IRREGULAR POLAROGRAPHIC CURRENTS OBEY FEIGENBAUM UNIVERSALITY ROUTE FROM ORDER TO CHAOS

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This article is dedicated to Professor Jaroslav Heyrovský to whom the Nobel Prize was awarded fifty years ago. The inventor of polarography and his disciples always stressed that electrochemical measurements should yield neat and regular polarographic waves. In this communication we present a case, in which a high degree of irregularity is observed and we seek its origin.

The DC polarograms of an oligomer with four repetitive units of 'extended viologen' yield in part irregular current fluctuation. The analysis of the current–time transients at different potentials confirms the periodicity, the period doubling and transfer to chaos. The periodicity doubling obeys the universal route to chaos. The estimated value of the Feigenbaum constant 4.68 is very close to the theoretical value $\delta = 4.6692...$

Keywords: Extended viologen; Pyridinium salts; Electroreduction; Feingenbaum constant; Polarography; Electrochemistry.

Periodic electric phenomena, electrochemical oscillations, occurring in electrochemical systems are known for many decades[1]. Most of the oscillating systems were found during anodic dissolution of metals (corrosion), where the electrode is subsequently passivated and re-activated[2]. Another type of oscillation was observed in electron transfer reactions accelerated by anionic[3] or cationic catalysis[4]. Desorption of the catalyst at a certain potential leads to negative differential resistance[5], that may cause under certain conditions instability of electric circuit which the electrochemical cell is placed in. Electrochemical oscillating systems are convenient models for in-

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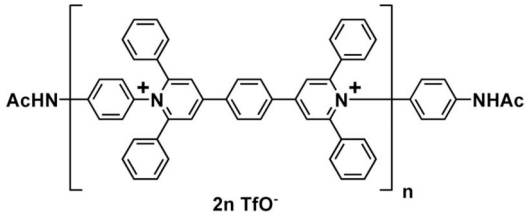
vestigation of periodic and chaotic processes[6] because system parameters (concentration, applied potential, temperature, overall resistance) can be conveniently changed. We recall that in the Nature many processes can easily switch between order and chaos[7]. The flow of a liquid can be laminar or turbulent. Also the heart beat changes from periodic to fibrillating. Unpredictability of chaotic dynamics for a long time was a puzzle because it seemed that those processes fail to obey any laws. The theory of chaos originates from the end of the 19th century. In this connection we should mention at least the names of Henry Poincaré, Mitchell Feigenbaum and Alexander M. Ljapunov. The discovery made by Feigenbaum was based on a numerical model of the so called quadratic iterator $x_{n+1} = ax_n(1 - x_n)$, where $n = 0, 1, 2, \ldots$ and a is a parameter[7]. This simple iteration is one of many examples confirming that order and chaos can be derived from the same mathematical description. Depending on the value of a, the final state of the quadratic iterator can be a single value, two values, four values, etc. The long term behavior may end up at a single state or it may alternate between two states, four states, etc. For all values of the parameter $a > 3.5699456...$, known as the Feigenbaum point, the branching ceases, the final values of the quadratic iterator fill the whole interval (0,1) and the system enters the chaos. Subsequent studies have shown that the route from stability to branching and to chaos is common not only for mathematical iterators but also for natural processes. This important finding has indicated that the law, by which a system approaches the chaotic behavior, can be deduced from branching periods and is manifested by a single number, the Feigenbaum constant, $\delta = 4.6692...$ The Feigenbaum constant is a universal constant for functions approaching chaos via period doubling. The value of δ for natural processes can be estimated as the ratio of duration of two subsequent branching intervals, which enables the prediction of the onset of chaos. Experiments confirming the existence of the period doubling and a remarkable degree of agreement with the δ value included hydrodynamics (helium, water, mercury), electronics (diods, transistors), laser feedback and acoustics in helium[8]. A rather artificial case of the quadratic iterator has shown the way to understand many physical processes. The appearance of δ in a large number of systems was called 'universality'. Methods were developed for distinction of periodic and chaotic time series, which otherwise seem to be almost identically irregular.

