New insight into the potential oscillations during iodate reduction in alkaline solution

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Potential oscillations during the reduction of iodate ions in alkaline solution under galvanostatic conditions have been re-investigated without adding iodide. The oscillations can take place only when the applied current is larger than the limiting current, and the oscillation amplitudes are within the plateau region of the limiting current. The bistability, i.e., iodate reduction and hydrogen evolution at different potentials, coupled with convection feedback, induced by hydrogen evolution, accounts for the oscillations. The mechanism was supported by the experimental results of current sweep and cyclic voltammetry. Our study shows that physical processes, i.e., alternately predominant mass transfer of the iodate by diffusion and by convection, play an important role in the oscillations.

Oxyhalogen anions, such as bromate, iodate and chlorite, are important components in known homogeneous oscillating chemical reactions.[1] Their heterogeneous oscillatory behavior has also been investigated by some researchers. Orbán and Epstein[2] found oscillations and bistability in hydrogen–platinum–oxyhalogen systems without external current and examined the effect of one-electron redox couples, such as Ce^{IV}/Ce^{III}, Mn^{III}/Mn^{II}, V^V/V^{IV}, Fe^{III}/Fe^{II} and Ag^I/Ag, on the oscillations. Electrically coupled Belousov–Zhabotinskii oscillators have been studied by Crowley and Field[3] and by Dechert and Schneider.[4] A series of studies on current oscillations, based on the reactions of bromate on mercury electrodes, were carried out by Treindl and co-workers.[5–9] Potential oscillations during the electrolysis of alkaline solutions of iodide plus iodate were briefly reported by Radkov and Ljutov with only one oscillating profile.[10] Although the authors sometimes observed weak hydrogen evolution during oscillations in this system, they did not give any explanation of how the oscillations were connected with the hydrogen evolution, and only listed possible chemical and electrochemical reactions in solution and on both electrodes (anode and cathode). They attributed the oscillations to the coupling reactions between anode and cathode because they placed the two electrodes very closely (2.5 mm apart). Actually, no convincing mechanism has been proposed to date.

The first author of this paper accidentally found a similar phenomenon to that described in ref. 10 when he employed the reaction $IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^-$, as Dahms[11] suggested, to change the surface pH of the electrode in a study of anomalous codeposition through carefully adjusting the applied current. The potential oscillations can take place without addition of iodide and with the two electrodes (cathode and anode) further apart (ca. 6 cm apart), which excludes the mechanism of coupling reactions between the anode and the cathode as described in ref. 10. The oscillations disappear with agitation, which means that mass transfer plays an important role in their formation. The potential oscillations can continue for hours, even days, under appropriately controlled conditions. We have studied the potential oscillations at various applied currents and iodate concentrations on different electrodes. A reasonable mechanism has been given with sound experimental support.

Experimental

An H-type glass cell was used, of which the two compartments have different sizes: the smaller one with a 2.5 cm id for the counter electrode (a strip of platinum); and the larger one with a 5 cm id for the working electrode (one of the three disks, silver, gold and platinum with diameters 2 mm, 2 mm and 3 mm respectively, insulated with epoxy resin). The two electrodes were placed vertically face-to-face at the two ends of the channel (1 cm id, 5 cm long) connecting the two compartments. An electrode of $Hg(l)|HgO(s)|1$ mol dm^{-3} NaOH, with a Luggin capillary, served as the reference electrode. The working electrode was polished with 600 mesh sandpaper and then was cleaned with ultrasonic waves. For each experiment, 100 cm^3 solution, freshly prepared from doubly distilled water and analytical grade chemicals, was used. Since dissolved oxygen has no effect on the oscillation phenomenon, nothing was done to eliminate it from the solution. Experiments were conducted at room temperature. Oscillations were obtained easily with the above conditions.

Electrochemical experiments were carried out with a CHI 660 Electrochemical Station (USA), which was interfaced with a Pentium 586 computer for acquiring and analyzing data. Digital potential–time series were sampled at 50 Hz.

