A general analytical treatment of modulated linear-ramp voltammetry for reversible processes

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Abstract

Studies of periodically modulated linear-ramp voltammetry have previously been undertaken by simulation coupled with Fourier analysis. Here, we develop a simple formula, based upon neither of these approaches, which permits the prediction of the magnitude of the ac current resulting from a reversible faradaic process. The formula is applicable to any periodic modulation, of any amplitude, and of any frequency, provided that the frequency/ramp rate quotient exceeds $4\pi n F/RT$. The formula has been validated using known results for sinusoidal and square-wave modulation.

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1. Introduction

Voltammetric experiments in which a ramped potential is modulated by a periodic signal of constant amplitude offer advantages over unmodulated ramps. The modulation provides a way of investigating processes at the electrode interface while the oxidant:reductant ratio is being slowly varied in response to the ramp. This year marks the 50th anniversary of voltammetry with a linear ramp modulated by a sinusoidal signal. Invented by Grahame [1] and others [2,3], this technique was developed extensively in the third quarter of the last century, especially by Smith [4] and the Sluyters [5]. Periodic modulation other than by sinusoids also has a 50-year history going back to the pioneering work [6] of Barker and Jenkins in 1952. An example is square-wave voltammetry, a sampled version of which was originated by Ramaley and Krause [7,8] in 1969 and popularized by O’Dea and Osteryoung more recently [9].

The development of modulated linear-scan voltammetry has been inhibited by the lack of comprehensive theory. Until quite recently, the theory for sinusoidal modulation existed only for amplitudes small in comparison with $RT/n F$. Likewise, for lack of a tractable analytical description, the interpretation of sampled square-wave voltammetry requires a concurrent simulation. That development, and many others, have been helped by the advent of laboratory-scale high-speed ample-memory computation. In a parallel development, computational power has allowed straightforward Fourier-transform methods to be used, not only in the modelling of modulated voltammetry [10,11] but also in voltammetric instrumentation [12,13]. High-speed computation also provides a means of testing and implementing new analytical solutions [10,14–16] proposed for modulated voltammetry.

In modern electroanalytical chemistry, it is no longer considered adequate to base conclusions on isolated points in a voltammogram. In cyclic voltammetry, for example, assurance that an experimental curve corresponds to a postulated mechanism, or to a particular rate constant, is far greater if the entire curve can be matched by a model, than if merely the peak potentials are used. Likewise in modulated linear-scan voltammetry, confidence would be heightened if all or many of the features of an experimental voltammetric study could be matched against model predictions. Among the features

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1 Not necessarily FFT-based.
that might be examined in sinusoidal ac voltammetry are: the height of the fundamental ac peak, the shape of that peak, the area under the peak, the dependence of the height and shape of the peak on frequency, the dependence of the peak height and shape on the amplitude of the modulating signal, all the aforementioned factors as they apply to harmonic voltammograms, and the effect of the ac signal on the dc component. Today, not all the theory needed to predict these features exist, even for reversible electrode reactions. The present study seeks to repair some of our ignorance by providing a means whereby features present in the current from modulated linear-ramp voltammetry may be predicted analytically, for a reversible reaction. In the general derivation, no constraint will be imposed on the shape of the modulation (be it sinusoidal, square-wave, sawtooth, or other) or on its amplitude, though a lower limit will be imposed on the frequency, for the reason discussed in the context of Eq. (3) below.

2. The experiment

A voltammetric experiment, fulfilling the following criteria will be modelled:

a) The working electrode (WE) supports the reversible reaction \( S(\text{soln}) - ne^- \rightarrow P(\text{soln}) \), where \( n \), the electron number, may have either sign. The standard potential of this reaction is \( E^\circ \).

b) The substrate \( S \) has a uniform concentration \( c_S^b \) initially, but the product \( P \) is absent.

c) The solution is quiescent and contains excess supporting electrolyte, so that transport of \( S \) and \( P \) is effectively by diffusion alone, with diffusivities of \( D_S \) and \( D_P \).

d) The spacing of the reference electrodes and other cell components is such that the diffusion field is effectively semiinfinite along the \( z \)-axis, which is normal to the WE.

