Reverse Scan as a Source of Information in Square Wave Voltammetry*

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Under the influence of recently published articles, reverse scans in square wave voltammetry were applied in a study of Eu^{3+}/Eu^{2+} redox system at increasing concentrations of several electrolytes, and gradually changing frequency or step potential. The electrode response is highly affected by all these factors and two peaks can appear though only one electroactive species is present in the solution and one electron included in the process, whereas adsorption of the reactant or product is not pronounced. Scanning in both directions appears as a potential tool for kinetic studies of the electrode processes although in the studied system its practical application meets various problems.

INTRODUCTION

When only the oxidized form of a redox pair is present in the electrolyte solution at a relatively high concentration, voltammetric study is generally performed by scanning in the negative direction.[1] In some techniques, such as square wave voltammetry (SWV),[2] successful application of the positive scan is also possible[3–7] under the same conditions, though (much) more negative initial potential should be applied. »Combined« measurements, *i.e.,* scanning in one and then in the other direction, give results that cannot be directly compared with cyclic voltammetry,[8] in which two opposite scans are the parts of the same cycle whereas in the discussed case they are completely independent.

In their recently published papers, Fatouros[3–5] and coworkers tested this approach on reactions of the type:

$$A + e^- \rightarrow B$$
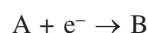
assuming that, in the experiments performed with a static mercury drop electrode, product B remains dissolved in the electrolyte solution. They concluded that recording of individual voltamograms by using both scan directions can be very useful in studies of electrode kinetics. The point is that the electrode response, even the number of peaks, highly depends on the scan direction if the process of interest is not reversible.

Obviously, the systems in which an amalgam is formed as the final reduction product are not included in the whole story. Irrespective of the problems that appear during theoretical treatment of such examples, some earlier experiments[6,7] point to the possible application of reverse scans even when this type of electrode reaction is studied. Suppression of the effects produced by adsorption of the negatively charged, surface active ligand (in $Cd^{2+} - I^-$ system)[6] and improvement of the peak shape when the electrode process is controlled by the kinetics

* Dedicated to the memory of the late Professor Marko Branica.

of the preceding reaction (as in perchlorate solutions of In^{3+})[7] can be achieved in the mentioned way.

On the other side, the number of systems with soluble products, which were studied by means of reverse scans in square wave voltammetry, is small. In fact, the UO$_2^{2+}$ / UO$_2^+$ redox pair in carbonate medium[3] and titanic salts in acidic solutions[4,5] are the only examples. Therefore it seems important to apply such an approach to some other redox pairs in order to find its »pluses« and »minuses« and/or to extract some new information.

In this article, an attempt to apply scanning in both directions is described taking the reaction

$$Eu^{3+} + e^- \rightarrow Eu^{2+}$$
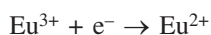
as a model. Its product is water soluble whereas the electrode reaction rate is governed by the type and concentration of the basic electrolyte.[9] The system is not of electrochemical interest only, because europium atypical behavior in different electrolyte solutions[10–12] (sometimes described as »anomalous hydration«)[11] was recorded by completely different methods, such as fluorescent or Raman spectroscopy.

EXPERIMENTAL

Salt solutions were prepared from reagent grade chemicals, produced by Kemika (Zagreb), Ventron (Karlsruhe) or Fluka, and water purified in a Millipore Milli-Q system.

Voltamograms were recorded using a static mercury drop electrode PAR 303 (Princeton Applied Research) attached to a μAutolab System (Eco Chemie, Utrecht). Platinum wire served as a counter electrode whereas all potentials were given with respect to the saturated Ag/AgCl (NaCl) reference electrode.

All measurements were performed with SW amplitude E_{sw} = 40 mV (i.e., 80 mV peak to peak) and delay time (defined in Figure 1) t_1 = 30 s while other potential and timing parameters were varied.

Before recording each set of voltamograms, the solution in the polarographic cell was deaerated with high purity nitrogen for 15 minutes. The room temperature was kept at 25 °C.

The influence of electrolyte concentration on the electrode response (obtained by forward and/or reverse scan) was followed at a constant level of dissolved europium (0.5 mmol dm^{-3}) and constant acidity (0.01 mol dm^{-3} HClO$_4$).

