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Electrochemical oscillators: an experimental study of the indium/thiocyanate oscillator

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Abstract

The “classical” indium/thiocyanate oscillator is studied in some more detail at the HMDE. Several qualitative dependences are investigated. Multiperiodic “mixed-mode” oscillations and aperiodic oscillations are observed near the system’s transition from steady state to oscillatory behaviour. These oscillations are very reminiscent of those observed in other (electro)chemical oscillators, and seem to indicate some kind of common mechanism.

INTRODUCTION

Among the known (temporal) oscillators in chemistry, the electrochemical ones go back farthest in time. As early as 1828 Fechner reported spontaneous current oscillations during the anodic polarization of iron in nitric acid [1]. Since then, numerous other examples of electrochemical oscillators have been investigated in the literature [1]. Most of these investigations were restricted to what may be called the “passive layer” or “corrosion oscillators” [2,3]. When interest is focused on the dynamic behaviour of (electrochemical) oscillators per se, it seems more obvious, however, to study first the simplest and best-defined systems available. Clearly, some “cathodic” oscillators, especially those pertaining to the potential-dependent catalysis or inhibition of a metal ion reduction at mercury [4–6], will most probably contain at least one variable less than the mentioned corrosion oscillators, because of the absence of a passive layer in such processes. In view of the fact that the mechanism of formation of such passive layers seems to be far from settled, cathodic oscillators might also be mathematically modelled more easily.

In this and in the subsequent paper [7] we will consider such cathodic oscillators, both experimentally and theoretically. The system whose dynamic behaviour we chose to investigate somewhat more in detail is the “In/SCN oscillator”, involving potential-dependent catalysis by thiocyanate of the indium(III) reduction. This

system was first studied extensively by de Levie and co-workers [4,8,9], who also discovered its ability to oscillate spontaneously without any "exotic" circuit elements in series with the electrochemical cell [10], clearly indicating the *chemical* origin of the observed oscillations.

EXPERIMENTAL

The experimental set-up consisted of an electrochemical cell, composed of a hanging mercury drop electrode (HMDE; EG&G Parc 303 Static Mercury Drop Electrode, the cathode) and a large mercury pool electrode (the anode), in series with an adjustable external resistance R_s . Potential control was performed by an Ecochemie "Autolab" polarograph. All electrode potentials were referred to that of the mercury pool, the solubility of mercury thiocyanate being sufficiently low. The cell was thermostated at 25 °C.

All solutions were prepared from freshly distilled water, $\text{In}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ (Merck), NaSCN (Merck, 98.5%) and HNO_3 (Baker, 65%). To all $\text{In}^{3+}/\text{SCN}^-$ solutions, a few drops of nitric acid were added to prevent the formation of indium hydroxides.

Because of the altogether not too high reproducibility of the HMDE's drop size, not much attention should be paid to the quantitative agreement of the various experiments. Obviously, in all experiments in which one specific dependence was under consideration, one and the same drop was used. This is not a problem since we are interested only in qualitative features. In all experiments the drop size was adjusted to "medium", conforming to a size of about 0.03 cm².

RESULTS

The dependence of several qualitative features of the observed oscillations (profile, amplitude, frequency, the occurrence of oscillations if at all) was studied as a function of the potential V , the external resistance R_s , the concentration of the electroactive component and the temperature. As the results will be discussed using some concepts from stability and bifurcation theory, we have included a small appendix dealing with the elementary nomenclature at the end of the second paper [7].