Results

General characteristics of the potential oscillations

In Fig. 1 we present boundaries measured on a silver electrode that separate the current–concentration parameter plane into two parts. The conditions in the shaded part (labeled 'so') were such that sustained potential oscillations were observed, whereas those in the other part (labeled 'ss') were such that only stable states were found. We measured different waveforms within the oscillatory region of Fig. 1 (labeled 'so'). Generally, periodic oscillations occurred in the inner part of the shaded area, and aperiodic oscillations appeared near and along the boundaries. A typical oscillation sequence on the silver electrode in the boundaries is shown on the left of Fig. 2, which was obtained in 1 mol dm^{-3} NaOH solution with
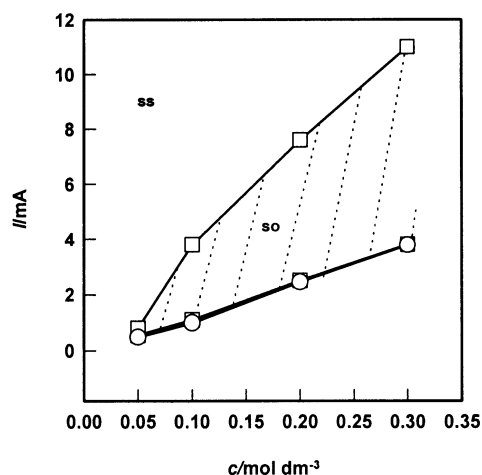
Fig. 1 Measured boundary points (□) in the parameter plane, applied current *vs.* iodate concentration, that separate the region in which sustained oscillations were observed (labeled 'so' and shaded) from the region in which only stable states were found (labeled 'ss'), and the relationship of limiting current with iodate concentration (○)

0.1 mol dm^{-3} iodate by increasing or decreasing the applied current monotonously. The system exhibits different oscillatory behavior at different currents. The oscillations in Fig. 2(c) and (d) are very stable with a limit cycle attractor. Increasing or decreasing the applied current induces some instability in the oscillations and the limit cycle becomes thicker [(b) and (e)]. Finally, at the bifurcation point the system displays some seemingly chaotic behavior [(a) and (f)]. We will explain this behavior in the Discussion section. Almost the same oscillatory sequence was observed on a gold electrode (Fig. 3), whereas the oscillation sequence on a platinum electrode (Fig. 4) is a little different from those on silver and gold electrodes. In most cases, a slightly damped time series was observed in Fig. 4, which may be due to a stronger adsorption of I_2, I or I^- on the electrode.[12] In addition, some induction time is required before the potential oscillations can be fully developed while the applied current is lower [Fig. 4(a)] and oscillations with smaller amplitudes appear [Fig. 4(e)] while the applied current is larger, both of which are basically coincident with the voltammogram in Fig. 5(c).

In Fig. 1, we show the relationship of limiting current with iodate concentration. In order to generate oscillations at a given iodate concentration, the minimum applied current should be larger than the limiting current.
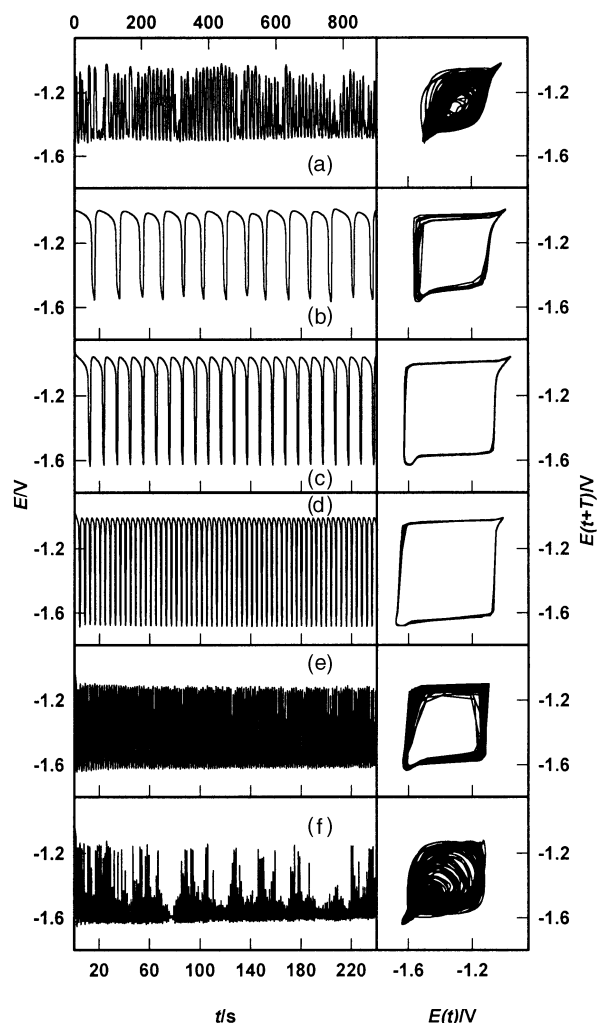