RESULTS AND DISCUSSION

Electrode Response

In the introductory part, the possibility of recording SW voltamograms by starting at positive or negative potentials was mentioned, assuming the presence of only the oxidized form of a redox pair in the aqueous phase and
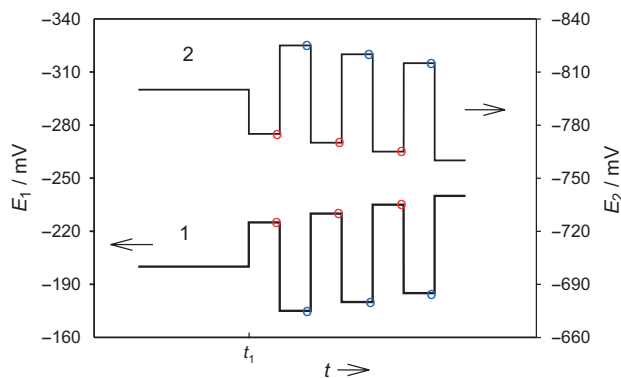

Figure 1. Excitation signals in square wave voltammetry for negative (1) and positive (2) scan directions. (Arrows indicate that the left y-axis is valid for curve 1 and the right one for curve 2.) Sampling points are schematically indicated for forward (red) and backward currents (blue). t_1 = delay time.

solubility of the reduction product in the electrolyte solution. In Figure 1, the excitation signals are given for both cases. The resulting voltamogram is generally ob-
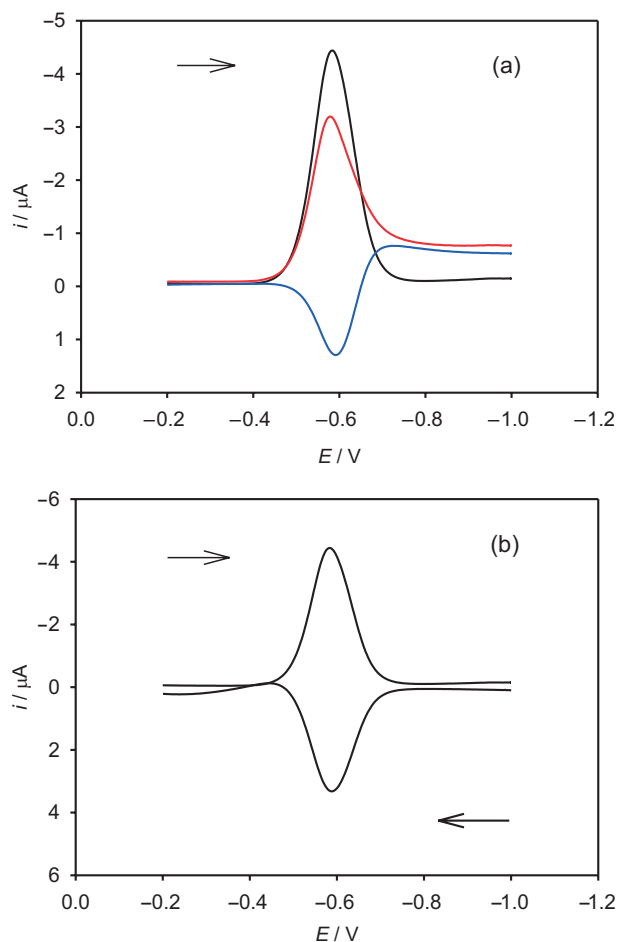

Figure 2. Square wave voltamogram of Eu^{3+} (0.5 mmol dm^{-3}) in 0.01 mol dm^{-3} HClO$_4$ and its forward (red) and backward currents (blue). Frequency: 20 s^{-1}; amplitude: 40 mV; step potential: 2 mV; delay time: 30 s; scan direction: negative (a). Net currents recorded in the same solution using both scan directions – indicated by arrows (b).