e) The WE is of large enough area \( A \), and of such geometry, that the equiconcentration surfaces are effectively planar.

f) The initial electrode potential, \( E(t \leq 0) \) equals the constant \( E_0 \), chosen to be sufficiently extreme that negligible current flows, \( I(t \leq 0) = 0 \).

g) Starting at time \( t = 0 \), the potential program \( E(t) = E_{dc}(t) + E_{ac}(t) \) is applied to the WE, and soon causes a measurable faradaic current \( I(t) \) to flow. This current, which on average has the same sign as \( n \), is accurately recorded.

h) The aperiodic component of the program, \( E_{dc}(t) \), is the simple ramp \( E_0 + vt \), where \( v \) is the sweep rate, a constant sharing the sign of \( n \).

i) \( E_{ac}(t) \), the periodic component of the program, has a period \( P \) and fulfils a number of conditions detailed in Section 3.

j) The effects of uncompensated resistance and non-faradaic current are either negligible or have been corrected for.

Though these 10 criteria are stringent, it is not difficult to meet them experimentally.

For the case in which the ac signal is a sinusoid of very small amplitude, Fig. 1 shows a plot of the total current as a function of the dc potential. The current may be decomposed into ac and dc components, the latter being shown by the medial curve. Because the ac amplitude is small, in this example, the dc current does not differ noticeably from the standard Randles–Sevčik behaviour [17]. This is not true [16], however, at the larger ac amplitudes in which we are mainly interested.

3. Periodicity

A periodic function of time is one that obeys the requirement

\[
\text{per} \left( \frac{t}{P} + m \right) = \text{per} \left( \frac{t}{P} \right) \quad m = 0, \pm 1, \pm 2, \ldots
\]  

(1)

Mathematically, this requirement is considered to apply for all times \( t \), though in voltammetric practice the modulating signal commences at \( t = 0 \). The constant \( P \), the period, is the smallest time interval that satisfies Eq. (1). As an alternative to designating the period \( P \) of the periodic function, \( \text{per}(t/P) \) may be characterized by its frequency \( \omega \), equal to \( 2\pi/P \).

One can imagine periodic signals in which maximum and minimum voltages are not symmetrically disposed about the mean voltage. However, we know of no cases in which such asymmetric signals have been employed or are anticipated by electrochemists. Accordingly, and for simplicity, it will be assumed that an amplitude \( \Delta E \) may be unambiguously ascribed to the modulating signal, such that \( 2\Delta E \) represents the total excursion of the periodic signal \( \Delta E \text{ per}(t/P) \).

Two conditions beyond periodicity will be imposed on the modulating potential signal. The first requires that its mean value be zero

\[ \text{This is not a necessary assumption; it was not made in a recent publication [16] of ours.} \]

2 More strictly \( E^\circ \) is the formal, or conditional, potential.
0 = \int \Delta E \frac{P}{\tau} d\tau = \frac{t + P}{t} \text{per} \left( \frac{\tau}{P} \right) d\tau \quad (2)

The second requires that the product of the period and the scan rate be small in comparison with the characteristic electrochemical voltage interval:

\[ |v|P \ll \frac{RT}{nF} \quad (3) \]

These two conditions are necessary to establish an unequivocal distinction between ‘dc’ and ‘ac’ phenomena. Gavaghan and Bond [11] investigated the effect of violating inequality (3) in sinusoidal cases.

The periodic modulation of the applied electrical potential elicits periodicity in the faradaic current. The period of the ac current \( I_{ac} \) exactly matches that of the modulation. The ac current is discerned from the dc component by the requirement, akin to Eq. (2), that

\[ 0 = \int_{t-P/2}^{t+P/2} I_{ac}(t) d\tau \quad (4) \]

The ac current is not truly periodic, however, because its amplitude, unlike \( \Delta E \), is not constant, being affected by the dc potential \( E_{dc}(t) \). Even the form of \( I_{ac} \) may\(^4\) be influenced by \( E_{dc}(t) \). This means that consecutive periods of the current are not exact duplicates of each other, though they will be very nearly so. The adjective ‘quasiperiodic’ is applicable in such cases.