Fig. 2 Left: time series of potential oscillations for 0.1 mol dm^{-3} iodate reduction on a silver electrode in 1 mol dm^{-3} NaOH solution at different applied currents: (a) 1.1; (b) 1.15; (c) 1.5; (d) 2.5; (e) 3.3; (f) 3.5 mA. Right: two-dimensional projection of the phase space plot constructed from the time series on the left by the time delay technique. The delay time T is: (a) 0.52; (b) 0.55; (c) 0.33; (d) 0.21; (e) 0.21; (f) 0.1 s.
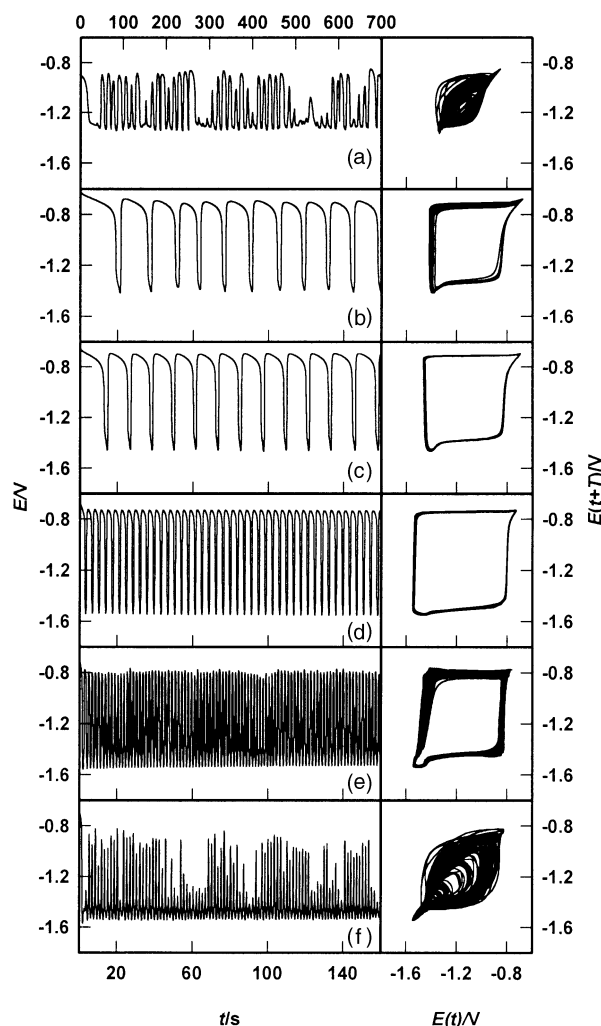
Fig. 3 Left: time series of potential oscillations for 0.1 mol dm^{-3} iodate reduction on a gold electrode in 1 mol dm^{-3} NaOH solution at different applied currents: (a) 1.18; (b) 1.3; (c) 1.5; (d) 3; (e) 4; (f) 4.1 mA. Right: two-dimensional projection of the phase space plot constructed from the time series on the left. The delay time T is: (a) 0.3; (b) 0.46; (c) 0.46; (d) 0.3; (e) 0.16; (f) 0.08 s.
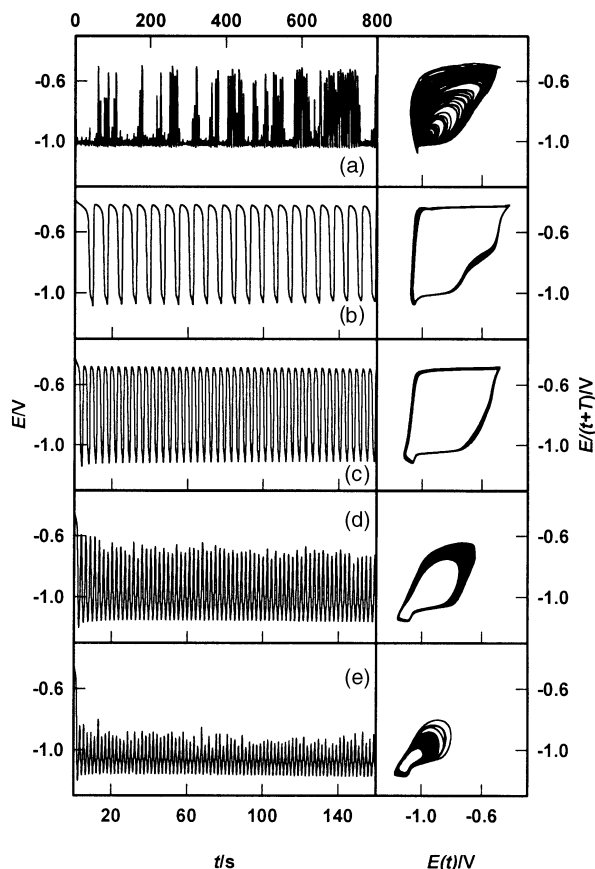
Fig. 4 Left: time series of potential oscillations for 0.1 mol dm^{-3} iodate reduction on a platinum electrode in 1 mol dm^{-3} NaOH solution at different applied currents: (a) 3.8; (b) 4; (c) 6; (d) 7.5; (e) 8 mA. Right: two-dimensional projection of the phase space plot constructed from the time series on the left. The delay time T is: (a) 0.32; (b) 0.3; (c) 0.3; (d) 0.22; (e) 0.22 s.

