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LETTERS

Demystifying an Electrochemical Oscillator

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The indium thiocyanate electrochemical oscillator has been studied experimentally, and by digital simulation based on independently determined rate parameters. The latter can reproduce the characteristic features of the oscillations, without any additional model assumptions.

Introduction

Electrochemical oscillators have a long history: the first electrochemical oscillator was described as early as 1828.[1] The early literature on electrochemical oscillators was reviewed by Heathcote[2] and by Hedges and Myers.[3] By now, some 170 years after Fechner's observations, many oscillating electrochemical systems are known; for recent reviews, see Wojtowicz,[4] Poncet et al.,[5] Hudson and Tsotis,[6] and Koper.[7] A survey of the experimental evidence indicates that all known electrochemical systems that oscillate under conditions of external voltage control share two characteristic features: (1) a rate process that has a *negative* charge-transfer resistance, and (2) an additional, resistive component that weakens the external, experimental control of the interfacial potential. The negative charge transfer resistance occurs when, within a limited range of potentials, the rate of oxidation decreases as the applied potential becomes more oxidizing or the rate of reduction becomes smaller with increasingly reducing electrode potential. Several mechanisms are known that can generate such negative charge-transfer resistances. The additional resistive element is often a film formed at the metal−solution interface, but an external resistance can serve as well.

The chemistry underlying electrochemical oscillators is often incompletely understood. This applies especially to film-forming processes, because the very existence of the resistive film makes it more difficult to extract qualitative and quantitative kinetic information from those systems. Fortunately, there are a few cases in which no films are formed and for which the mechanism has been clarified. Even so, it has not been possible so far to convert that understanding into a satisfactory replication of the trajectories of those oscillations. Here we report such a replication, for the so-called indium thiocyanate oscillator.

The Indium Thiocyanate Oscillator

In a great variety of near-neutral aqueous electrolyte solutions, In(III) is readily reduced at a mercury electrode. However, in noncomplexing solutions (of, e.g., perchlorate or nitrate) at pH $\leq$ 3.5, In(III) is not polarographically reducible until the potential is reached where hydrogen ions are reduced, at which point the *interfacial* pH increases and indium reduction can take place. Consequently, the species reduced in neutral, noncomplexing aqueous solutions is most likely a hydroxy complex.[8]

Nonetheless, In(III) is reducible in acidic solution in the presence of a number of surface-active species, among them the surface-active halides and pseudo-halides. In this case, the polarograms show a polarographically reversible wave leading

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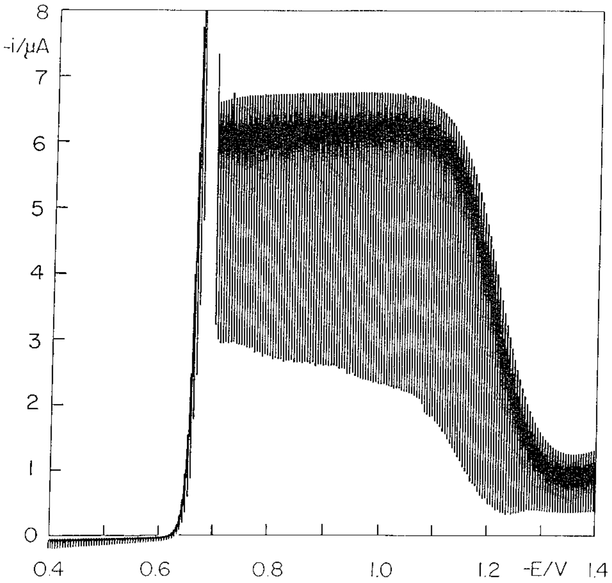

Figure 1. Dc polarogram of the reduction of aqueous 1 mM In(NO$_3$)$_3$ in 2.5 M NaSCN at 18 °C, pH = 3.15. Drop time mechanically controlled at 5.0 s. The region of interest for the oscillatory behavior is between −1.0 and −1.35 V vs SCE, where the reduction current decreases as the potential becomes increasingly more negative. The feature around −0.7 V is a polarographic maximum.

to a normal diffusion-limited current. However, as the potential is gradually made more negative, a *decrease* in the current is observed[9] until the onset of the hydrogen reduction. The latter gives rise to the already mentioned interfacial formation and subsequent reduction of complexes such as $In(OH)_2^+$ and hence to the eventual return of the current to its normal, diffusion-limited value, in addition to the simultaneously flowing hydrogen reduction current.

