Chaos during the Reduction of Iodate in Alkaline Solution: Geometrical Effect of the Electrode

Zelin Li,*,† Jiale Cai,‡ and Shaomin Zhou‡

Department of Chemistry, Hunan Normal University, Changsha 410012, People's Republic of China, and State Key Laboratory for Physical Chemistry of Solid Surface and Department of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

Geometrical effects on the oscillatory behavior during the reduction of iodate in an alkaline solution have been studied in detail. We have found that the geometrical factors greatly affect the oscillatory behavior when the iodate concentration is smaller, and chaos appears on the electrodes with smaller size or smoother surface, whereas at higher iodate concentration, the influence from the geometrical factors is minor and periodic behavior occurs instead, though some differences still exist in the waveforms with different roughness. The geometrical factors affect mainly the convection mass transfer of the iodate induced by the hydrogen evolution, in addition to the different adsorption.

1. Introduction

Nonlinear phenomena involving oxyhalogen anions, such as bromate, iodate, and chlorite, which appeared both in homogeneous systems[1] and in heterogeneous systems,[2−8] have been vital research subjects since the late 1960s. Chaos was observed in the Belousov−Zhabotinskii reactions by Hudson et al.[9] Simple and complex resting potential oscillations during the oxidation of hydrogen on the surface of platinum by strong oxidants, such as bromate and chlorite, as well as by some other oxidants, without applying external voltage or current, were reported by Orbán and Epstein[10] and by Kurin-Csörgei and Orbán,[11] but the authors seem to have given some totally different observations about the effects of the size and the quality of the platinum surface on the oscillations in their former[10] and latter[11] papers without further explanation. For instance, in their former paper (the second paragraph of the Discussion section), the authors claimed that the characteristics of the oscillatory curve depend greatly on the size and the quality of the platinum surface, and no oscillations could be produced with a platinum wire electrode; whereas in their latter paper (the fourth paragraph in the Results section), the authors stated that the oscillations were insensitive to the geometric surface of the electrode, and a platinum needle showed potential oscillations as well. Recently, geometrical effects have been discussed also in the electrodissolution with arrays of iron electrodes[12] and in the "beating mercury heart".[13] Geometrical factors seem to play different roles in different systems.

Potential oscillations during the electrolyses of alkaline solutions of iodide plus iodate were briefly described by Radkov and Ljutov[14] with only one oscillating profile. Although the authors observed weak hydrogen evolution sometimes during the oscillations in this system, they did not give any interpretation on how the oscillations were connected with the hydrogen evolution. We found similar phenomena[15] as in ref 14 accidentally while employing the reaction $IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^-$, as Dahms [16] suggested, to change the surface

pH of the electrode in study of anomalous codeposition through carefully adjusting the applied current. The potential oscillations, unlike those in ref 14, can take place without addition of iodide and with the two electrodes (cathode and anode) separated far away (about 6 cm), which excludes the mechanism of the coupling reactions between the anode and cathode as proposed in ref 14. Our studies[15] show that the potential oscillations, accompanying periodic hydrogen evolution, can occur only when the applied current is larger than the limiting reduction current of the iodate, and the oscillatory amplitudes are within the plateau region of the limiting current. The overlap of a negative feedback (depletion of the surface concentration of the iodate by reduction under diffusion control) and a positive feedback (replenishment of the surface concentration of the iodate by convection mass transfer induced through the hydrogen evolution) between the bistable states (the reduction of the iodate at the higher potential side of the limiting current plateau, and the hydrogen evolution at the lower potential side of the plateau) accounts for the oscillations. With the understanding of the mechanism, we have found[17] a series of similar potential oscillators not only on the cathode but also on the anode (with periodic oxygen evolution) and have extended[17] the application of the mechanism to a series of current oscillators.

In this paper, we present some new observations, namely, the chaotic behavior during the iodate reduction in an alkaline solution which results from the geometrical factors of the electrode, both the size and the roughness, and give some detailed discussion on the phenomena. We hope this work can act as an example for the understanding of the geometrical effect on the electrochemical oscillatory behavior, since the effect is important but less reported and generates some perplexing phenomena sometimes.