tained by sampling the currents under conditions schematically presented by red and blue circles and recording their difference as a function of potential. In such a way, the peak presented in Figure 2a was obtained applying a forward (*i.e.,* negative) scan to the solution of Eu^{3+} in 0.01 mol dm^{-3} $HClO_4$. The signal corresponds to a (nearly) reversible reduction process as follows from the height and shape of its components, *i.e.,* forward and backward currents obtained by sampling at red and blue circles, respectively (Figure 1, curve 1). Reverse (*i.e.,* positive) scan from the same solution (Figure 2b) also gives one (but oppositely oriented) signal with the same value of the peak potential (E_p) as before but somewhat lower peak current (i_p). The latter could reflect the difference in the diffusion coefficients of Eu^{3+} and Eu^{2+} though similar results sometimes appear for pure kinetic reasons.[3] Strictly speaking, in such a dilute electrolyte solution (0.01 mol dm^{-3} $HClO_4$) the signal should be additionally influenced by IR drop[13] but under applied conditions, *i.e.,* relatively low frequency ($f = 20$ s^{-1}) and not too high metal concentration, it is not pronounced.

If europium solution, in addition to 0.01 mol dm^{-3} $HClO_4$, also contains 0.1 mol dm^{-3} $NaClO_4$ and frequency is increased to 125 s^{-1}, the SW voltamogram obtained in a forward (*i.e.* negative) scan corresponds to an irreversible reduction process (Figure 3a). (Such an effect cannot be achieved from the dilute perchloric acid by the corresponding frequency increase without addition of the dissolved salt.) Reverse (*i.e.,* positive) scan, however, gives two peaks instead, as shown in Figure 3b, from which their origin also becomes obvious. Namely, forward and backward (»red« and »blue«) signals are separated by about 300 mV and therefore the resulting (*i.e.,* net) peaks are relatively well defined, though in the previously mentioned examples[3–5] the separation was even better and consequently overlapping was completely absent. Both peaks are oriented in the same direction because subtraction of negative currents from the positive ones (for the more negative signal) gives positive values whereas a more positive peak is obtained by subtraction of lower positive currents from the higher ones. By inspection of Figures 3a and 3b it can be concluded that in the first of them no reoxidation signal appears because at the corresponding potentials (with the SW amplitude applied) the reduced form virtually does not exist.

If the signals obtained by reverse scans are recorded in a frequency range 10–300 s^{-1}, the results presented in Figure 4a arise. For $f = 10$ s^{-1} only one peak is obtained at – 0.6 V but for higher values an additional peak, located nearly 300 mV more positively, gradually develops and finally becomes higher than the initially present signal whose height is virtually independent of frequency.

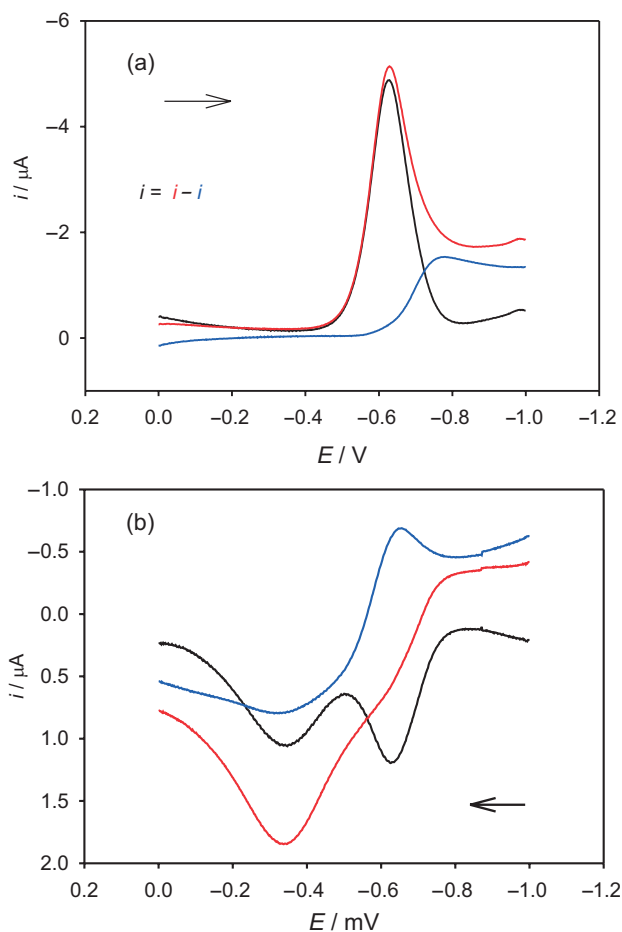If the measured currents are divided by the corresponding $f^{½}$ values, Figure 4a is transformed to Figure

Figure 3. Square wave voltamogram recorded in acidified 0.1 mol dm^{-3} $NaClO_4$ and its forward (red) and backward (blue) currents. Frequency: 125 s^{-1}; scan direction: negative (a), positive (b). Other conditions as in Figure 2.