This communication describes currents observed during the electron transfer of a higher oligomer **1** of the extended viologen **2**. Numerous derivatives of 2,2′- or 4,4′-bipyridinium dications were frequently studied. Generally, two reversible one-electron waves are observed in aprotic sol-

vents[9]. The resulting cation radicals and fully reduced neutral forms are highly reactive, being often used as redox mediators. The reduced forms can react among themselves[10] or with the parent oxidized form[11]. Adsorption effects are also common[12]. In this communication we deal with two derivatives of 'extended viologens', polycation **1** bearing eight positive charges and simple dication **2** as a reference (Chart 1). Electrochemical properties of **2** have been described in our previous publications[13]. This communication is aimed at the description of unusual phenomena encountered in electrochemistry of **1**.



1 n = 4
2 n = 1

CHART 1

It was expected that **1** behaves as a compound with four communicating redox centers. Instead, vigorous instability was observed. The full electrochemical description of a series of these polycations will be given elsewhere. Here we limit ourselves to observation of the periodicity, bifurcations and chaos-related properties.

EXPERIMENTAL

The syntheses and identification of compounds **1** and **2** was described in our previous communication[14]. Both compounds were used in a form of triflates. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and acetonitrile were supplied by Sigma Aldrich. The indifferent electrolyte $TBAPF_6$ was recrystallized and dried in vacuum. Acetonitrile was dried over activated molecular sieves. Electrochemical measurements were done using a system for DC polarography, cyclic voltammetry, phase-sensitive AC polarography, AC voltammetry and electrochemical impedance spectroscopy (EIS). It consisted of a fast rise-time potentiostat, a lock-in amplifier (Stanford Research, model SRS830) and a frequency response analyzer (Stanford Research, model SRS760). The instruments were interfaced to a personal computer via an IEEE-interface card (PC-Lab, AdvanTech Model PCL-848) and a data acquisition card (PCL-818) using 12-bit precision for both A/D and D/A conversion. The drop time was 1.5 s for DC polarography and 4 s for the phase-seneitive AC polarography. Sine-wave frequency and amplitude were from 16 to 43 kHz and 1 mV, respectively. Current–time curves were recorded by means of a fast digital oscilloscope Tektronix, model TDS1012B, which uses the 8-bit resolution. The degassed solution was briefly mixed by passing a stream of argon, which should ensure the homogeneity of the solution after previous measurements. A fresh

mercury drop was formed and the current–time transient was recorded. At each constant potential the transient was recorded with a different sampling time (typically 10 ms, 40 ms, 1 s). A three-electrode electrochemical cell was used. The reference electrode, Ag|AgCl|1 M LiCl, was separated from the test solution by a salt bridge. The working electrode was a valve-operated static mercury electrode (SMDE2, Laboratorní přístroje, Prague) with an area 2.73 × 10^{-3} cm^2 and a computer-controlled drop time. The auxiliary electrode was cylindrical platinum net. The scan rate of the applied DC potential was in the range 5–10 mV s^{-1}. Oxygen was removed from the solution by passing a stream of argon saturated with vapors of the solvent. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

The first electron transfer to viologens or to extended viologens, such as **2**, yields the cation radical. Higher oligomers of **2** with two or three repetitive viologen units give polarograms with the first wave split to a doublet or a triplet, respectively. This is an expected behavior for compounds having equivalent communicating redox centers. The octo-cation **1** behaves differently. Figure 1 shows the comparison of the first polarographic reduction wave of **1** and **2**. The DC polarogram of **1** rises almost discontinuously at –0.5 V and from this potential the current is characterized by a considerably higher noise level. At potentials of the limiting current, the noise level again decreases. This increased noise was observed for concentrations as low as 60 μmol l^{-1}. The increased noise is present in polarograms registered with the expanding dropping electrode and also with the static valve-operated mercury drop electrode. Therefore, these irregular currents cannot