2. Experimental Section

An H-type glass cell was used, the two compartments of which have different sizes: the smaller one has a 2.5 cm inner diameter for the counter electrode, a strip of platinum; and the larger one has a 5 cm inner diameter for the working electrode, either a silver disk with a diameter of 1 or 2 mm, or a platinum
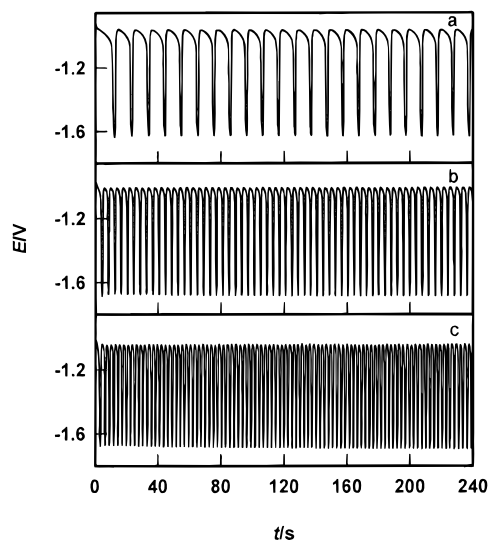
---

† Hunan Normal University.
‡ Xiamen University.

Figure 1. Potential oscillations for 0.1 mol dm^{-3} iodate reduction on a rougher silver electrode with a 2 mm diameter in 1 mol dm^{-3} NaOH solution at different applied currents (mA): (a) 1.5; (b) 2.5; (c) 3.

Figure 2. Potential oscillations (column 1), phase space projections (column 2), and power spectra (column 3) for the same solution and the same electrode in Figure 1 but with a smoother electrode surface at different applied currents (mA): (a) 2; (b) 2.5; (c) 2.8. The delay time T (s) in column 2: (a) 0.48; (b) 0.24; (c) 0.24.

disk with a diameter of 1 or 3 mm, insulated with epoxy resin. We denote the electrode with a diameter of 1 mm as a smaller one, and 2 or 3 mm as a larger one. The counter electrode and the working electrode were placed vertically face to face at the two ends of the channel (1 cm inner diameter and 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 reference electrode. Unless indicated otherwise, the working electrode was polished with 600 mesh sandpaper for a rougher surface, which was further smoothened with alumina powders down to 0.05 μm for a smoother surface for comparison, and then the working electrode was cleaned with ultrasonic waves. A solution of 100 cm^3 was used each time, which was freshly prepared from doubly distilled water and analytical grade chemicals. Since dissolved oxygen has no effect on the oscillation phenomena, nothing was done to eliminate it from the solution. Experiments were conducted at room temperature with the CHI 660 Electrochemical Station (USA), which was interfaced with a computer for acquiring and analyzing data.

3. Results

Effect of the Roughness of the Electrode Surface. Apparently stable periodic potential oscillations occurred (Figure 1) within a range of currents from 1.5 mA (a) to 3 mA (c) when the electrode surface was polished with 600 mesh sandpaper (a rougher surface). By further smoothing the electrode surface to a mirrorlike finish with alumina powders down to 0.05 μm (a smoother surface), seemingly period-doubling chaos[18] appeared (column 1 in Figure 2) in the same range of currents, as we can see that all the oscillations have the so-called strange attractors[19] (column 2 in Figure 2) and their power spectra in column 3 have broadened peaks with highly noisy background.[20]

Other differences in the oscillations between the rougher (Figure 1) and the smoother (Figure 2) surfaces for the same electrode with a larger size are that the oscillatory amplitudes are smaller in the latter case than in the former case, and the minima of the potential peaks in the latter case shift to the positive direction by about 200 mV. While using a smaller size electrode (1 mm diameter) but with the same roughness as the smoother one in Figure 2, the larger amplitudes which appeared intermittently (Figure 5a) were nearly the same as those
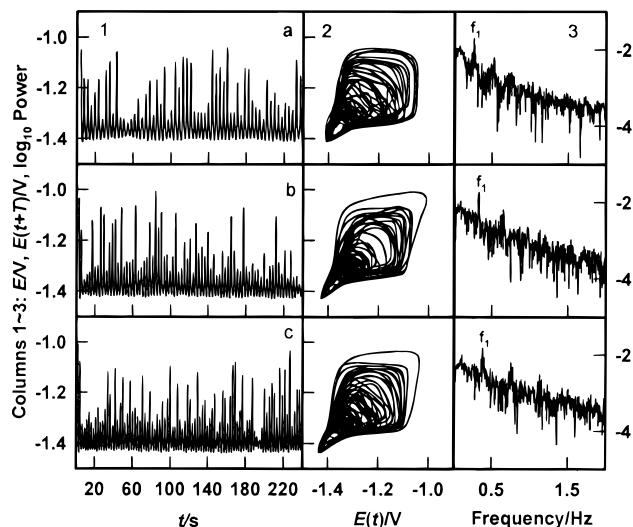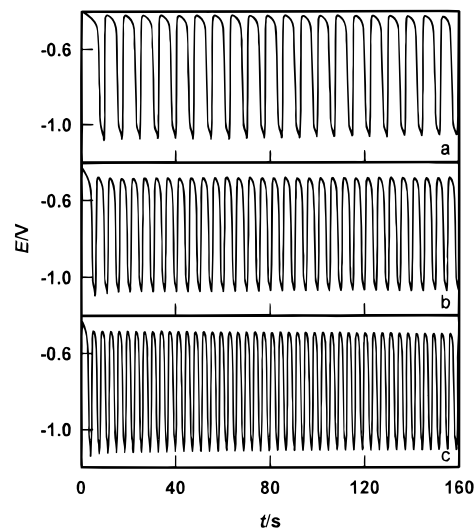

