

Reversible Electrode Potentials in Rapidly Reacting Redox Systems. Application of Phase Selective Second Harmonic AC Voltammetry

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Phase selective second harmonic AC voltammetric responses for stable, reacting, and rapidly reacting redox systems were examined. A critical comparison of the theoretical and experimental responses in rapidly reacting redox systems was made. Theory predicts that the reversible potential E^{rev} should be obtainable from the zero current crossing potentials of the in phase (I) and the quadrature (Q) components of the second harmonic AC current providing that k , the rate constant of the chemical follow-up reaction, is less than 3 times the angular frequency ω . We find that the I response for rapidly reacting systems in non-aqueous solvents, perhaps due to complications of uncompensated resistance, does not give reliable potential measurements while results using the Q component were found to be in accord with theoretical predictions. The limitations of the method are discussed with regard to the measurement of the oxidation potential of anthracene in acetonitrile containing pyridine derivatives which is accompanied by rapid reactions of the anthracene cation radical.

Reversible redox potentials are thermodynamically significant and can be used for the determination of equilibrium constants of chemical reactions. Such potentials are frequently required in order to establish the mechanisms of organic electrode reactions. Recent applications include the estimation of solvation energies of aromatic ions,^{1,2} the proposal of an "absolute" electrode potential scale^{1,2} and the estimation of pK_a values of weakly acidic hydrocarbons.^{3–9}

The most common measurement technique is cyclic voltammetry.^{10–12} Accurate measurements can only be made by the latter technique when the product of the electrode reaction is relatively stable under the conditions of the experiment. Methods have recently been developed which extend the lifetime of some reactive intermediates so that reversible potentials for their formation can be obtained by cyclic voltammetry.^{11,12} It is much more desirable to be able to measure potentials under conditions where the electrode generated intermediates are undergoing rapid chemical follow-up reactions since it is under these conditions that mechanistic conclusions are to be drawn.

Smith and coworkers have shown that second harmonic AC voltammetry at high frequencies should be capable of providing reversible potentials for the formation of very reactive intermediates.^{13,14} Calculations indicate that the reversible potential should be measurable as long as $k < 3\omega$ where k is the first order or pseudo first order rate constant for the reaction of the intermediate and ω is the angular frequency of the applied AC signal.¹³ Breslow^{7–9} has reported potentials measured by second harmonic AC voltammetry which appear to support the theoretical results. We have recently applied the technique to some organic systems and have been able to measure reversible potentials for the reduction of perylene to the anion radical in the presence of acetic acid under conditions where the pseudo first order rate constant for the protonation reaction was as great as 340 s^{-1} .¹⁵

The quest for kinetic and thermodynamic data from electrode potential measurements represents

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a two dimensional problem. As we have recently discussed, kinetic parameters (rate constants) are linearly related to thermodynamic properties (shifts from reversible potentials) of electrode processes.¹⁶ This means that if one or the other, rate constant or reversible potential, is known, the other can be obtained from electrode potential measurements. There are many cases where the product of an electron transfer reaction is inherently unstable and the rate constants for the follow-up reactions are usually not known. In such a case we have one equation and two unknowns and another measurable quantity, related in a known way to either the reversible potential or the rate constant, is required. While either current^{17,18} or absorbance¹⁹ fulfills this requirement for slow or moderately fast reactions following charge transfer, these quantities

are of no help for reactions with rate constants of 10^5 s^{-1} or greater.¹⁶

Phase selective second harmonic AC voltammetry brings in two new dimensions, the frequency and the phase of the current relative to the applied AC potential, which can be used in the determination of reversible potentials in cases where a direct measurement is not possible. In this paper we demonstrate the application of the technique to the study of rapidly reacting redox systems.