4b. Such a presentation is analogous to the way in which theoretical results are usually given[2,3] (*i.e.,* in the form of dimensionless currents – proportional to $i/f^{½}$). It indicates that the normalized peak current of the more negative (*i.e.,* cathodic) signal decreases with increasing frequency whereas under the same conditions the height of the other (*i.e.,* anodic) signal becomes constant. At first glance, such a result seems to be opposite to the theoretical prediction (Figure 2 in Ref. 3) but it is not. The point is that mathematical modeling was performed assuming a constant ratio between delay time (t_1) and pulse duration (Δt) whereas the real experiments were performed at a constant value of t_1 and decreasing Δt. Under such conditions, the results presented in Figure 4b seem acceptable or, in other words, the change of the mentioned ratio is more important than the decrease of pulse duration at increasing square wave frequency, which is analogous to the decrease of the standard rate constant (k^o). With the negative scans, only one peak is obtained, which increases and shifts negatively by 42 mV in the frequency range 10–300 s^{-1}. Here, the results are not influenced by the ratio $t_1/\Delta t$.

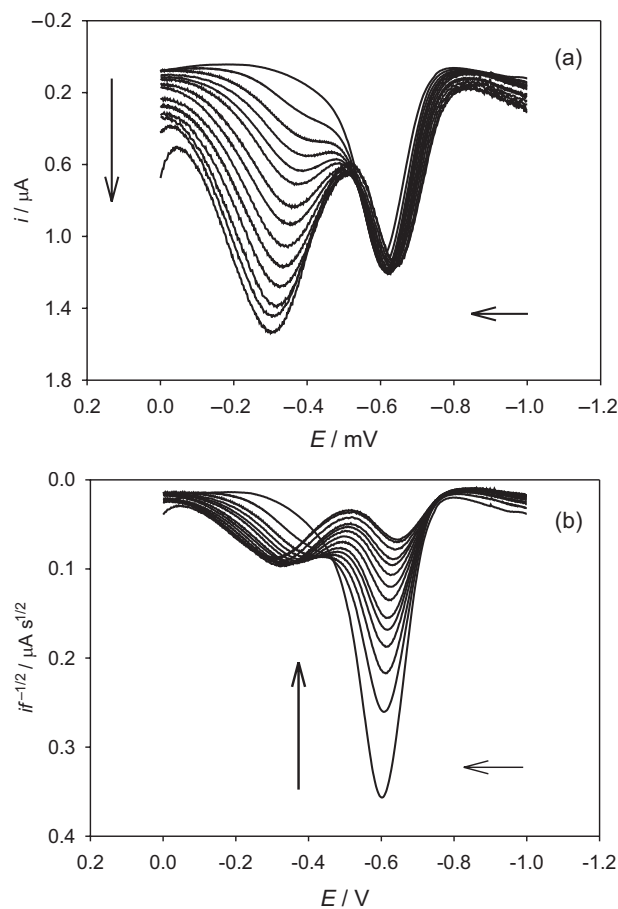Figure 4. Real square wave voltamograms of Eu^{3+} in acidified 0.1 mol dm^{-3} NaClO$_4$. Frequency range: 10–300 s^{-1} (a). The same curves obtained after dividing all the currents by the corresponding $f^{1/2}$ values (b). Other conditions as before. Scan direction is indicated by a horizontal arrow and frequency increase by a vertical one.
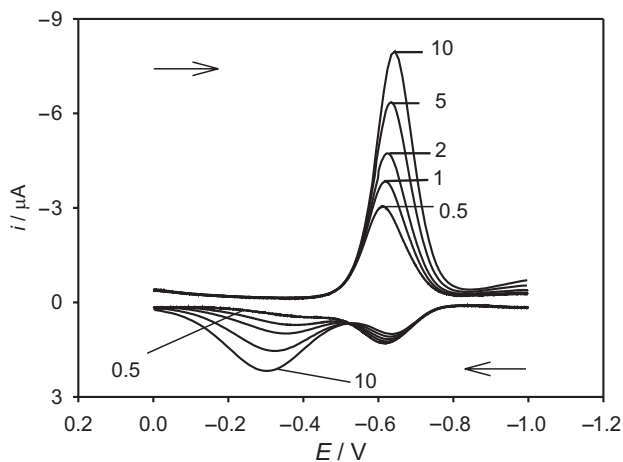