Figure 1 shows some typical oscillation profiles that can be observed at the HMDE. Figure 2 gives the V - R_s stability diagram of the In/SCN oscillator, i.e. the occurrence of either a stationary state or an oscillatory state under the various adjustments of the potential V and the external resistance R_s . Figures 3, 4 and 5 show the dependence of the oscillation amplitude and frequency on the potential, external resistance and temperature, respectively. Typical oscillation profiles for a ten-fold higher concentration of $\text{In}(\text{III})$ are depicted in Fig. 6. For obvious reasons the external resistance then has to be reduced by the same order of magnitude. Especially interesting behaviour appears near the stability boundaries of Fig. 2. In that region multiperiodic "mixed-mode" oscillations (combination of large and

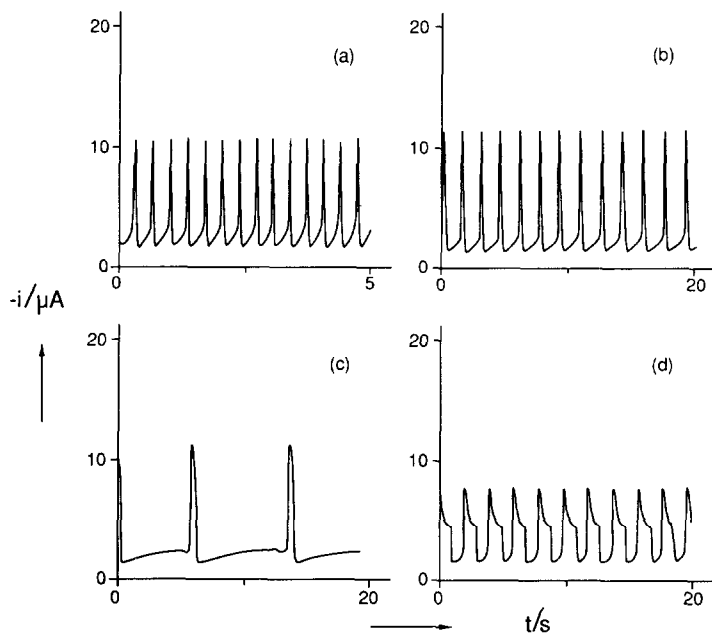


Fig. 1. Some typical oscillation profiles observed at the HMDE for 1.2 mM In^{3+} in 5 M NaSCN solution. (a) $V = -0.95$ V, $R_s = 35$ k Ω ; (b) $V = -1.05$ V, $R_s = 50$ k Ω ; (c) $V = -1.10$ V, $R_s = 60$ k Ω ; (d) $V = -1.15$ V, $R_s = 90$ k Ω .

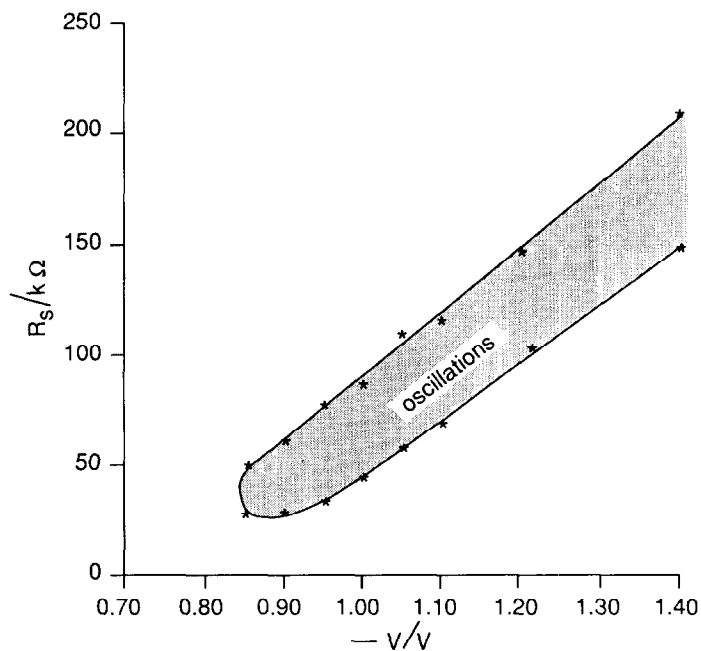


Fig. 2. V - R_s stability diagram for the In/SCN oscillator.