RESULTS AND DISCUSSION

Phase selective second harmonic AC voltammetry. The theory and some of the practical aspects of second harmonic AC voltammetry have been treated in detail.^{13,14,20} However, the emphasis was

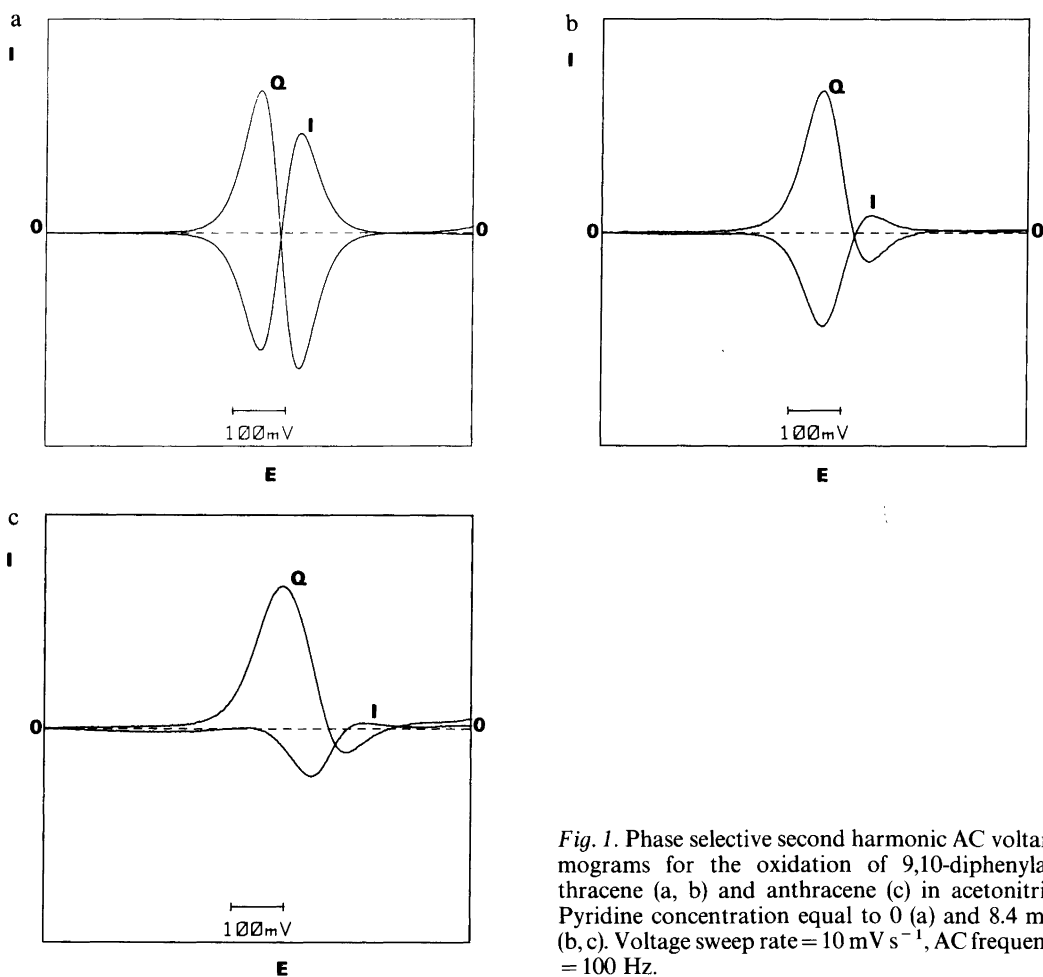


Fig. 1. Phase selective second harmonic AC voltammograms for the oxidation of 9,10-diphenylanthracene (a, b) and anthracene (c) in acetonitrile. Pyridine concentration equal to 0 (a) and 8.4 mM (b, c). Voltage sweep rate = 10 mV s^{-1} , AC frequency = 100 Hz.

on the total magnitude second harmonic AC current-potential response with only brief discussion of the phase selective mode. A more recent discussion dealing with phase selective response in rapidly reacting organic redox systems has led to some confusion and misapplication.⁷ Therefore, a brief illustration of the method for stable and reacting systems is necessary.

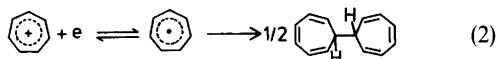
A recommended procedure for determining a reversible potential for an electrode process is to record the I and Q component voltammograms.^{13,14} If the oxidized and the reduced forms of the redox couple are stable in solution, both components will be symmetrical and appear as mirror images about the zero current axis. The I and Q components then intersect at zero current and this intersection defines the reversible potential, E^{rev} . An example is shown in Fig. 1a which was recorded during the oxidation of 9,10-diphenylanthracene (DPA) to the stable cation radical in acetonitrile. On the other hand, if the product of the electrode reaction is not stable and undergoes a chemical follow-up reaction as in eqn. (1), the I and Q component voltammograms lose their symmetry.