The dependence of the polarographic minimum on the applied potential indicates that it is controlled by an interfacial rather than a bulk process. Analysis of the experimental data showed[10,11] that the most likely mechanism is the attachment of an incoming indium(III) species to two adsorbed thiocyanate anions (the rate-determining step), followed by the reduction of this surface complex, resulting in the formation of indium amalgam and recovery of the two adsorbed SCN^- ions. It is the electrostatic repulsion of the adsorbed SCN^- anions by the increasingly more negatively charged electrode that leads to the gradual desorption of the electrocatalytic anion and, therefore, to a decrease in the reduction current as the electrode potential is made increasingly more reducing. The quantitative description is complicated by the apparent need[11] to consider the interfacial activity βa of thiocyanate rather than its interfacial excess Γ.

Typically, the reduction rate constant k increases as the potential E is made more negative, i.e., more strongly reducing. In the region of the polarographic minimum of indium in acidic thiocyanate solutions, the current, and the corresponding reduction rate constant k, instead *decreases* as the potential E is made more negative, see Figure 1. This gives rise to a *negative* charge-transfer resistance over a range of potentials.[10] (Usually, model expressions for the potential dependence of electrode kinetics, such as the relation of Erdey-Grúz and Volmer,[12] are used to describe $k(E)$. We have shown earlier[10] that this standard formalism is not very useful in the case of the indium thiocyanate oscillator. Fortunately, in the present case, the electrochemical rate constants $k(E)$ are directly, experimentally accessible, without any reliance on such models.) When the electrode potential E lies inside the range of negative charge-transfer resistances, electrochemical oscillations can result[13] when an external resistor R_{ext} is placed in series with the cell, and a voltage V is applied to that combination. The introduction of the series resistance R_{ext} inside the potentiostatic control loop partially relinquishes the potentiostatic control of the metal−solution interface because we now have $E = V - iR_{\text{ext}}$, where i is the current.

Experimental Results and Simulations

The experimental methods used were traditional dc polarography, using a dropping mercury electrode with an externally controlled drop time, and ac and transient measurements on hanging mercury drop electrodes. For the latter we used a Princeton Applied Research model 303 under computer control. The rate constants $k(E)$ were obtained from the dc polarogram using the Koutecký formalism[14,15]

$$F(\chi) = \frac{i}{i_{\lim}} \tag{1}$$

$$\chi = k\sqrt{\frac{12\tau}{7D}} \tag{2}$$

combined with an extension of the Oldham−Parry algorithm[16]

$$F(\chi) = \frac{3}{2}\left[1 + \xi - \sqrt{1 + \frac{2\xi}{3} + \xi^2}\right] - \frac{1}{117} \times \exp[-2.75(\log \xi)^2] \tag{3}$$

$$\xi = \frac{8\chi}{9} = \frac{16k}{9}\sqrt{\frac{3\tau}{7D}} \tag{4}$$

Here i is the polarographic current at the end of drop life, $i_{\lim}$ is its mass-transport-limited value, χ is the Koutecký parameter[14] in the absence of significant oxidation (as is the case here[10]), ξ is the closely related parameter used by Oldham and Parry, k is the reduction rate constant, D the diffusion coefficient, and τ the drop time. The drop time τ was controlled mechanically at 5.0 s. The value of the diffusion coefficient D (in cm^2 s^{-1}) was obtained from the polarogram, using the Ilkovič equation,[17,18] as

$$D = \{i_{\lim}/(708ncm^{2/3}\tau^{1/6})\}^2 \tag{5}$$

where $i_{\lim}$ is the limiting current (in μA), $n = 3$, c is the indium concentration in solution (in mM), and m is the mercury mass flow rate (in mg s^{-1}). We obtained $D = 4.5 \times 10^{-5}$ cm^2 s^{-1}.