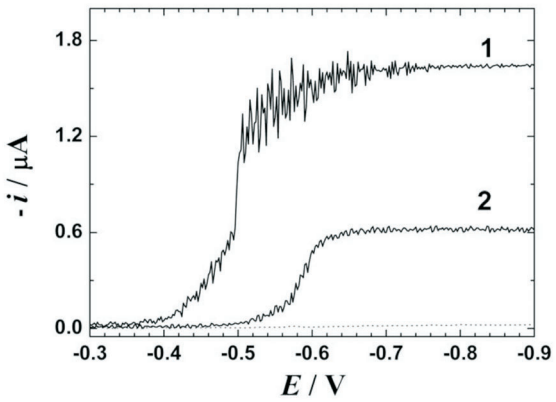


FIG. 1
The DC polarograms of 0.5 mM **1** and **2** in 0.1 M $TBAPF_6$ in acetonitrile. The dashed line is for the supporting electrolyte

be attributed to well-known streaming maxima caused by an uneven distribution of the surface tension. The fast Fourier transform (FFT) of a section of polarograms is shown in Fig. 2. Compound **1** yields the power spectrum with a rather high noise level. This spectrum shows the presence of a distinct frequency line pointing to the periodicity of the current variation. The power spectrum of **2** and the spectrum of **1** calculated at the limiting current show a low noise and an absence of any periodicity. On the basis of these findings we have undertaken a more thorough study of transitions from stability to instability.

Electrochemical oscillating systems are conveniently investigated by impedance techniques assessing conditions at which the cell is characterized by a negative (NDR) or a hidden negative differential resistance (HNDR)[1,5]. This task was not simple to accomplish for the studied system. The phase sensitive AC polarogram of **1** (Fig. 3) shows that **1** is strongly adsorbed, as inferred from the imaginary faradaic admittance component being much larger than its real counterpart. The objective of our AC measurements was to prove the existence of NDR, which would require the application of very low frequencies and consequently long measurement time. At potentials of interest, the system slowly evolves in time. Hence, we could not complete reliable impedance measurements at the lowest frequencies. Nevertheless, the AC polarogram in Fig. 3 shows faradaic maxima with a narrow dip located exactly at the potential of a discontinuity on DC polarograms and

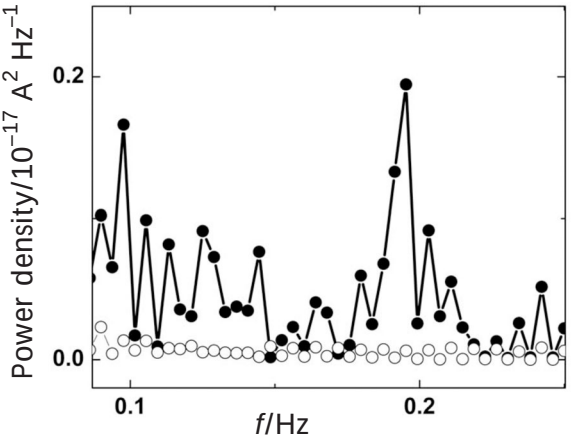


FIG. 2
The FFT power spectra of parts of DC polarograms given in Fig. 1. ●, a section of the DC polarogram of **1** between –0.5 and –0.65 V; ○, compound **2**

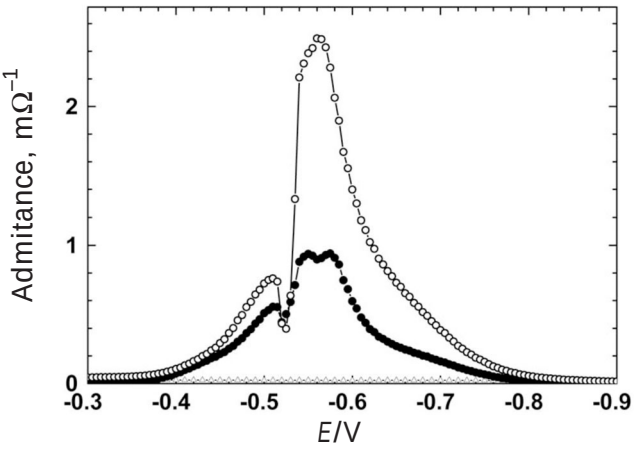


FIG. 3

The phase-sensitive AC polarogram of 0.5 mM **1** in 0.1 M $TBAPF_6$ in acetonitrile. The real and imaginary admittance components are plotted as ● and ○, respectively. The imaginary admittance component of the blank is shown as △. The AC frequency was 160 Hz