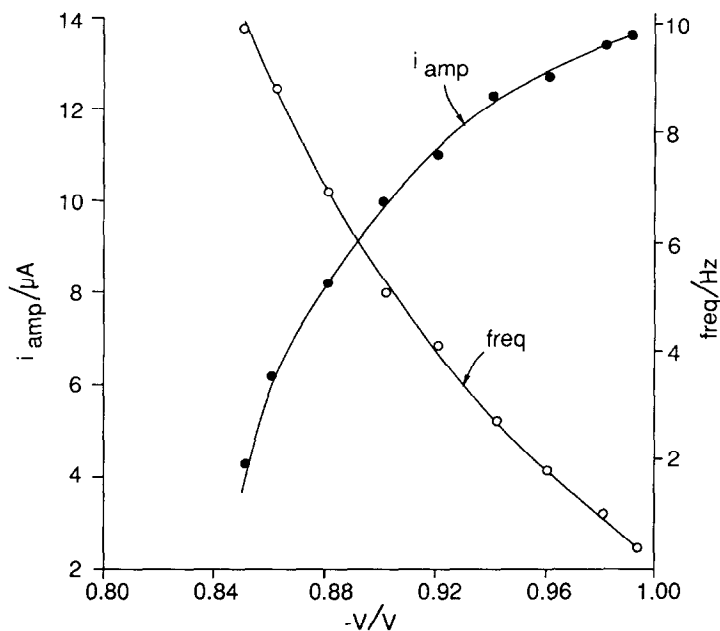


Fig. 3. Dependence of the oscillation amplitude and frequency on the potential V . R_s adjusted to $40\text{ k}\Omega$ (same system as in Fig. 1).

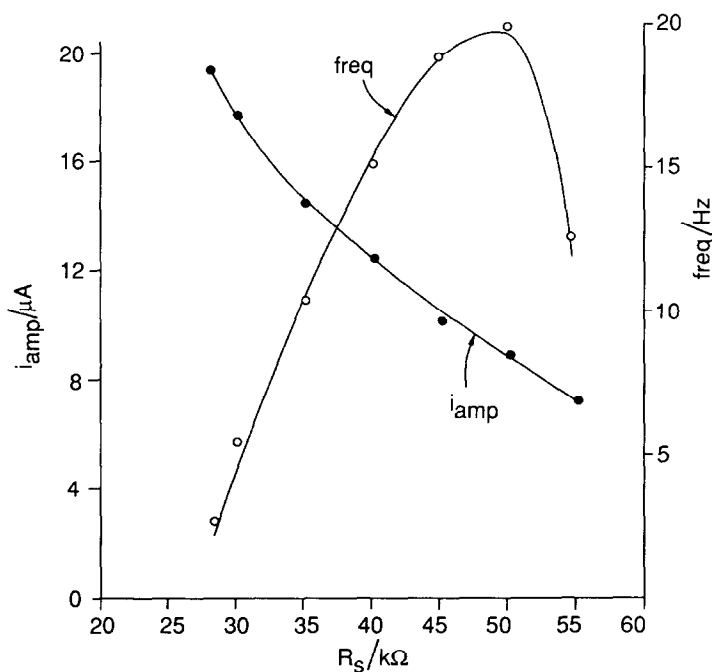


Fig. 4. Dependence of the oscillation amplitude and frequency on the external resistance R_s . V adjusted to -0.90 V (same system as in Fig. 1).