Figure 5. Influence of step potential on the electrode response in acidified 0.1 mol dm^{-3} NaClO$_4$. Applied value in mV indicated near each voltamogram; frequency: 20 s^{-1}; scan direction: indicated by an arrow. Other conditions as in Figure 2.

Another parameter that modifies the electrode response is step potential (E_s) – also known as scan increment. If under otherwise identical conditions its value is

gradually increased, the results presented in Figure 5 arise in 0.1 mol dm^{-3} NaClO$_4$. With the forward scan at the frequency of 20 s^{-1}, the peak becomes higher and shifted negatively by 16 mV when step potential increases from 0.5 to 10 mV. In the reverse scans, the second, more positive signal develops instead. In other words, similar effects appear in measurements performed at a constant frequency and increasing scan increment as in the opposite case, *i.e.,* increasing frequency and a constant scan increment. »Formal« scan rate (v) is equal to their product (*i.e.,* $v = f \cdot E_s$) but such a value does not have the same role here as, for example, in linear scan voltammetry.[1] In other words, the resulting signals, obtained at a constant scan rate with different pairs of f and E_s values, are similar but not identical. They were not obtained at a constant $t_1/\Delta t$ ratio and their similarity could perhaps be improved by taking into account this factor as well.

As already mentioned, the electrode response is highly affected by the concentration of sodium perchlorate in the aqueous phase.[9] The corresponding voltamograms, given in Figure 6, clearly indicate that under the influence of the increasing salt concentration in the range 0.1–1.0 mol dm^{-3}, suppression of the cathodic and enhancement of the anodic signal is obtained by the reverse scan. Under the same conditions, reduction peaks obtained by forward scans become lower and shifted negatively,[9] indicating that the electrode process becomes slower. (In highly concentrated solutions such as 8 mol dm^{-3} NaClO$_4$, only one peak is obtained in a reverse scan.)

Similar results, *i.e.,* the appearance of two, though poorly resolved, peaks, were also obtained by reverse scans in solutions of other salts such as LiNO$_3$ and CsCl, which compared to perchlorate media have somewhat different properties. Chloride and cesium ions exhibit (relatively weak) surface activity[14] whereas nitrate is a ligand[15] that gives the inner sphere complex EuNO$_3^{2+}$.

Electrode Kinetics

From Figure 6 it follows that the two peaks obtained in a reverse scan are best defined when 0.1 mol dm^{-3} sodium perchlorate is used as a basic electrolyte whereas in more concentrated salt solutions the height ratio changes significantly and overlapping becomes more pronounced. According to the literature data,[13] with respect to the possible effects of IR drop (at relatively high frequencies, which should be applied), this electrolyte concentration is just on the border. Anyway, an attempt was made to calculate the corresponding kinetic parameters using the method of Fatouros and Krulic,[3] *i.e.,* properties of SW signals, recorded by using both scan directions. In such a procedure it should be possible to calculate all the kinetic parameters (k^o, E^o and both transfer coefficients) from the potentials and widths of the signals (obtained under the same well defined conditions) and the value of the diffusion coefficient.
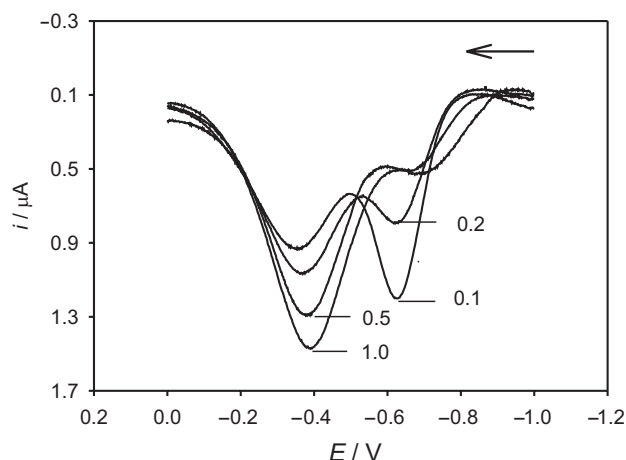
Figure 6. Square wave voltamograms of Eu^{3+} obtained by reverse scans. Concentration of $NaClO_4$ (in mol dm^{-3}) indicated near each curve. Frequency: 100 s^{-1}. Other conditions as in Figure 2.