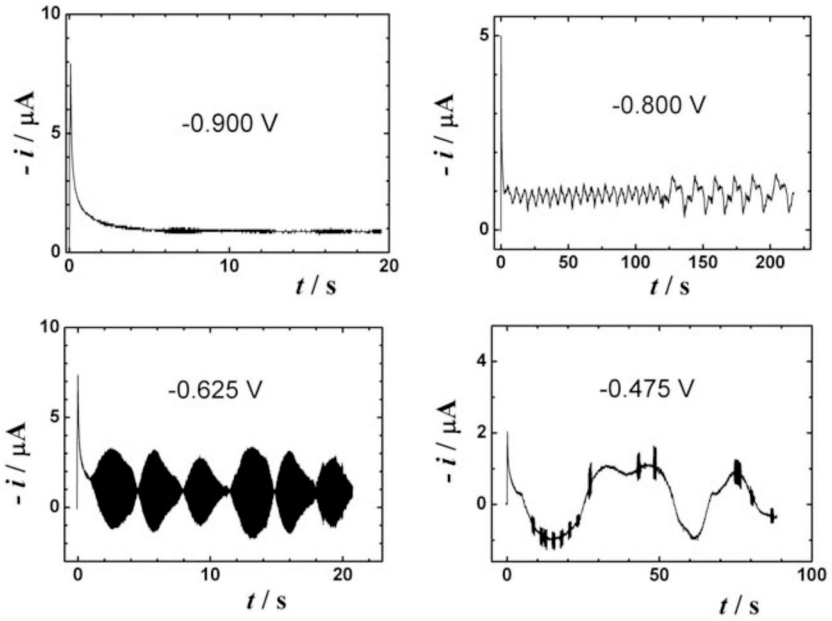


FIG. 4

Current–time transients at different constant potentials obtained for 0.5 mM **1** in 0.1 M $TBAPF_6$ in acetonitrile. The SMDE was freshly formed at a potential indicated in each graph

at the on-set of the electrical instability. The reader may ask why the AC polarogram is neat and regular while the DC polarogram under the same conditions shows irregularity. We recall that the phase sensitive detection rectifies only the AC current components of the same frequency as the reference sinusoidal perturbation. All different frequencies, including electrochemical oscillations, are discriminated.

A typical development of the current periodicity and instability at different constant potentials is shown in Fig. 4. The current–time curve (the *i–t* curve) at potentials of the limiting polarographic current (–0.900 V) is a featureless current decay, as expected from the theory of diffusion-limited currents. Very small disturbances at low current values stem from the 8-bit digitization. This transient confirms that our experimental setup does not suffer the pick-up of noise from the power line or other sources of electronic disturbances. All other curves in Fig. 4 were recorded at potentials where the DC polarogram showed pronounced irregularity. We can see a periodic behavior changing the frequency of oscillations at –0.800 V. The frequency doubling is a well known feature in oscillating and chaotic systems. A periodic burst of oscillations was observed at –0.625 V. Note that this transient is a smooth function for the first one or two seconds and periodic bursting begins afterwards. The last example is a transient at –0.475 V, which shows a low-frequency periodicity combined with an irregular appearance of small-amplitude bursts.

One of the typical features of systems governed by chaos is a high degree of sensitivity to a very small system perturbation, which becomes amplified. The perturbation of the present system can be a small variation in the potential distribution at the SMDE, screening effects of the glass capillary, uneven distribution of an adsorbate, mass transport fluctuations of the parent species or their products, just to name some of them. As a result, transients repeatedly measured at the same potential always have a somewhat different form. Figure 5 shows another *i–t* curve at –0.475 V sampled in 10-ms intervals. It is characterized by bifurcation points, where the frequency doubling occurs. Figure 5 closely resembles the famous Feigenbaum diagram of the final-state based on a numerical model of so called quadratic iterator $x_{n+1} = ax_n(1 - x_n)$, where $n = 0, 1, 2, \ldots$ and a is a parameter (see introducting part). The multiplication of final values is termed *frequency doubling* and the corresponding coordinates determine the bifurcation point. The lengths δ_{k-1} and δ_k of two successive branches of the Feigenbaum diagram, in our case the time duration between bifurcations, are precisely related to the Feigenbaum constant $\delta = \delta_{k-1}/\delta_k = 4.6692...$ The constant δ matches the importance of the number π and is universal for natural pro-