The reason for the latter is that as the electrode potential is being traversed through the region of potential where reaction occurs the concentration of A, and hence B, is continually depleted resulting in a decrease in the flow of AC current. Thus, the current at the lower potential peak is greater than that at the higher. If the angular frequency is high relative to the rate constant for the follow-up reaction, the mirror image relationship still holds and the I and Q components intersect at zero current and give E^{rev} . An example of this type of behaviour is shown in Fig. 1b for the oxidation of DPA in the presence of pyridine (8.4 mM). The AC frequency, 100 Hz (628 radians s^{-1}), was great enough to "out-run" the chemical reaction and the I and Q components intersected at zero current. But even with this relatively slow follow-up reaction, both voltammograms were decidedly asymmetric. In the case where the chemical reaction is fast relative to the frequency, the mirror image relationship no longer is observed and the intersection of the I and Q components does not occur at zero current and it is not possible to deduce E^{rev} from the experiment. Such is the case shown in Fig. 1c for the oxidation of anthracene (AN) in acetonitrile containing pyridine (8.4 mM). The rate constant for

the reaction of AN^{+} with pyridine under the latter conditions is apparently very large. The frequency was much too low to overcome the perturbation caused by the follow-up reaction and the zero current intersection was not observed. These examples illustrate situations frequently encountered in the study of electrode reactions by second harmonic AC voltammetry. It should be pointed out that the theoretical relationships are not exact for the experimental systems. For example, in Fig. 1a, the I and Q component currents are not equal.

A number of "reversible" potentials for rapidly reacting redox systems, taken from symmetrical or nearly symmetrical second harmonic AC voltammograms have recently been reported.⁷ This is inconsistent with the discussion above and with the illustrations in Fig. 1. We have re-examined one of the redox systems, the reduction of the tropylium cation, which is described by eqn. (2). We find the rate constant (k) for the dimerization of cycloheptatrienyl radical in acetonitrile at 20 °C, determined



by double step chronoamperometry,¹⁷ to be equal to $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The voltammogram reported earlier was measured at 45 Hz.⁷ The I and Q component voltammograms measured at 45 Hz in our laboratory are shown in Fig. 2a. In accord with the discussion in the previous paragraph, the I and Q components are asymmetric and do not intersect at zero current. The symmetrical trace shown in Fig. 2b was obtained from measurement on the same solution after shifting the phase 23°. In order to observe the zero current intersection of the I and Q components it was necessary to decrease the concentration of the cation drastically (0.05 mM) and use higher frequency (300 Hz). The reason for the discrepancy⁷ could possibly be due to faulty instrumentation. However, such problems can be avoided by recording both the I and Q components as recommended by Bond and Smith.¹⁴ The conclusion cannot be avoided that the potentials reported for tropylium ion and related systems⁷⁻⁹ are not reliable estimates of E^{rev} .

Frequency effects upon electrode potential measurements. Calculations¹³ suggest that the Q and I component voltammograms will intersect zero current at E^{rev} during measurements on redox systems with irreversible chemical reactions follow-

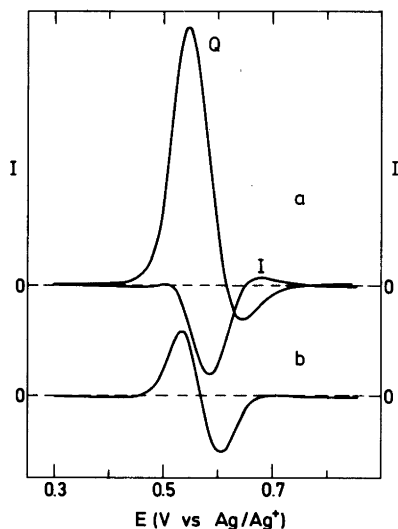


Fig. 2. Phase selective second harmonic AC voltammograms for the reduction of tropylium ion in acetonitrile. Quadrature and in phase components (a) and the phase shifted 23° from the I component (b). Voltage sweep rate = 50 mV s^{-1} , AC frequency = 45 Hz .

ing charge transfer as in eqn. (1) providing the conditions of eqn. (3) pertain. In most organic redox systems it is possible to employ AC frequencies as high as 1 kHz without interference from

$$k < 3\omega \quad (3)$$

charge transfer kinetics. Thus, theory predicts that E^{rev} will be measurable from the crossing points of the I and Q voltammograms as long as the pseudo first order rate constant for reaction (1) does not exceed about 2×10^4 . The theory has not been adequately tested, the experiments reported were conducted with a maximum value of the

pseudo first order rate constant of approximately 10 s^{-1} .¹⁴ The oxidation of DPA and AN in the presence of nucleophiles provides test systems where the rates of reaction following charge transfer can be varied over a very wide range. Thus, we are able to rigorously test theory and determine the possible errors in electrode potentials measured over the kinetic range where essentially all electrode reactions will fall.