A consequence of the condition (4) is that the dc current may be identified with the average value of the current over a period, so that

\[ I_{ac}(t) = I(t) - I_{dc}(t) = I(t) - \frac{1}{P} \int_{t-P/2}^{t+P/2} I(\tau) d\tau \quad (5) \]

This identification is evidently inexact inasmuch as it neglects any non-linear change in the dc current during the period. Nevertheless, if \( v \) and/or \( P \) are small enough, it should be an excellent approximation. In a similar vein, it should be an excellent approximation to ignore the small change in dc potential that occurs during a single period. Thus, in the analysis of a single ac period, \( E_{dc} \) will be treated as a constant.

How much information do we need to find in order that we ‘know’ the ac current waveform at a particular dc potential? Let us choose a large even integer\(^5\) \( K \), and posit that the waveform is known if the value of the ac current is known at \( K \) instants distributed evenly through the period. Thus the goal of our study is to determine the \( K \) values of \( I_{ac}(E_{dc}/v + kP/K) \), where \( k \) takes the values 0, 1, 2, \ldots, \( K-1 \), for any chosen value of \( E_{dc} \).

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\(^4\) When the modulation is sinusoidal, the form of the ac current (as manifested in its harmonic content), is dependent on the dc potential, but this is not the case for square-wave modulation [15].

\(^5\) In much of our work we used \( K = 128 \).
4. Derivation

When the composite signal

\[ E(t) = E_{dc}(t) + E_{ac}(t) = E_0 + vt + \Delta E \per(t) \]  

(6)

is imposed on an electrode meeting the conditions prescribed in Section 2, there is ‘cross-talk’ between the ac and dc components, the current for one being affected by the potential for the other. The objective of this section is to answer, for any reversible modulated ramp experiment, the question ‘What mathematical relationship is there between \( I_{ac} \) and the parameters, not only of the ac signal, but also of the dc signal?’ The complementary question ‘What mathematical relationship is there between \( I_{dc} \) and the parameters, not only of the dc signal, but also of the ac signal?’ has already been answered in the literature [16].

Criteria (c) and (e) imply that Fick’s second law is obeyed by the concentrations \( c_S(z, t) \) and \( c_P(z, t) \). This law, together with the initial and semiinfinite boundary conditions implicit in criteria (b) and (d) leads, via a Laplace transform argument, to the exact requirement that

\[ \sqrt{D_S} \frac{\partial}{\partial z} c_S(z, t) = \frac{\partial^{1/2}}{\partial t^{1/2}} [c_S(z, t) - c_S^0] \]

(7)

\[ X = S \text{ or } P, \quad c_P^0 = 0 \]

At the \( z = 0 \) surface of the WE, the relationships

\[ -D_S \frac{dc_S}{dz}(0, t) = \frac{I(t)}{nAF} = D_P \frac{dc_P}{dz}(0, t) \]

(8)

hold by virtue of Fick’s first and Faraday’s laws, while the Nernst relationship

\[ \frac{c_P(0, t)}{c_S(0, t)} = \exp \left( \frac{nF}{RT} [E(t) - E^*] \right) = \exp \left( \frac{D_P}{D_S} \exp \left( \frac{nF}{RT} [E(t) - E_{1/2}] \right) \right) \]

(9)

is a consequence of criterion (a) and of the definition of the halfwave potential \( E_{1/2} \). By straightforward algebra, it is possible to combine the last three equations into

\[ I(t) = - \frac{nAFc_S^b}{\sqrt{D_S}} \frac{d^{1/2}}{dt^{1/2}} \left( 1 + \tanh \left( \frac{nF}{2RT} [E(t) - E_{1/2}] \right) \right) \]

(10)

This last equation has been used many times to relate current and voltage in reversible voltammetry, but the above thumbnail sketch of its origin has been included to demonstrate the rigour of its derivation and the generality of its applicability.