Figure 3. Potential oscillations for 0.1 mol dm^{-3} iodate reduction on a rougher platinum electrode with a 3 mm diameter in 1 mol dm^{-3} NaOH solution at different applied currents (mA): (a) 4; (b) 5; (c) 6.

in Figure 1 for the larger electrode with a rougher surface, and a whole shift also occurred toward the higher potential direction.

Effect of the Size of the Electrode Surface. On varying the area (size) of the electrode surface about one decade while retaining the same roughness, completely different oscillatory behavior was observed as well. Stable periodic oscillations occur (Figure 3) on an electrode with a larger size surface (3 mm diameter), but when the surface size is smaller (1 mm diameter), the oscillations (column 1 in Figure 4) exhibit seemingly chaotic behavior too, for they also have the strange attractors[19] (column 2).

Some noiselike small amplitudes appear during the oscillations (column 1 of Figure 4) with a smaller size electrode surface (rougher), which are consistent with the case in Figure 5a (same size but smoother), and their intermittent larger amplitudes (Figure 4) are almost the same as those in Figure 3 with a larger size electrode surface (rougher). No apparent potential shift was observed by only varying the size of the electrode surface.
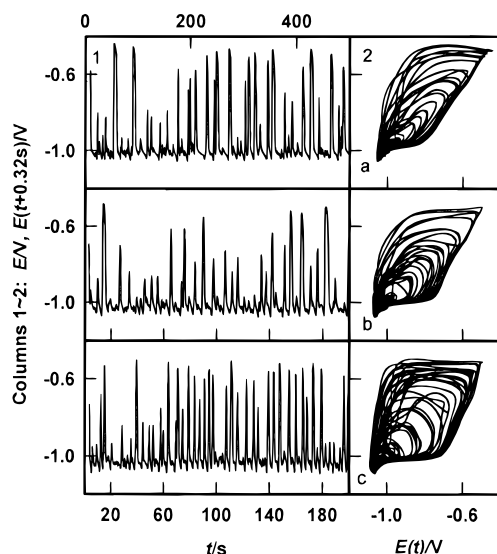
Reduction of Iodate in Alkaline Solution

J. Phys. Chem. B, Vol. 102, No. 9, 1998 **1541**

Figure 4. Potential oscillations (column 1) and phase space projections (column 2) for the same solution in Figure 3 on a rougher platinum electrode with a 1 mm diameter at different applied currents (mA): (a) 0.4; (b) 0.5; (c) 0.6.
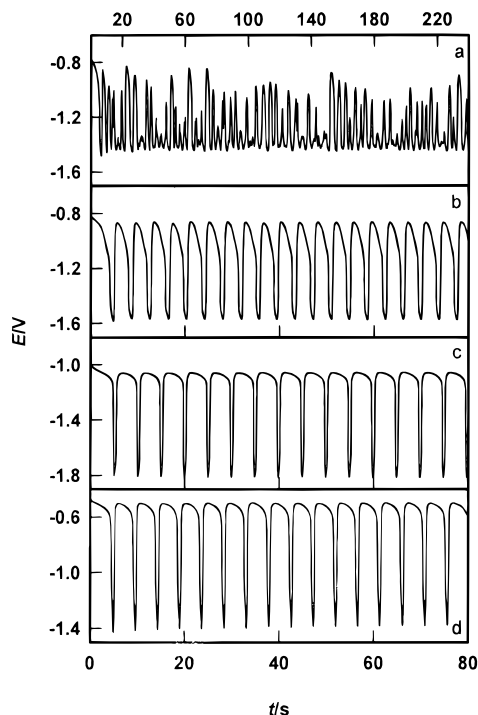

Figure 5. Potential oscillations (a) on a smoother silver electrode with a 1 mm diameter in the same solution of Figure 1 at 0.5 mA; (b) on a smoother silver electrode with a 2 mm diameter for 0.3 mol dm^{-3} iodate reduction in 1 mol dm^{-3} NaOH solution at 6 mA; (c) at the same conditions in (b) except for a rougher surface; (d) on a rougher platinum electrode with a 1 mm diameter in the same solution of (b) at 1.7 mA.