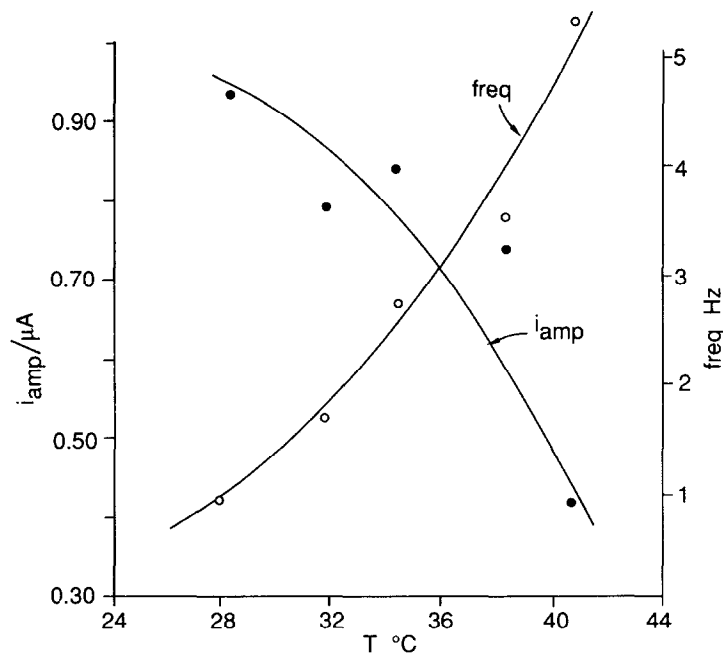


Fig. 5. Dependence of the oscillation amplitude and frequency on the temperature. $V = -1.05$ V, $R_s = 60$ k Ω (same system as in Fig. 1).

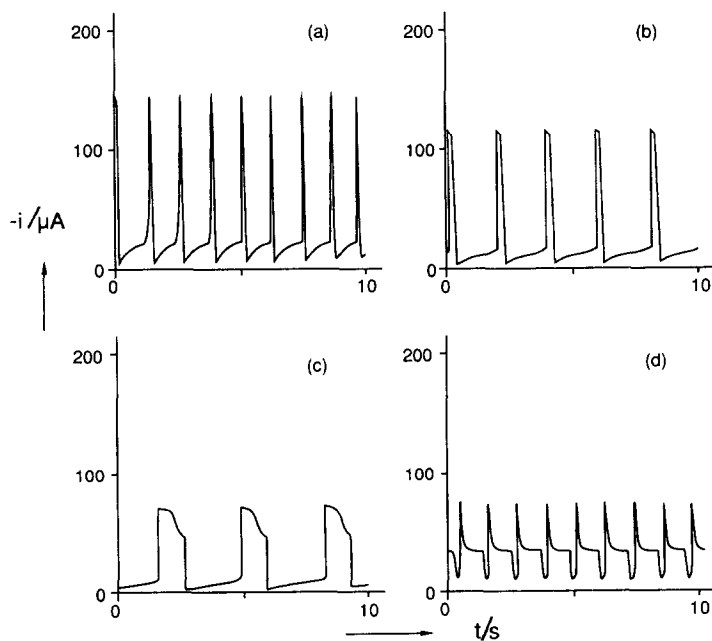


Fig. 6. Some typical oscillation profiles observed at the HMDE for 11 mM In^{3+} in 5 M NaSCN solution. (a) $V = -0.90$ V, $R_s = 3.5$ k Ω ; (b) $V = -0.95$ V, $R_s = 5$ k Ω ; (c) $V = -1.00$ V, $R_s = 9$ k Ω ; (d) $V = -1.05$ V, $R_s = 10$ k Ω .