To curtail the notation, it is beneficial to adopt the following definitions

\[ M_L = nAFc_S^b \sqrt{D_S} \]

\[ \xi_{dc}(t) = \frac{nF}{2RT} [E_0 + vt - E_{1/2}] \]

\[ \Delta \xi = \frac{nF \Delta E}{2RT} \]

The first and third of these are constants. The second describes a variable linearly related to time; however, for the reasons discussed above, \( \xi_{dc} \) will, in Section 5, be treated as a constant during discussion of a single ac period. By also incorporating Eq. (6), these definitions permit the conversion of Eq. (10) to

\[ I(t) = \frac{M_L}{2} \frac{d^{1/2}}{dt^{1/2}} \left( 1 + \tanh \left( \xi_{dc}(t) + \Delta \xi \per(t) \right) \right) \]

\[ = \frac{M_L}{2} \frac{d^{1/2}}{dt^{1/2}} \text{qer}(t) \]

(11)

where the symbol ‘qer’ represents the quasiperiodic function \( 1 + \tanh(\xi_{dc}(t) + \Delta \xi \per(t)) \). This equation is exact. Its combination with Eq. (5) leads\(^6\) to

\[ I_{ac}(t) = \frac{M_L}{2} \frac{d^{1/2}}{dt^{1/2}} \text{qer}(t) = \frac{M_L}{2P} \frac{d^{-1/2}}{dt^{-1/2}} \text{qer}(t) \]

\[ \times \frac{d^{1/2}}{dt^{1/2}} \left( 1 + \tanh \left( \frac{nF}{2RT} [E(t) - E_{1/2}] \right) \right) \]

\[ = \frac{M_L}{2} \left( \frac{d^{1/2}}{dt^{1/2}} \text{qer}(t) \right) \]

\[ - \frac{1}{P} \int_{t-P/2}^{t+P/2} \frac{d^{1/2}}{dt^{1/2}} \text{qer}(t) \, dt \]

(12)

\[ \text{This equation, which is also exact, forms the basis of our derivation.} \]

\[ \text{Though it leads to very lengthy computation, it is possible to exploit Eq. (13) directly. A very large array (we used 128,000) of qer(t/P) values is created, then semidifferentiated numerically. Being the speediest, the Grünwald algorithm [18] is used to produce Fig. 1 and the full lines in Figs. 3 and 4.} \]

\[ \text{\(^6\) We have exploited the ‘composition law’ which, though not universally true, applies in the present circumstance [18].} \]
5. The periodic approximation

Next, we explore the effect of regarding \( \text{qer}(t/P) \), which is a quasi-periodic function, as a truly periodic function. We expect this changed viewpoint to be unimportant to an extent that reflects how well inequality (3) is satisfied. The motive for the substitution is that the operations of the fractional calculus become massively abbreviated for periodic functions as will now be demonstrated.

The semiintegral of a function \( f(t) \) is given, according to the Riemann–Liouville definition [18], by

\[
\frac{d^{-1/2}}{dt^{-1/2}} f(t) = \frac{1}{\sqrt{\pi}} \int_0^t \frac{f(\tau)}{(t-\tau)^{1/2}} \, d\tau
\]

(15)

The semiderivative of \( f(t) \) is simply the derivative of Eq. (15) with respect to \( t \). These definitions are valid for any \( f(t) \) function, but if this function is periodic and has a mean value of zero (i.e. it satisfies a relationship akin to Eq. (4)), then replacement of the lower limit by \( -\infty \) provides an excellent approximation to the semiintegral, provided that very many periods have elapsed during the \( t > 0 \) interval. In these circumstances, which are generally satisfied experimentally, the integral in Eq. (15) may be dismembered into

\[
\frac{d^{-1/2}}{dt^{-1/2}} f(t) = \frac{1}{\sqrt{\pi}} \sum_{j=0}^{\infty} \int_{t-jP}^{t-(j+1)P} \frac{f(\tau)}{(t-\tau)^{1/2}} \, d\tau
\]

(16)

Next, change the integration variable to \( \lambda = [t(1-jP)] - j \) and invert the order of summation and integration, whereby the formula

\[
\frac{d^{-1/2}}{dt^{-1/2}} f(t) = \sqrt{\frac{P}{\pi}} \sum_{j=0}^{\infty} f(t - jP \lambda) \left( \frac{j + \lambda}{P} \right)^{1/2} \, d\lambda
\]