Electrode potentials measured by phase selective second harmonic AC voltammetry in acetonitrile solutions of DPA and AN containing various nucleophiles are summarized in Tables 1 and 2.

The data obtained using the I component are summarized in Table 1. The fastest reaction in the table had a pseudo first order rate constant no greater than about 10^3 s^{-1} . The lowest frequency, 100 Hz ($\omega = 628 \text{ radians s}^{-1}$), fulfills the requirements of eqn. (3) for rate constants up to about 2×10^3 . Therefore, all of the zero current crossing potentials listed should have been equal to E^{rev} . The potentials were found to be frequency dependent and were all more than 5 mV higher than E^{rev} ($889.5 \text{ mV vs. Ag/Ag}^+$) and the last entry in the table measured at 1 kHz was in error by as much as 25 mV . It should be mentioned here that the I component potentials measured for the oxidation of DPA in the presence of pyridine were dependent upon the setting of the IR compensation on the potentiostat. This was not the case for the oxidation in the absence of pyridine under which conditions the measurements were both frequency and IR setting independent. Thus, we conclude that the I component data are influenced by adsorption of reactants, which does take place in this case, and therefore of questionable value in the measurement of reversible potentials in rapidly reacting systems.

Fortunately, the measurement of the Q component zero current crossing potentials met with more success. Data gathered in Table 2 for the

Table 1. Second harmonic AC in phase component zero current crossing potentials during the oxidation of 9,10-diphenylanthracene in acetonitrile containing pyridine.

$\Delta E(10 \text{ Hz})^a$	$E(100 \text{ Hz})^b$	$E(300 \text{ Hz})^b$	$E(1 \text{ kHz})^b$
19.9	884.9	885.0	888.4
25.7	887.6	883.5	895.1
31.1	892.5	896.9	904.2

^a Quadrature component zero current crossing potential relative to E^{rev} . ^b Supporting electrolyte = Bu_4NBF_4 (0.1 M), DC sweep rate = 10 mV s^{-1} at 20°C , all potentials in mV vs. Ag/Ag^+ in acetonitrile.

Table 2. Second harmonic AC quadrature component zero current crossing potentials during the oxidation of anthracenes in acetonitrile containing nucleophiles.^b

Substrate/Nucleophile	$\Delta E(10 \text{ Hz})/\text{mV}^a$	$E(100 \text{ Hz})/\text{mV}^b$	$E(300 \text{ Hz})/\text{mV}^b$	$E(1 \text{ kHz})/\text{mV}^b$
DPA/pyridine	19.9	877.6(4)	878.9(2)	880.3(6)
DPA/pyridine	25.7	876.1(4)	877.7(3)	879.7(4)
DPA/pyridine	31.1	875.6(7)	878.8(5)	880.8(6)
DPA/pyridine	36.1	873.0(6)	877.2(8)	878.6(11)
AN/water	30.0	917.8(4)	920.7(3)	920.1(2)
AN/methanol	39.3	908.1(6)	913.7(4)	921.2(7)
AN/methanol	47.7	901.6(4)	911.6(4)	920.2(8)
AN/4-cyanopyridine	55.7	893.5(4)	904.8(3)	915.6(4)
AN/4-cyanopyridine	58.1	891.0(6)	901.0(3)	916.7(9)
AN/ α -picoline	71.5	880.1(18)	899.0(7)	914.3(4)
AN/ α -picoline	88.7	866.3(4)	882.0(3)	889.1(4)
AN/pyridine	106.9	848.0(5)	864.2(6)	886.9(23)

^a Potential measured at 10 Hz relative to E^{rev} . ^b Phase selective second harmonic AC zero crossing potential. Supporting electrolyte = Bu_4NBF_4 (0.1 M), DC sweep rate = 10 mV s^{-1} at 20°C , all potentials vs. Ag/Ag^+ in acetonitrile. The number in parentheses indicates the standard deviation of the last digit(s).

oxidation of DPA and AN in acetonitrile, E^{rev} equal to 877.2 and 920.4 mV vs. Ag/Ag^+ , respectively, bear this out. All values listed are the average of ten determinations and the parentheses contain one standard deviation. Data were processed with an on-line computer and the resolution was 0.2 mV per data point.