Typical voltammetry characteristics for the oscillations

Fig. 5 shows the typical cathodic current–potential curves for iodate reduction on silver, gold and platinum electrodes in 1 mol dm^{-3} NaOH solution, which were obtained by current scan. They have a broad limiting current plateau. Under current sweep, the system is destabilized when the applied current is larger than the limiting current, and the amplitudes of the potential oscillations are within that region.
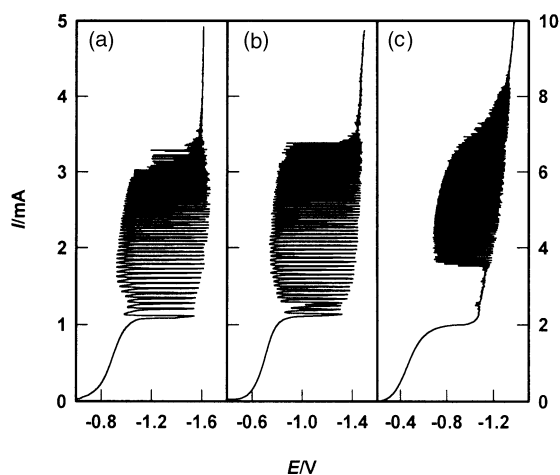

Fig. 5 Voltammograms on (a) silver, (b) gold and (c) platinum electrodes in a solution of 0.1 mol dm^{-3} iodate with 1 mol dm^{-3} NaOH. Current sweep at 0.01 mA s^{-1}.
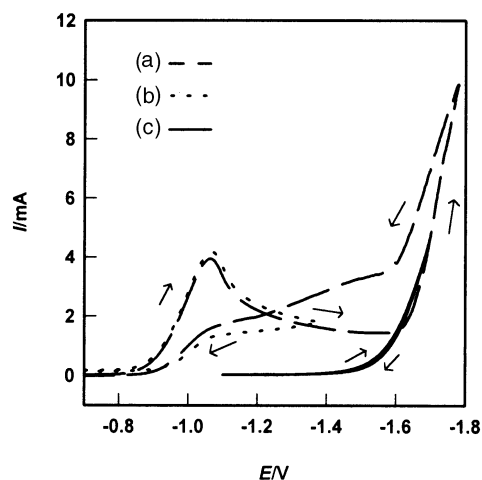

Fig. 6 Cyclic voltammograms on a silver electrode in 1 mol dm^{-3} NaOH solution. (c) Without and [(b) and (a)] with iodate (0.1 mol dm^{-3}); [(a) and (c)] with and (b) without hydrogen evolution. Potential sweep at 100 mV s^{-1}.

Cyclic voltammograms in Fig. 6 were obtained under different conditions, *i.e.*, with or without iodate ions, and with or without hydrogen evolution. An N-shaped curve appears in the forward scan between −0.7 and −1.8 V in (a), and a crossing cycle occurs by reverse scan, *i.e.*, the reverse scan current is larger than the forward scan current. When there is no iodate [as in (c)] or no hydrogen evolution [as in (b)] (reverse scan at −1.4 V), ordinary cyclic voltammograms appear.

Discussion

Mechanism of the oscillations

Since the potential oscillations occurred only when the applied current was over the limiting current (Fig. 1 and Fig. 5) and periodic hydrogen evolution was observed during the oscillations, hydrogen evolution must have played an important role in the phenomenon. From Fig. 5, a qualitative explanation for the oscillation mechanism is given here. With an increase of the applied current, three different stages occur in the current–potential curves of Fig. 5. In the first stage, where the applied current is less than the limiting current, only iodate reduction takes place. The second stage begins when the applied current reaches the limiting current, where a bistability appears; *i.e.