Dependence of the Oscillatory Behavior on the Concentration of the Iodate. Although such a section seems to be unrelated to the subject of this paper, the observations are helpful in the understanding of the geometrical effect on the oscillatory behavior. It is interesting and unexpected that, at a higher concentration of iodate, 0.3 mol dm^{-3}, for example, the chaotic behavior from the geometrical factors disappears, no matter what quality the electrode surface has, smoother (Figure 5b) or smaller (Figure 5d). Only two minor differences exist in the oscillatory behavior for the different roughness of the electrode surfaces

(Figure 5, b and c): one is that the system stays longer at upper potentials with the rougher electrode surface (c) than with the smoother electrode surface (b), but less time was spent at lower potentials with the rougher electrode surface than with the smoother one, both of which can be easily seen from the facts that the peaks are wider in (c) than in (b), and the intervals between the jumps, down and then up, are narrower in (c) than in (b); and the other is that the range of the potential oscillations with the smoother electrode surface (b) also shifts to a higher location by about 200 mV while remaining the same amplitudes as in (c).

4. Discussion

The above observations appear to be very confusing, but they all actually have some intrinsic connection and can be explained reasonably.

Although the mechanism for the oscillations has been discussed in detail in our previous work,[15,17] a brief description here may be necessary. When an applied current larger than the limiting current is imposed, the surface concentration of the iodate depletes to zero due to the limited supplying rate by diffusion. Meanwhile the potential moves to the negative direction with the decrease of the iodate surface concentration till hydrogen evolution takes place in order to keep up the applied current. Because the formation and detachment of bubbles produce an enhanced convection mass transfer by penetration effect, microconvection effect, and macroconvection effect,[21] which replenishes the surface concentration of the iodate, hydrogen evolution is completely repressed and the potential rises again. This is a typical period-one potential oscillation. The stronger the agitation and the larger the bulk concentration of the iodate, the more completely the iodate surface concentration is restored and the hydrogen evolution is repressed, so periodic behavior occurs, or else aperiodic behavior will appear.

For a larger electrode, a rougher surface facilitates the gas evolution by providing more nucleation sites than a smoother surface does, and more uniform hydrogen evolution on the whole electrode surface, which has a stronger agitation, can take place at a rougher surface than at a smoother surface, so periodic behavior usually occurs with a rougher surface (Figure 1). When the surface is smoother, hydrogen evolution mainly exhibits some local behavior and can hardly be developed uniformly on the whole electrode surface because of its fewer nucleation sites and weaker adhesion to the bubbles. It is this nonuniformity and the weaker agitation of the hydrogen evolution on the smoother electrode surface, which cannot restore the iodate surface concentration completely when its bulk concentration is lower, that results in the chaotic behavior (Figure 2) and the smaller amplitudes in the oscillations (Figure 2); i.e., the oscillations in Figure 2 should have a larger upper potential near −0.8 V as in Figure 5a,b, if a stronger agitation were imposed, as well as the shorter relaxation time in Figure 2 than in Figure 1.

When the bulk concentration of the iodate is increased, its limiting reduction current increases. A larger applied current (beyond the limiting current) is required in order to generate the potential oscillations as we have discussed above, which means that the current for the hydrogen evolution is increased too when the iodate surface concentration depletes to zero. In this case, the convection mass transfer of iodate is enhanced by not only the increase of its bulk concentration but also the stronger agitation from more hydrogen evolution, so periodic behavior usually occurs at higher iodate concentration no matter

what geometrical characteristics the electrode has, larger or smaller, rougher or smoother. The relaxation time is longer at higher iodate concentration with the rougher surface (Figure 5c) than with the smoother surface (Figure 5b) because the former has a slightly larger limiting current for the iodate reduction (3.8 and 3.5 mA for the rougher and the smoother surfaces, respectively) owing to the larger real surface area and the larger the difference between the applied current and the limiting current, the longer the time for the iodate depletion; and the jump time is a little shorter for the rougher surface (Figure 5c) than for the smoother surface (Figure 5b) because the former can promote hydrogen evolution on its whole surface which generates a stronger agitation to replenish the surface concentration of the iodate more rapidly.