It turned out that the logarithms of the resulting rate constants k, in cm s^{-1}, could be fitted to within their experimental uncertainty by the simple relation

$$\ln k = a_0 - a_1 E \tag{6}$$

where E is in V versus a saturated calomel electrode (SCE). No theoretical basis is claimed for eq 5, which is used here merely to represent the experimental data in a form suitable for digital simulation. (While eq 6 can be described *formally* in terms of a negative transfer coefficient,[19] it more realistically reflects the approximately exponential decay of the interfacial activity βa of thiocyanate ions with increasingly negative electrode potential E.[20]) For the test solution, aqueous 1 mM In(NO$_3$)$_3$ in 2.5 M NaSCN acidified with HNO$_3$ to pH 3.15, we find $a_0 = 19._9$ and $a_1 = 22._3$ V^{-1} for E in the range between −0.8 and −1.3 V vs SCE.

All measurements were made in a three-compartment, three-electrode cell with a Pt auxiliary electrode and an external SCE, both in aqueous 2.5 M NaSCN. A three-compartment cell was used because, to obtain reproducible results, we found it necessary to isolate the auxiliary electrode from the measurement compartment. Before each measurement, a fine stream of argon bubbles was passed through the solution; the same stream was redirected over the solution during the measurements.

For our transient measurements, after the solution had been deaerated, measurements were made on individual, freshly hung mercury droplets. Argon was bubbled through the solution for about 30 s, after which three mercury droplets were expelled, spaced about 1 s apart. A measurement was then made on the fourth extruded droplet. Five seconds after its extrusion, at an applied voltage of -0.2 V (at which potential no indium reduction takes place), the applied voltage was stepped to its final value V. The resulting current was amplified, digitized, and stored. The same cell and test solution were used as in the dc polarography: 1 mM $In(NO_3)_3$ in 2.5 M NaSCN acidified with HNO_3 to pH 3.15. The external resistance was placed in series with the mercury electrode, inside the potential control loop. The uncompensated solution resistance was estimated (from the positive feedback necessary to destabilize the potentiostat) as about 110 Ω; this value was so much smaller than the values of the external resistance R_{ext} used (typically 20 kΩ, at minimum 10 kΩ) that it was not taken into account in the simulations.

The interfacial capacitance was also measured on hanging mercury droplets, using the same equipment and protocol, except that these measurements were made in the absence of the external resistance R_{ext} . Moreover, in this case, the potential was scanned rather than stepped, a small alternating voltage was added, and the in-phase and quadrature components of the resulting alternating current were measured. The interfacial capacitance was extracted from the quadrature component of the alternating current and could be represented reasonably well over the limited range of interest by the simple expression

$$C_{dl} = b_0 + b_1 E \tag{7}$$

where $b_0 = 1.33$ μF and $b_1 = 0.71$ μF V^{-1}. In these experiments, the electrode area was 0.022 cm^2.

To simulate the oscillatory transients we have used the fast implicit finite difference algorithm, which has been shown to be both stable and efficient in its applications to cyclic voltammetry.[21-23] The simulation assumes a spherical electrode geometry.

Figures 2 and 3 illustrate some of the experimental transients and the corresponding simulations. The satisfactory fit between the measured oscillations and the simulations based on independently determined parameters, for a variety of applied voltages V and external resistances R_{ext} , demonstrates that these oscillations are simply the predictable result of the particular values of the electrochemical rate parameters used. The fit between simulation and experiment is not perfect, since the rate parameters all have their inherent uncertainties. It might well be possible to optimize the parameters to obtain an improved fit, but that was not the purpose of our exercise.