The deviation of measured second harmonic AC potentials from the reversible value as a function of frequency and the rate of the chemical follow-up

reaction is demonstrated by Fig. 3. Potentials measured at 10 Hz were subtracted from the corresponding values at other frequencies listed in Table 2. In Fig. 3, the kinetic potential shift at 10 Hz, $\Delta E(10 \text{ Hz})$, is plotted on the x axis vs. the differences described in the previous sentence. The deviation from the reversible potential for the three frequencies, 100, 300 and 1000 Hz, at a particular value of the kinetic potential shift at 10 Hz is the difference between the curve describing the measurements and the diagonal in the plot. If we assume that $E(10 \text{ Hz})$ begins to deviate from E^{rev} at $k = 3\omega$ (or 189 Hz) as suggested by eqn. (3) and that $dE/d \log \omega = (\ln 10)RT/2F$ (or 29.6 mV at 25°C), we can write an approximate relationship (4) between $\Delta E(10 \text{ Hz})$ and $\log k$, where k is a pseudo first order rate constant as in eqn. (1). If this

$$\log k = (29.6)^{-1} \Delta E(10 \text{ Hz}) + \log 189 = 0.034 \Delta E(10 \text{ Hz}) + 2.3 \quad (4)$$

relationship is valid, we would expect the plateau regions of the curves (Fig. 3) to intercept the diagonal and the right hand margin at 30 mV (100 Hz), 44 mV (300 Hz) and 60 mV (1000 Hz). Since the deviation from the predictions is not very great, eqn. (4) along with Fig. 3 can be used as a rough guide to predict the deviation of E measured at a particular frequency from E^{rev} . For example, eqn. (4) leads to the prediction that when $\Delta E(10 \text{ Hz})$ is 120 mV, $\log k$ will be about 6.4 and the deviations

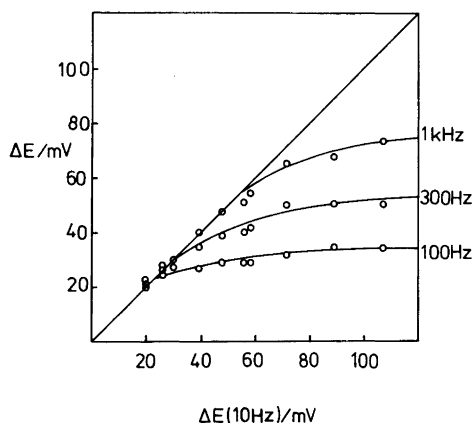


Fig. 3. Differences between second harmonic AC crossing potentials at 100, 300 and 1000 Hz compared to 10 Hz. The vertical deviation of the curves from the diagonal gives the difference between the measured and the reversible potentials.

from E^{rev} will be 90 mV (100 Hz), 76 mV (300 Hz) and 60 mV (1000 Hz). Thus, $E(1000 \text{ Hz})$ is not expected to deviate much more than 100 mV from E^{rev} even when k is as large as 10^8 s^{-1} .

In conclusion, we would like to emphasize that the measurements reported here support the results of the theoretical studies^{13,14} and show that phase selective second harmonic AC voltammetry is indeed a valuable tool for determining reversible electrode potentials for rapidly reacting redox systems. The work also points out that care must be taken in the interpretation of the measurements and that the observation of zero current crossing potentials is not always sufficient for establishing the reversible potential for a reaction.

EXPERIMENTAL

The instrumentation, cells, electrodes and reference electrodes as well as solvent, electrolyte and reagent purification were described recently.¹⁶

The collection and the treatment of the data were carried out in the same manner as before.¹⁶ We stress that the collection of data was accomplished with an on-line computer and the precision reported cannot be duplicated with analog instruments. Attempts to use an X-Y recorder led to much greater error.

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