(17)

emerges. In the second step, it is the periodicity of the \( f(\lambda) \) function that allowed its removal from within the summation. The integral converges only if the mean value of \( f(t) \) is zero. The expression in square brackets in Eq. (17) is, by definition [19], the Hurwitz function of moiety order and argument \( \lambda \). The computation of this function is described in Appendix A. The simple definite integral

\[
\frac{d^{-1/2}}{dt^{-1/2}} f(t) = \sqrt{\frac{P}{\pi}} \int_0^1 f(t - \lambda P) \zeta(1/2; \lambda) \, d\lambda
\]

(18)

is the final result. Differentiation of Eq. (18) leads to the corresponding result

\[
\frac{d^{1/2}}{dt^{1/2}} f(t) = \frac{1}{2\sqrt{\pi P}} \int_0^1 [f(t) - f(t - \lambda P)] \zeta(3/2; \lambda) \, d\lambda
\]

(19)

for semidifferentiation of a periodic function.

Formulas (18) and (19) clearly demonstrate that the semioperators convert a periodic function of mean value zero into another periodic function of the same period. Thus if the quasiperiodic function \( \text{qer}(\lambda) \) is treated as periodic, the second (semiintegral) term in Eq. (13) disappears and there remains

\[
I_{ac}(t) = \frac{M_L}{4\sqrt{\pi P}} \int_0^1 \left[ \text{qer} \left( \frac{t}{P} \right) - \text{qer} \left( \frac{t-k}{P} \right) \right] \zeta(3/2; \lambda) \, d\lambda
\]

(20)

This is an extremely simple formula, reminiscent of a convolution, that can be implemented via the simple algorithm that is presented below. It provides a method of predicting the periodic portion of the current, during a single period, without needing to make use of data relating to times prior to that period. In this respect, it represents a distinct departure from simulative procedures, which are cumulative solutions, continually building on what has gone before.

6. Periodicity algorithm

To implement Eq. (20) for any single value of \( t \), let us once more subdivide the integration range \( 0 \leq \lambda \leq 1 \) into \( K \) subranges by creating nodes at \( \lambda = 0, 1/K, 2/K, \ldots, k/K, \ldots, 1 \). Then, making use of the temporary abbreviation

\[
Q_k = \text{qer} \left( \frac{t}{P} \right) - \text{qer} \left( \frac{t-k}{P} \right)
\]

\[
= \tanh \left\{ \xi_{ac} + \Delta \xi \, \text{per} \left( \frac{t}{P} - \frac{k}{K} \right) \right\}
\]

\[
- \tanh \left\{ \xi_{ac} + \Delta \xi \, \text{per} \left( \frac{t}{P} - \frac{k}{K} \right) \right\}
\]

(21)

and an approximation in which \( \text{qer}(\lambda) \) is treated as a linear function between adjacent nodes, we find from Eq. (20) that

\[
I_{ac}(t) = \frac{M_L}{4\sqrt{\pi P}} \sum_{k=0}^{K-1} \int_{k/K}^{(k+1)/K} [(k+1)Q_k - kQ_{k+1}]
\]

\[
+ \lambda K (Q_{k+1} - Q_k) \zeta(3/2; \lambda) \, d\lambda
\]

(22)

Parts integration yields

\[
I_{ac}(t) = -\frac{M_L}{2\sqrt{\pi P}} \sum_{k=0}^{K-1} \left[ \zeta(1/2; \lambda)
\]

...
\[ \times [(k + 1)Q_k - kQ_{k+1} + K\lambda(Q_{k+1} - Q_k)]_{(k+1)/K} \]
\[ - K(Q_{k+1} - Q_k) \int_{k/K}^{(k+1)/K} \zeta(1/2; \lambda) \, d\lambda \]  
(23)

which evaluates to

\[ I_{ac}(t) = -\frac{M_{L}K}{2\sqrt{\pi P}} \sum_{k=0}^{K-1} Q_k \zeta(-1/2; (k+1)/K) \]
\[ - Q_k \zeta(1/2; k/K) - 2K(Q_{k+1} - Q_k) \]
\[ \times [\zeta(-1/2; (k+1)/K) - \zeta(-1/2; k/K)] \]  
(24)