Discussion

Although chemical kinetics often lead to monotonically changing concentrations, potentials, etc., there are many oscillatory reactions, in which such changes are nonmonotonic, in bulk chemistry, in interfacial chemistry, and in biochemistry. They often have strikingly similar appearances, which has sometimes led investigators to assume a deeper similarity. For instance, Lillie[24-26] demonstrated that the action potentials traveling along nerves were in many respects analogous to those traveling along passivating metal wires. However, since both processes were poorly understood at that time, such an analogy was akin to setting up one equation between two unknowns. We now realize that nerve transmission and metal passivation are quite different phenomena, based on underlying processes that have little in common beyond a shared dimensionality and a highly nonlinear response. To understand oscillatory processes, each system must be understood in terms of its individual chemistry and physics and preferably be amenable to reconstitution from its independently determined rate parameters.

In the present case we have exploited the advantage that we can study the indium reduction in aqueous thiocyanate solution in the absence of external resistance, so that we have direct access to the rate parameters. We also have the advantage of being able to make our measurements on well-defined, easily renewable, and highly reproducible mercury electrodes. These favorable conditions were not accidental.

Since our initial description of the main features of the indium thiocyanate oscillator,[10,11,13] there have been several attempts to describe the observed oscillatory waveforms using theoretical models. The first of these was by Keizer and Scherson.[27] Unfortunately, these authors introduced a number of model assumptions for which there was no supporting evidence in the experimental record, such as double-layer relaxation, mass transport by diffusion plus migration, and an abrupt rather than gradual change in the amount of adsorbed *thiocyanate* ions (switching from full coverage to zero coverage) at a potential that was assumed to depend on the interfacial *indium* concentration. Because of these ad hoc assumptions, Keizer and Sherson could not compute oscillation waveforms resembling those reported for this system.

More realistic attempts have recently been made by Koper and co-workers.[28-30] In their first paper on this topic,[28] they assumed a gradual variation of thiocyanate interfacial excess with potential, and described indium mass transport in terms of a Nernst diffusion layer of fixed thickness. To limit the potential excursions at negative potentials, they introduced a parallel, uncatalyzed reduction pathway, which in their model was not related to hydrogen reduction and the resulting change in interfacial pH but, instead, was a formal term anchored at the reversible half-wave potential. In subsequent papers, Koper et al.[29,30] have slightly refined their model by replacing the single Nernst diffusion layer by two concentric, spherical Nernst diffusion layers. This modification led to somewhat more realistic current−time oscillations, although its authors still considered their model “a parody of reality”.[30]

Both Keizer and Sherson and Koper et al. tried to describe the experimental system in terms of solvable differential equations, and in so doing had to make a number of simplifying assumptions. Our approach is quite different, since the digital simulation makes it unnecessary to introduce simplifying assumptions and allows us to use directly measured rate parameters instead. We find that such a digital simulation, based on independently determined rate parameters, can reproduce the major experimental features of the oscillations. Note that there are no adjustable parameters in our simulation and that all simulations were made using the same set of parameters, except for the values of V or R_{ext}, which corresponded to the experimental values. The present simulations show that *there*