*, reduction of iodate ions occurs at the higher potential side of the plateau and hydrogen evolution at the lower side of the plateau. Then, sustained oscillations follow in addition to the bistability with a continued increase of the applied current. As a current larger than the limiting current is imposed, the surface concentration of iodate ions is depleted to zero by reduction owing to the limited supply rate by diffusion mass transfer. Meanwhile, the potential moves negatively to the other side of the plateau where hydrogen evolution takes place to maintain the applied current. Because growth, detachment and movement of the hydrogen bubbles produce a forced convection mass transfer which replenishes the surface concentration of iodate ions, *i.e.*, a non-linear feedback, hydrogen evolution is thus completely repressed and the potential rises again to the higher side of the plateau. This is a typical period-one potential oscillation. The mechanism not only explains why the amplitudes of the oscillations are within the plateau region, but also shows that physical processes, *i.e.*, diffusion and convection mass transfer, as well as the (electro)chemical reactions, play an important role in the oscillations. The bistability and the sustained oscillations last for a limited range of currents because the convection mass transfer induced by the hydrogen evolution can raise the stationary limiting current plateau to a higher level like rotating the elec-

trode. Experimentally, at a given applied current in the current range where the oscillations occur, if a constant agitation, with a strength equal or larger than that caused by the hydrogen evolution, is employed instead of the convection effect induced by hydrogen evolution, no iodate depletion at the electrode surface can occur, so the oscillations stop and the potential stabilizes at the higher potential side of the plateau where only iodate is reduced. This is a simple way, similar to that in ref. 2, to show the one stable state of the bistability in that current range, and it explains why the oscillations disappear with agitation as we mentioned in the introduction. Removing the agitation, the potential shifts to the lower potential side of the plateau with the depletion of the iodate surface concentration by reduction under diffusion control, and hydrogen evolution takes place again, which is the other stable state of the bistability, and so the oscillations between the bistable states are restored. When the applied current is over the current range for the oscillations, the third stage occurs, where hydrogen evolution becomes the predominant reaction and can not be repressed by the replenishment of the iodate ions through the limited convection effect (which is now less than the blockage effect of the gas film formed on the electrode to the iodate reduction) induced by hydrogen evolution, and so the oscillation stops.