On summing and recognizing that \(Q_0 = Q_K = 0\), all terms involving Hurwitz functions of order 1/2 cancel. There remains, on collecting terms

\[ I_{ac}(t) = -\frac{K M_{L}}{\sqrt{\pi P}} \sum_{j=1}^{K-1} Q_j \zeta(1/2; (k+1)/K) \]
\[ - 2\zeta(-1/2; k/K) + \zeta(-1/2; (k-1)/K) \]  
(25)

Note that \(K - 1\) values of the quantity in square brackets are needed, but they require calculating only once.

It is convenient to represent this square-bracketed quantity by \(Z_k\) and to name it ‘the doubly differenced Hurwitz function’ of order \(-1/2\).

To profile an entire period, we need to replace \(t\) in definition (21) by \(\kappa P/K\). Then, abandoning the \(Q\) and \(K\) abbreviations

\[ I_{ac} \left( \frac{E_{dc} + \kappa P}{v} \right) \]
\[ = -\frac{K M_{L}}{\sqrt{\pi P}} \sum_{j=1}^{K-1} \left[ \tanh \left( \zeta_{dc} + \Delta \zeta \text{ per } \left( \frac{\kappa}{K} \right) \right) - \tanh \left( \zeta_{dc} + \Delta \zeta \text{ per } \left( \frac{\kappa - k}{K} \right) \right) \right] Z_k \]  
(26)

The summation in Eq. (26) calls for some values of \(\zeta\) relating to the period prior to the one being profiled.

7. Validation

Because there have been a number of approximations built into Eq. (20), we decided to validate this formula in two distinct ways.

For sinusoidal modulation, there exists an exact solution7 [10] describing the harmonic components of the current at the halfwave potential only. There is no current at even harmonics and the formula for the fundamental \(h = 1\) and the odd harmonics, \(h = 3, 5, 7, \ldots\) is

7 The cited reference deals with the cosine, rather than the sine function. Signs differ in the two cases.
limitation

We have validated the Hurwitz equation (20), and its implementation via algorithm (26), for the case \( nFvP/RT = 0.02 \), which was the parameter combination employed in Figs. 1–3. It is expected that the validity of Eq. (20) will break down at larger values of \( nFvP/RT \) and, to investigate this, figures analogous to Fig. 3 were constructed for \( nFvP/RT = 0.1, 0.2, 0.5 \), and 1.0. The agreement, though imperfect, was acceptable in the 0.1 and 0.2 cases, but for \( nFvP/RT = 0.5 \), the case illustrated in Fig. 4, or larger, we regard the Hurwitz approximation as no longer valid.

The conclusion therefore is that, provided \( (nFvP/RT) < 0.5 \), it is permissible to treat the ac current as a periodic function of time (or of dc potential), given by

\[
\frac{2\sqrt{\pi P} I_{ac}}{M_L} = \frac{1}{2K} \int_0^K Q_k \xi(3/2; k/K) dk
\]

\[
\approx -2K \sum_{k=1}^{\infty} Q_k [\xi(-1/2; (k+1)/K) - 2\xi(-1/2; k/K) + \xi(-1/2; (k-1)/K)]
\]

(28)

where

\[
Q_k = \tanh \left\{ \xi_{dc} + \Delta \xi \left( \frac{t}{P} \right) \right\} - \tanh \left\{ \xi_{dc} + \Delta \xi \left( \frac{t}{P} - \frac{k}{K} \right) \right\}
\]

(29)

The limitation implies that (for \( n = 1 \) and \( T = 298.15 K \), with a sweep rate of 0.1 V s\(^{-1}\), the frequency of the
modulation must exceed 49 Hz. If \( v = 1 \text{ V s}^{-1} \), \( \omega > 490 \text{ Hz} \).

9. Non-sinusoidal applications

To this point, our only applications of Eq. (28) have been to sinusoidal modulations, whereas the formula applies to any waveform satisfying Eqs. (1)–(3).