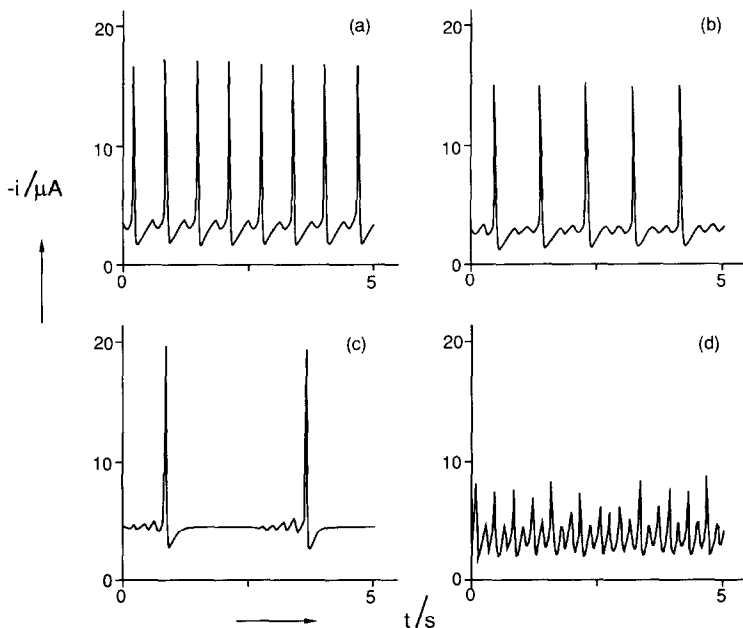


Fig. 7. Multiperiodic and aperiodic oscillations observed at the HMDE for 1.2 mM In^{3+} in 5 M NaSCN solution. (a) $V = -0.95$ V, $R_s = 25$ k Ω ; (b) $V = -0.95$ V, $R_s = 30$ k Ω ; (c) $V = -0.90$ V, $R_s = 25$ k Ω ; (d) $V = -0.92$ V, $R_s = 25$ k Ω .

small amplitude oscillations, Figs. 7a–7c) or even aperiodic oscillations can be observed (Fig. 7d). (These were not observed or not reported by de Levie in his previous study of the In/SCN oscillator [4].)

DISCUSSION

The qualitative properties of the In/SCN oscillator investigated above are intended to serve mainly as a comparison with those dependences predicted by a mathematical model [7]. However, some comments can be made in advance.

The observed bifurcation behaviour seems to correspond to either a supercritical Hopf bifurcation (Fig. 3) or a saddle-loop or SNIPER bifurcation, with a frequency going to zero (the experimental conditions were not really favourable enough to study the presence of a hysteresis region, which can distinguish between the two). A simple quantitative test for a supercritical Hopf bifurcation is the plot of Fig. 8. As the oscillation amplitude near a Hopf bifurcation should reach a root dependence on its distance to the bifurcation point asymptotically [11], such a plot is expected to have a theoretical slope of 0.5. The least-squares value for the slope of Fig. 8 is 0.497. As mentioned, at first sight the other bifurcations of Figs. 3 and 4 are identified as infinite period bifurcations. However, the observation of the mixed-mode oscillations of Fig. 7 indicates that more complex things can also happen.

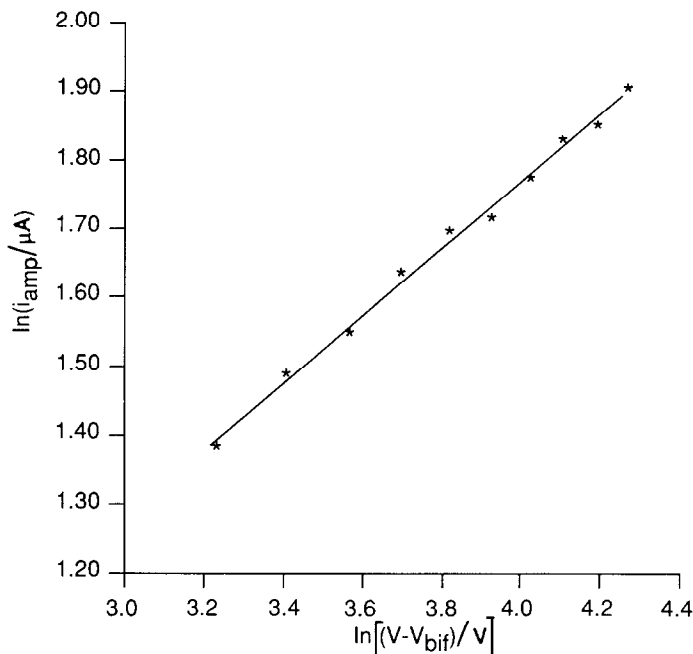


Fig. 8. Logarithmic plot of the oscillation amplitude vs. the potential (with respect to the bifurcation potential), indicating Hopf bifurcation.