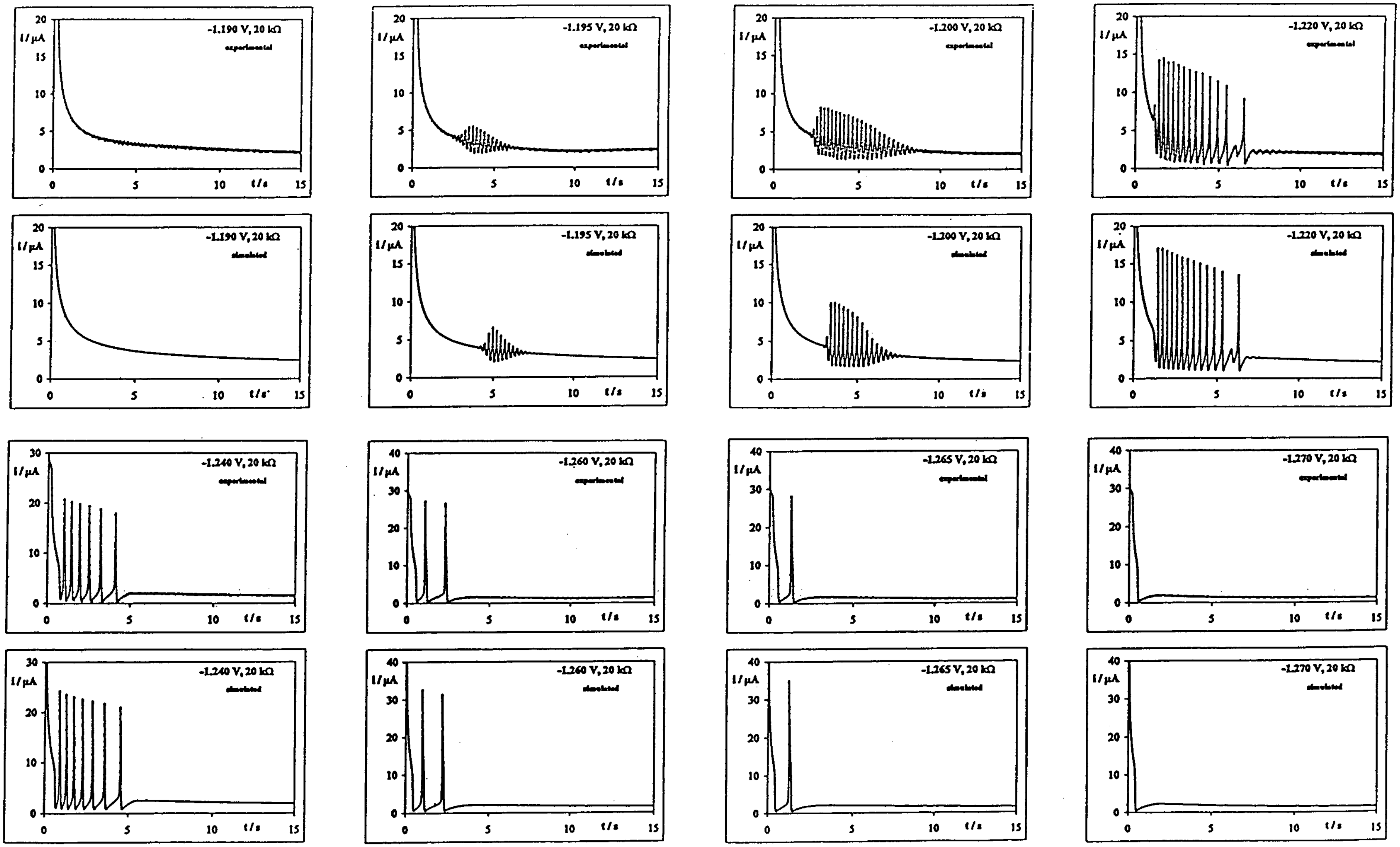

Figure 2. First and third rows: oscillatory transients obtained on a hanging mercury drop electrode at the potentials indicated with the data, in V vs SCE, when a 20 kΩ resistance was inserted in series with the working electrode. Second and fourth rows: oscillatory transients simulated using the independently obtained rate parameters plus the applied potential. Experimental data rates: 100 points per second; simulation 1000 points s^{-1}.