According to the equation:

$$\alpha = 1.7RT \,/\, FW_{\frac{1}{2}}$$

cathodic transfer coefficient ($\alpha = 0.76$) was calculated from the width of the forward signal. In fact, $W_{\frac{1}{2}}$ denotes the distance between the first half peak potential and the peak potential – but not the full width of the signal at half of its height, because such a response is generally not symmetric. In the same way, the anodic transfer coefficient ($\beta = 0.34$) was calculated from the reverse anodic signal.

Literature data for this ionic strength are scarce but in the article by Elzanowska et. al[16] $\alpha = 0.82$ was given, which is in reasonable agreement with the above result. However, it indicates that the reaction of interest is asymmetric and, strictly speaking, cannot be studied in more depth by the equations given[3] because one of them, which takes into account the measuring conditions, is valid only in the range $\alpha = 0.3 – 0.7$. If all the problems are ignored, kinetic parameters calculated by the straightforward application of the calculation procedure[3] still give reasonable results (log k^o/cm s^{-1} = -3.0, $E^o = -590$ mV vs. SCE).

In more concentrated perchlorate solutions, the cathodic transfer coefficient becomes lower as follows from the dependence of the peak potential on SW frequency and the slope of dc polarograms, but the problem of overlapping signals increases. (The peaks are not fully resolved even in 0.1 mol dm^{-3} $NaClO_4$.) Taking into account that transfer coefficients are calculated from the $W_{\frac{1}{2}}$, it is extremely important to have well defined signals. Therefore, resolution of close peaks by deconvolution,[17] often applied in our laboratory, is not applicable here because the method »produces« better resolved signals by making them narrower. In some other procedures, based on nonlinear curve fitting, independence of peaks is assumed.[18] Hence their applicability in the present case seems questionable.
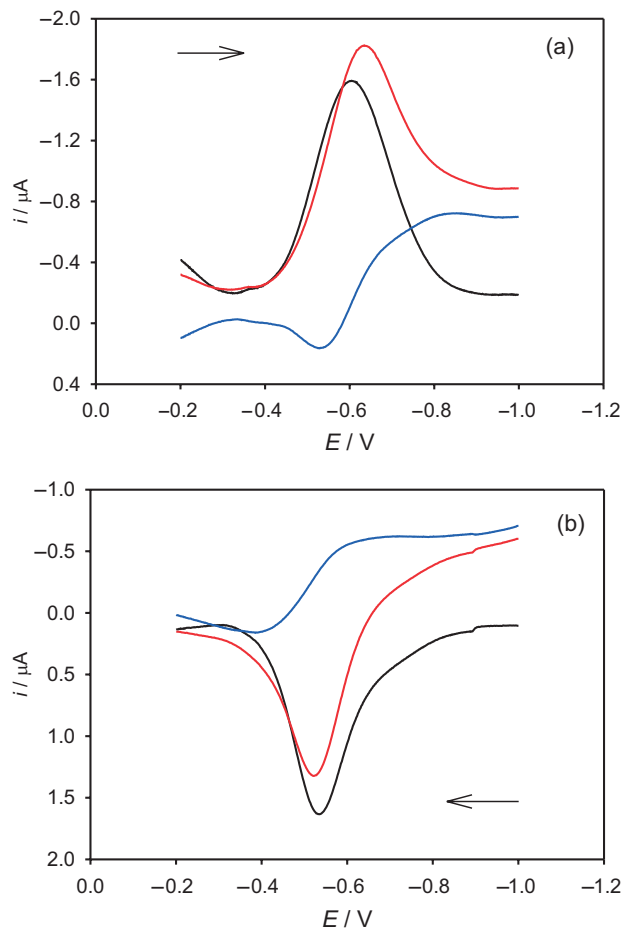

Figure 7. Square wave voltamograms of Eu^{3+} recorded in acidified solution of 0.5 mol dm^{-3} $NaClO_4$ + 0.5 mol dm^{-3} NaBr by negative (a) and positive scans (b) together with the corresponding forward (red) and backward (blue) currents. Frequency: 20 s^{-1}. Other conditions as in Figure 2.