cesses. The number δ was observed in such diverse fields as the dynamics of liquid helium, the fluctuation of the gypsy moth population and in many branches of physics. The Feigenbaum constant opens a route for prediction when the next bifurcation will happen and proves that at a certain point the system will change to chaos. Two current branches in Fig. 5 yield the experimental value of δ = 4.68, which is indeed quite close to the theoretical value. This confirms that the irregular polarogram in Fig. 1 is not caused by the negligence of an operator or the malfunction of the current sensor. Instead it indicates a complex system behavior that obeys the 'universality' rule governing a change from order to chaos.

The *i*–*t* transient at –0.800 V depicted in Fig. 4 shows a change of periodicity together with a change of the amplitude of oscillations. Similar small and large amplitude oscillations were observed in many electrochemical systems (for references see refs[15,16]). This transient shows its periodicity at the first glance. However, it may not be so obvious in other cases. An experimental time series can be just a noise without any structure. Another similarly looking series can hide in itself an underlying deterministic governing law, like it is the case of the quadratic iterator. These two cases can be distinguished by the method of time delays, which allows the construction of an attractor. The attractor of the *i*–*t* series at –0.8 V is shown in Fig. 6. It was made by having plotted current data in a 3D graph having *i*(*t*) values as the

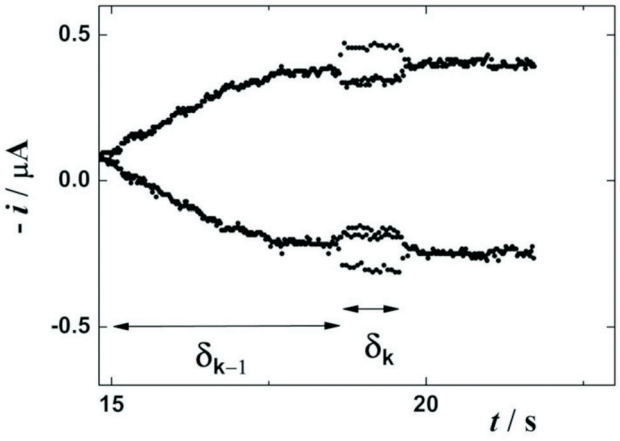


FIG. 5
Current–time transient at a constant potential –0.475 V obtained for 0.5 mM **1** in 0.1 M $TBAPF_6$ in acetonitrile. The sampling interval was 10 ms. Arrows indicate the duration of two subsequent branching periods, which yield δ very close to the Feigenbaum constant

x-axis and phase-shifted (or time-delayed) values $i(t - 3\tau)$ and $i(t - 6\tau)$ as the other two axes. The delay was $\tau = 0.2$ s. The resulting form of the attractor is insensitive to the value of τ. The attractor in Fig. 6a clearly shows a dense larger orbit corresponding to the large amplitude periodicity, whereas the inner part is characteristic for a chaotic behavior. For a better clarity, Fig. 6b reproduces just few orbits of Fig. 6a, namely the last large amplitude orbit and the first low amplitude orbit. If the measured time series were a random noise, the graphical construction would only yield points spread all over the phase space of Fig. 6. An example, in which the first impression is not so obvious, is given in Fig. 7. The time series of the current (Fig. 7a)