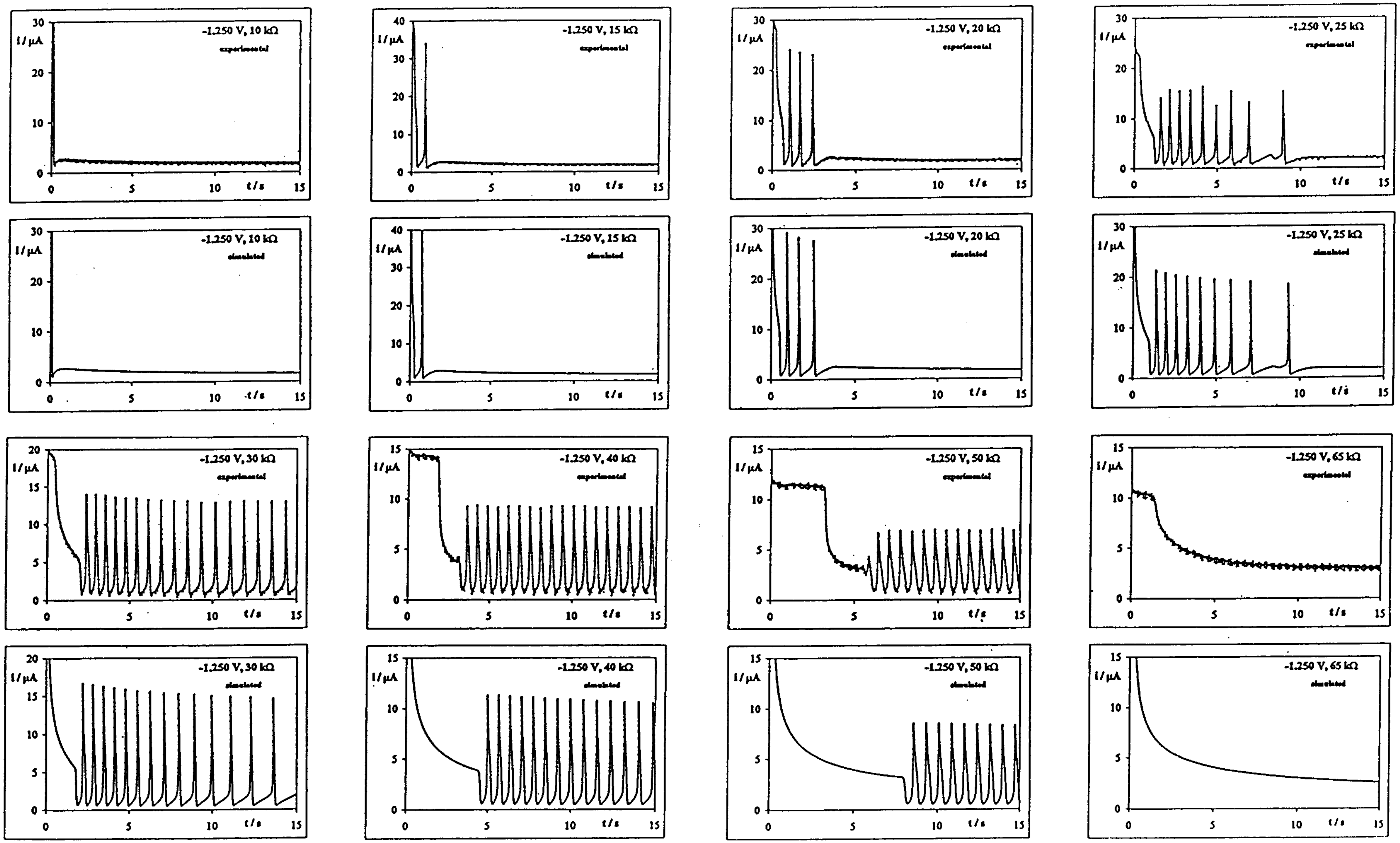

Figure 3. First and third rows: oscillatory transients obtained on a hanging mercury drop electrode at −1.25 V vs SCE upon insertion of a resistance of indicated value (in kΩ) in series with the working electrode. Second and fourth rows: the corresponding simulated oscillatory transients for those same series resistances. Experimental data rates: 100 points per second; simulation 1000 points s^{-1}.

is nothing strange, mysterious, or unexpected in such oscillations: they simply follow from the generally accepted formalism given these particular rate parameters. In the present case, the latter reflect an electrocatalytic sequence in which two adsorbed thiocyanate anions catalyze the electrochemical reduction of In(III).[10,11]

Our approach has some additional benefits. It allows us, for instance, to examine what happens with experimentally unobservable parameters such as the interfacial indium concentration c', or to vary experimental parameters that, in practice, cannot be varied independently, such as the interfacial capacitance C_{dl}. Likewise, we can now more readily study the effect of different modes of mass transport, such as planar instead of spherical diffusion. We will report separately on such more detailed studies.

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