Fig. 5 shows the results of applying Eq. (28), implemented by algorithm (26), to a square-wave modulated ramp, at the halfwave potential. Unlike sinusoidal modulation, in which the shape of the ac current during a period depends on both \( \Delta \xi \) and \( \xi_{dc} \), the corresponding shape for square-wave modulation is known [15] to depend on neither of these factors. Indeed, we found the shape shown in Fig. 5 to be reproduced for all values of these parameters. Expressed as a Fourier series, the published [15] formula for the ac current at \( \xi_{dc} \) is

\[
I_{ac}(t) = \sum_{h=1,3}^{\infty} I_h(t)
\]

where

\[
I_h(t) = M_L \sqrt{\frac{2}{\pi \Phi_h}} \left[ \tanh\left(\xi_{dc} + \Delta \xi\right) - \tanh\left(\xi_{dc} - \Delta \xi\right) \right] \times \sin\left(\pi \Omega t + \frac{\pi}{4}\right)
\]

To compare with this formula, we Fourier transformed the data in Fig. 5. The comparison of the harmonic amplitudes and phase angles is shown in Table 1 and the agreement is seen to be good.

For several values of the ac amplitude, we also investigated triangular-wave modulation, via Eq. (28). For a typical large amplitude, the results are shown in Fig. 6, at three different values of the dc potential: \( E_{1/2} \) and \( E_{1/2} \pm 2RT/nF \). We discovered that, like the sine-wave, but unlike the square-wave modulated linear-scan voltammogram, the shape of the ac current depends on both the dc potential and the ac potential amplitude.

10. Summary

We have verified that, provided the frequency is not too small, the ac voltammetric current resulting from periodic modulation of a linear potential ramp is accessible via a simple formula. A convenient and accurate algorithm has been devised to implement this formula. We have applied this technique to sinusoidal, square- and triangular-wave modulations.

### Table 1
Comparison of the Fourier analysis of the data in Fig. 5 with the theoretical ac current from square-wave modulated linear-scan voltammetry

| Harmonic number \( h \) | \( \frac{2|I_h|}{\sqrt{\pi \Phi}}/M_L \) | Phase angle |
|--------------------------|--------------------------------|-------------|
|                          | Fourier analysis | Formula (31) | Fourier analysis | Formula (31) |
| 1                        | 4.3083           | 4.3082       | 45.0863       | 45.0000 |
| 2                        | 0                | 0            | 45.2553       | 45.0000 |
| 3                        | 2.4877           | 2.4874       | 45.4214       | 45.0000 |
| 4                        | 0                | 0            | 45.5853       | 45.0000 |
| 5                        | 1.9273           | 1.9267       | 45.7473       | 45.0000 |
| 6                        | 0                | 0            | 45.9077       | 45.0000 |
| 7                        | 1.6292           | 1.6284       | 45.9077       | 45.0000 |
| 8                        | 0                | 0            | 45.9077       | 45.0000 |
| 9                        | 1.4371           | 1.4361       | 45.9077       | 45.0000 |
| 10                       | 0                | 0            | 45.9077       | 45.0000 |
| 11                       | 1.3002           | 1.2990       | 45.9077       | 45.0000 |
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Appendix A: The Hurwitz function

The function \( \zeta(\mu; \lambda) \) may be defined as \( \sum (j+\lambda)^{-\mu} \), where \( j \) runs from 0 to \( \infty \). This summation, however, converges only for \( \mu > 1 \) and convergence is painfully slow even for larger \( \mu \) values. In this study, we calculated numerical values of the Hurwitz function from

\[
\zeta(\mu; \lambda) = \sum_{j=0}^{J-1} (j+\lambda)^{-\mu} + \frac{(J+\lambda)^{-\mu}}{2} + \frac{(J+\lambda)^{1-\mu}}{\mu - 1} \times \left[ 1 - 2 \sum_{k=1}^{K} \frac{(\mu - 1)_{2k} \zeta(2k)}{(-4\pi^2(J+\lambda)^2)^k} \right] \tag{A.1}
\]

with \( J = 25 \) and \( K = 4 \). For further information on the function, see Ref. [19].

References