The depletion and replenishment can also be seen from the cyclic voltammograms of Fig. 6. In the forward scan between -0.7 and -1.8 V in (a) an N-shaped curve appears and its descending branch is due to the limited supply rate of iodate ions by diffusion mass transfer, i.e., from the depletion of the iodate surface concentration by reduction even though the potential value keeps on increasing towards the negative direction. The occurrence of a crossing cycle in (a), where the reverse scan current is larger than the forward scan current even after the hydrogen evolution ceases, can be explained only by the enhanced mass transfer of iodate ions through convection (which cannot stop as soon as the hydrogen evolution ceases) caused by hydrogen evolution, because only ordinary cyclic voltammograms were found when there is no iodate [as in (c)] or no hydrogen evolution [as in (b)] (reverse scan at -1.4 V).

We would like to point out that (i) not all reactions involving hydrogen evolution can generate oscillations unless they have similar voltammetry characteristics to that which we have discussed; especially, there should be a limiting current plateau in the current–potential curve obtained by potential sweep (not shown) or by current sweep or by both. Based on this typical characteristic, we have found a series of similar oscillators and will report them elsewhere.[13] (ii) Even though condition (i) is necessary, it is not sufficient to guarantee oscillations in all situations. For instance, we did not find oscillations when the iodate concentration is less than 0.05 mol dm^{-3} (Fig. 1) even though it also has a limiting current plateau. At lower iodate concentration, the iodate convection flow is too small to repress the hydrogen evolution, i.e., no effective or sufficient non-linear feedback. So although a limiting current plateau is a necessary condition for this kind of oscillation, it is not the only condition. This may be the reason why otherwise common oscillators have not been widely recognized.

Reason for different oscillatory behavior at different currents

According to ref. 14, the aperiodic oscillations result from the non-uniformity in bubble sizes of the hydrogen evolution and in nucleation sites at lower current (near and along the lower boundaries of Fig. 1), which only induces a weaker convection, or from the unstable gas film, which repeatedly collapses and reforms at larger current (near and along the upper boundaries of Fig. 1) and has some blockage effect towards iodate reduction. For both cases the iodate surface concentration cannot be restored completely. As the gas film transforms into a stable one at a still larger current, the oscillations stop because the hydrogen evolution becomes the predominant reaction and cannot be repressed by the replenishment of iodate ions. In contrast, periodic oscillations result from uniform hydrogen evolution which produces a stronger agitation and restores the iodate surface concentration completely.

Conclusions

The potential oscillations, during the reduction of iodate in 1 mol dm^{-3} NaOH solution, under galvanostatic control, have been discussed in detail. The oscillations have a typical current–potential curve, in which a broad limiting current plateau exists and the oscillation amplitudes are within that region. The characteristics of the current–potential curve can be used as a preliminary criterion for finding similar oscillations.

The reason for the oscillations is attributed to the occurrence of a bistability, i.e., iodate reduction and hydrogen evolution at different potentials, coupled with convection feedback induced by hydrogen evolution. This is the answer to the main question, unsolved in ref. 10, of why the oscillations depend on the hydrogen evolution. Therefore, the mechanism involving coupling reactions between cathode and anode, proposed in ref. 10, is rejected.

The sequence of aperiodic, periodic, aperiodic oscillations was obtained by increasing the applied current between the lower and upper boundaries at fixed iodate concentration. These phenomena result from the different behavior of hydrogen evolution at different currents.

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