50 V) was smaller than the scan range used to acquire the voltammogram in Figure 3 (1.50 V). Using a narrow scan range to isolate a redox couple of a series in order to simplify a subsequent analysis is called wave clipping.[2,4] The technique is useful when studying multiple redox systems. The remaining simulation parameters for Figure 3 were obtained by carefully fitting the overall waveform as was done in Figure 1. Small adjustments to the initial values of the first redox couple were necessary to fit the overall waveform. Generally, the simulation of a multiple redox system provides more accurate parameters than the simulation of a single redox couple because you fit additional features present in the more complex voltammogram.[2]

To fit the experimental voltammogram in Figure 3, it was necessary to add rate constants for the removal of the radical anion by reaction with trace water in the solvent (Figure 2; reaction 3). Two rate constants ($k_{1,1\,(anion)}$, $k_{1,2\,(anion)}$) were used because there are two sources of the radical anion: (1) reduction of benzophenone and (2) reoxidation of the dianion. These two rate constants were kept equal while fitting the reduction wave at −2.34 V because they are associated with the same reaction. After the reduction wave was fitted at −2.34 V, it was noted that the absolute value of the oxidation current peak located at −1.67 V was still too large. The simulation in this region was improved by adding an additional rate constant that corresponded to the removal of the dianion by reaction with trace water in the solvent (Figure 2; reaction 5; $k_{1,2\,(dianion)}$).

The discrepancy between the simulation in Figure 3 and the experimental data from about −2.42 to −2.85 V is because the reduction of solvent contributed to the current. This is the reduction limit of the electrochemical domain for this solvent system. The shoulder on the first reduction wave between −1.80 and −2.18 V is perhaps an adsorption peak underneath the wave.[1,2] This shoulder becomes more prominent at larger scan rates. Adsorption peak currents increase linearly with scan rate in contrast to diffusion peak currents, which increase by the

square root of the scan rate.[1,2] Adsorption peaks were not included in the simulations. The deviation seen between the simulation and experimental CV during the forward scan from −1.35 to −1.58 V is perhaps from impurities in the solvent or electrolyte contributing to the current. This current was also present in the background scans of the solvent/electrolyte system and not entirely subtracted from the experimental voltammograms. Attempts to subtract this contribution to the current any further resulted in distortions in other regions of the experimental waveforms. The simulation parameters obtained for the first redox couple in Figure 3 were then put back into the simulation of Figure 1 to improve the model. Small adjustments to the simulation parameters were necessary to obtain the best fit of the experimental waveform.

Few CV experiments designed to teach undergraduate students utilize wave clipping as a technique to simplify experimental data to aid in the simulation of a more complex system. This experiment involves the determination of parameters from a single redox couple obtained from wave clipped voltammograms, which are then used to analyze two redox couples in series for the same compound. The new solvent system provides improved waveforms with fewer distortions and an extended electrochemical domain. The experiment incorporates the use of a spreadsheet simulator to analyze one, and then two redox couples in a series for benzophenone with simple changes to the acquisition parameters. The addition of wave clipping and the simulation of a two redox system increases the experience gained by the students in the laboratory as compared to the original procedure, which was limited to a single redox couple. See Supporting Information for the CV spreadsheet simulator used in this work.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00052.

> Table of simulation parameters with units, equations, derivations; example diffusion grid (PDF, DOCX)
> Microsoft Excel spreadsheet (CV_EC Simulator v_6); experimental and background data can be copied/pasted into the first page of the spreadsheet using Excel; a simulation mechanism is selected by clicking one of the tabs at the bottom of the spreadsheet; an example data set was included in the spreadsheet for practice; critical cells in the spreadsheet were locked to avoid accidental alterations. The spreadsheet can be operated in protected mode or unprotected and modified as needed; it supports up to four redox couples in a series and is capable of modeling oxidations and reductions. The spreadsheet is provided with no guarantee; it may not be suitable for all applications (XLS).

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Notes

The authors declare no competing financial interest.

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