These oscillations, together with the aperiodic (probably chaotic) state of Fig. 7d, are typical for a so-called homoclinic orbit associated with a saddle focus point. Such an orbit involves a steady-state point of the saddle-focus type, whose unstable spiralling trajectory is reinjected from a third dimension (after a large detour through phase space) exactly into the same steady-state point. Every such closed trajectory which has on it a steady-state point of the saddle type (i.e. the unstable trajectory leaving it is reinjected as a stable trajectory) is called homoclinic. Figure 7c shows such a nearly homoclinic oscillation (a real homoclinic oscillation is of infinite period, of course).

Homoclinic orbits of the saddle-focus type are well known as originators of mixed-mode oscillations and of so-called “Shil’nikov chaos” [12–14]. It is interesting to note that this kind of mixed-mode oscillation has been observed earlier both in homogeneous chemical oscillators (Belousov–Zhabotinskii reaction [15,16] and in a large number of heterogeneous electrochemical oscillators [14,17–20]. (We ourselves observed the same kind of mixed-mode oscillations at a HMDE in the Cu(II)/tribenzylamine oscillator, which was studied earlier in ref. 5.) The fact that exactly the same kind of saddle-focus homoclinicity is discerned in so many electrochemical oscillators seems indicative of some kind of common or “universal” mechanism at their origin. Because all these systems are kinetically different, we surmise that mass transfer might be responsible for it.

REFERENCES

- 1 J. Wojtowicz in J.O'M. Bockris and B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, Vol. 9, Plenum Press, New York, 1973, pp. 47–120.
- 2 U.F. Franck and R. FitzHugh, *Z. Elektrochem.*, 65 (1961) 156.
- 3 P. Russell and J. Newman, *J. Electrochem. Soc.*, 133 (1986) 59.
- 4 R. de Levie, *J. Electroanal. Chem.*, 25 (1970) 257.
- 5 H. Jehring and U. Kuerschner, *J. Electroanal. Chem.*, 75 (1977) 799.
- 6 H.-D. Dörfler and E. Müller, *J. Electroanal. Chem.*, 135 (1982) 37.
- 7 M.T.M. Koper and J.H. Sluyters, *J. Electroanal. Chem.*, 303 (1991) 73.
- 8 R. de Levie and A.A. Husovsky, *J. Electroanal. Chem.*, 22 (1969) 29.
- 9 L. Pospisil and R. de Levie, *J. Electroanal. Chem.*, 25 (1970) 245.
- 10 R. Tamamushi, *J. Electroanal. Chem.*, 11 (1966) 65.
- 11 F. Verhulst, *Nonlinear Differential Equations and Dynamical Systems*, Springer Verlag, Berlin, 1989.
- 12 P. Gaspard and X.-J. Wang, *J. Stat. Phys.*, 48 (1987) 151.
- 13 P. Gaspard, R. Kapral and G. Nicolis, *J. Stat. Phys.*, 35 (1984) 697.
- 14 M.R. Bassett and J.L. Hudson, *J. Phys. Chem.*, 92 (1988) 6963.
- 15 J.L. Hudson, M. Hart and D. Marinko, *J. Chem. Phys.*, 71 (1979) 1601.
- 16 J. Maselko and H.L. Swinney, *J. Chem. Phys.*, 85 (1986) 6430.
- 17 F.N. Albahadily and M. Schell, *J. Chem. Phys.*, 88 (1988) 4312.
- 18 F.N. Albahadily, J. Ringland and M. Schell, *J. Chem. Phys.*, 90 (1989) 813.
- 19 N. Fetner and J.L. Hudson, *J. Phys. Chem.*, 94 (1990) 6507.
- 20 Y. Xu and M. Schell, *J. Phys. Chem.*, 94 (1990) 7137.