A smaller size electrode is more sensitive to the convection effect, which is the reason for the smaller noiselike oscillations in Figures 4 and 5a, and the surface concentration of iodate can be restored more easily by the convection, which is the reason the intermittent larger amplitudes nearly have the same magnitudes as those for the larger and rougher electrode surface (Figure 4 with Figure 3, and Figure 5a with Figure 1). Hydrogen evolution not only has the agitation effect but also the blockage effect with the bubbles adhered tentatively on the electrode surface. The smaller size electrode is more sensitive to the latter effect, for a larger bubble may occupy tentatively a larger part of the whole electrode surface available for the iodate reduction, which produces another nonuniformity. The chaotic behavior on a smaller size electrode at a lower iodate concentration results from this nonuniformity.

That the potentials shift toward positive direction with a smoother electrode should be due to the weaker adsorption of the product iodide on the smoother electrode surface. A larger surface concentration ratio of iodate against iodide accounts for a more positive potential and the shift in contrast with the rougher surface.

We have shown how the geometrical factors affect the oscillatory behavior during the iodate reduction. The geo-metrical factors have much greater effects on the oscillatory behavior at the lower iodate concentration by affecting the convection mass transfer of the iodate induced by the hydrogen evolution besides the different adsorption with different roughness. The seemingly confusing oscillatory behavior at different conditions can thus be clearly understood.

References and Notes

(1) Field, R. J.; Burger, M. *Oscillations and Traveling Waves in Chemical Systems*; John Wiley & Sons: New York, 1985.

(2) Crowley, M. F.; Field, R. J. *J. Phys. Chem.* **1986**, *90*, 1907.

(3) Dechert, G.; Schneider, F. W. *J. Phys. Chem.* **1994**, *98*, 3927.

(4) Treindl, L.; Olexová, A. *Electrochim. Acta* **1983**, *28*, 1495.

(5) Olexová, A.; Treindl, L. *Chem. Zvesti.* **1984**, *38*, 145.

(6) Olexová, A.; Treindl, L. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1156.

(7) Olexová, A.; Treindl, L. *Electrochim. Acta* **1990**, *35*, 1095.

(8) Olexová, A.; Král, D.; Treindl, L. *React. Kinet. Catal. Lett.* **1992**, *48*, 470.

(9) (a) Hudson, J. L.; Hart, M.; Marinko, D. *J. Chem. Phys.* **1979**, *71*, 1601. (b) Hudson, J. L.; Mankin, J. C. *J. Chem. Phys.* **1981**, *74*, 6171.

(10) Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1981**, *103*, 3723.

(11) Kurin-Csörgei, K.; Orbán, M. *J. Phys. Chem.* **1996**, *100*, 19141.

(12) Fei, Z.; Kelly, R. G.; Hudson, J. L. *J. Phys. Chem.* **1996**, *100*, 18986.

(13) Smolin, S.; Imbihl, R. *J. Phys. Chem.* **1996**, *100*, 19055.

(14) Radkov, E. V.; Ljutov, L. G. *J. Electroanal. Chem.* **1988**, *241*, 349.

(15) Li, Z.; Cai, J.; Zhou, S. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3519.

(16) Dahms, H. *J. Electroanal. Chem.* **1964**, *8*, 5.

(17) Li, Z.; Cai, J.; Zhou, S. (a) *J. Electroanal. Chem.* **1997**, *432*, 111. (b) *J. Electroanal. Chem.* **1997**, *436*, 195.

(18) Weiss, C. O.; Abraham, N. B. In *Measures of Complexity and Chaos*; Abraham, N. B., Albano, A. M., Passamante, A., Rapp, P. E., Eds.; Plenum Press: New York, 1989; pp 269−280.

(19) Hudson, J. L.; Tsotsis, T. T. *Chem. Eng. Sci.* **1994**, *49*, 1493.

(20) Eckmann, J. P. *Rev. Mod. Phys.* **1985**, *57*, 617.

(21) Vogt, H. In *Comprehensive Treatise of Electrochemistry*; Yeager, E., Bockris, J. O'M., Conway, B. E., Sarangapani, S., Eds.; Plenum Press: New York, 1983; Vol. 6, Chapter 7.