It follows that appearance of two peaks on the square wave voltamogram recorded in a reverse scan does not guarantee that kinetic parameters of the studied reaction can be calculated without difficulties. Additional requirements obviously include as high as possible peak separation and not too different values of the two transfer coefficients. In the present case, the problem of peak separation in nitrate and chloride solutions is even more pronounced than in perchlorate media.

In addition to the salts that make the electrode process less reversible as their concentration increases, there are some anions that can change the trend, i.e., increase the rate[19] at the same ionic strength. Bromide and iodide belong to this group and their role is explained in terms of the bridge effect, i.e., exchange of electrons between the electrode and the reducible species in the solution via adsorbed anion. If adsorption of bromide is really crucial for the whole process, it should be possible to find the conditions under which the apparent reversibility depends on the scan direction. The point is that the surface concentration of adsorbed bromide is much

lower at (highly) negative potentials compared to the situation near 0.0 V. Such result was really obtained when a mixture of 0.5 mol dm^{-3} NaBr and 0.5 mol dm^{-3} NaClO$_4$ was used as the electrolyte. Although the effect is not highly pronounced, it can be clearly seen that backward current obtained by the negative scan (Figure 7a) does not reflect a totally irreversible process whereas with the changed scan direction it does (Figure 7b).

CONCLUDING REMARKS

Recording of a SW voltamogram from a reducible analyte solution by scanning in the positive direction is a good way to check the reversibility of the electrode process. Such an opportunity is not so important in measurements with modern instruments because forward and backward (*i.e.,* »red« and »blue«) currents can be used for the same purpose. With older polarographic analyzers, such as PAR 384B for example, only the net current can be obtained and reverse scan is definitely a tool for extraction of more information.

In addition, experimental results should depend on the scan direction if the electrode process is affected by the presence of a surface active anion. In the Eu^{3+}–Br$^-$ system, the forward scan starts at a potential characterized by a relatively high surface concentration of the adsorbed bromide and the electrode process is not totally irreversible, as follows from the shape of the backward current. In a reverse scan that starts at a highly negative potential and a very low surface concentration of Br$^-$, the electrode process is obviously slower. The mentioned approach could be also useful in studies of other potential dependent adsorptions.

From the practical point of view, especially because the whole effect does not appear in SWV only, it seems important to accept generally that formation of two voltammetric signals is possible even in extremely simple cases, *i.e.,* with only one electroactive species present, which exchanges only one electron in the electrode process without pronounced adsorption of the reactant or product.

According to the present state of the art, scanning in both directions cannot be applied when an amalgam forming metal appears as a reduction product (because an adequate theory is lacking) or in measurements at trace concentrations and remains limited to the systems in which both forms of the redox pair are soluble in electrolyte solutions.

The impression is that additional work on the theory and practice of the mentioned approach is needed in order to clarify the observed effects and make the whole story useful and applicable in practice.

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SAŽETAK

»Obrnuti« smjer promjene potencijala kao izvor informacija u pravokutnovalnoj voltametriji

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Pod utjecajem nedavno objavljenih radova, »obrnuto« skeniranje u pravokutnovalnoj voltametriji primijenjeno je u izučavanju redoks sustava Eu^{3+}/Eu^{2+} pri rastućoj koncentraciji nekoliko elektrolita i postepenoj promjeni frekvencije ili koraka potencijala. Svi ovi faktori snažno utječu na elektrodni odziv pa se i dva vrha mogu pojaviti iako u otopini postoji samo jedna elektroaktivna tvar, u proces je uključen samo jedan elektron, a adsorpcija reaktanta ili produkta nije izražena. Pokazuje se da je skeniranje u oba smjera potencijalno »oruđe« za izučavanje kinetike elektrodnih procesa iako je njegova praktična primjena u ispitivanome sustavu povezana s različitim problemima.