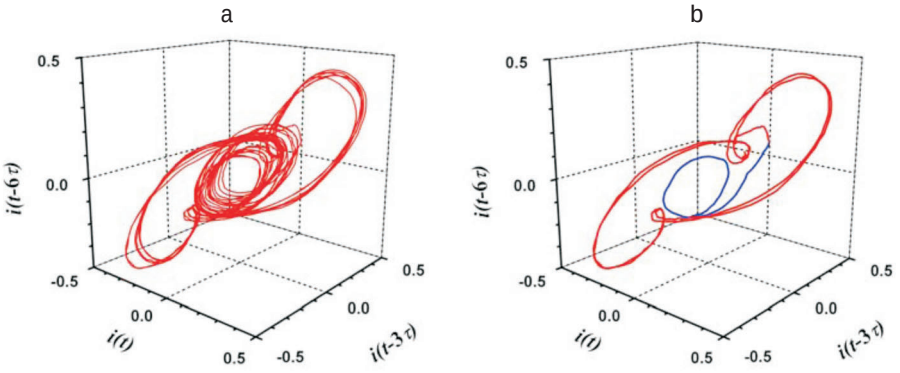


FIG. 6
Construction of an attractor from the current–time transient at –0.800 V. a The trajectory of the current–time series in the phase space obtained at the time delay $\tau = 0.2$ s. b Selected trajectories from graph a showing a change of the attractor

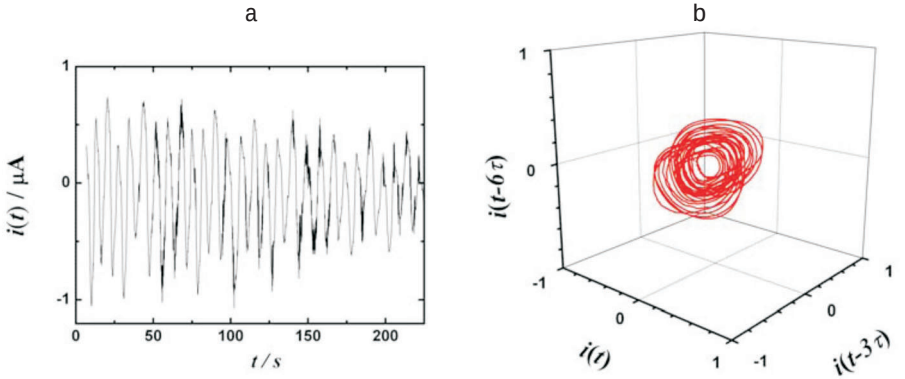


FIG. 7
Construction of an attractor from the current–time transient at –0.450 V. a The current–time series. b The corresponding attractor constructed at $\tau = 1.2$ s

could be a random fluctuation. The time-delay analysis in Fig. 7b shows the behavior of a deterministic chaos.

The analysis given above confirms that an irregular polarogram shown in the beginning of this communication carries information about a rather complicated interfacial processes. The underlying process obeys the universal characteristics of chaotic systems. Further experiments and modeling will be needed for identification of equations governing the observed behavior. We can only suggest a hypothesis on the origin of reactions causing the observed complexity. Compound **1** is exceptional in the sense that it can take up to sixteen electrons, where of eight in the first step. Redox centers of **1** are mutually communicating and should yield eight more or less separated redox potentials. This is certainly not observed in the data given in Figs 1 and 3. In a compound like **1** it is not possible to predict the order in which the redox centers will accept the single electron. Most likely, the order of reduction will be stochastic. Another aspect is the acceleration of the interfacial reaction of this polycation by the field of the electric double layer (the Frumkin effect). The sequential transfer of electrons to redox centers will diminish the positive charge of the polycation **1** and, hence, the electrostatic acceleration will decrease. We suppose that the observed chaotic faradaic currents are results of mutual interplay of the distribution of redox potentials, randomness in redox site reduction, electrostatic forces and also the adsorption interaction. At present a more precise estimation of the principal influence governing the chaos of this system is not feasible. We assume that a systematic variation of large number of external parameters (temperature, concentration, double-layer properties, solvent polarity, electrode size, etc.), which influence rates of heterogeneous and homogeneous reactions, electrostatic and adsorption effects[17], will shed more light in the system complexity. Another strategy is the comparison of the transition from the order to chaos in a series of shorter and longer oligomers similar to **1**. Further work will require a change of the fast data acquisition system from the 8-bit to 16-bit resolution. Work along these lines is in progress.

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