ISOPOTENTIAL POINTS IN SQUARE-WAVE VOLTAMMETRY OF REVERSIBLE ELECTRODE REACTIONS

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of 50th anniversary of his Nobel Prize for polarography.

Isopotential points in square-wave voltammetry are described for the first time. Model calculations and real measurements (performed with UO_2^{2+} and Eu^{3+} in perchlorate and bromide solutions, respectively) indicate that such an intersection could be observed when backward components of the net response, resulting from an increase in frequency or reactant concentration, are presented together. The electrode reaction should be fully reversible because quasireversible or slower electron transfer processes give the isopoints only at increasing reactant concentrations but not at increasing square-wave frequencies. The effect could be used as an additional diagnostic criterion for recognition of reversible electrode reactions where products remain dissolved in the electrolyte solution.

Keywords: Square-wave voltammetry; Reversible electrode reaction; Backward current; Isopotential point; Uranium(VI); Europium(III); Electrochemistry.

In order to study an unknown redox process or to find the optimum conditions for some electroanalytical measurements, a series of voltammograms is often recorded at different values of individual potential/timing parameters or at gradually increasing concentrations of an electroactive substance. As a result of such (and some other) experiments, the so-called isopoints (or isopotential points), i.e., intersections of all current-potential curves from the same series, sometimes appear[1–13]. The effect was mainly studied by cyclic voltammetry (CV) where isopotential points could be obtained in multisweep experiments, too[5]. Depending on the properties of the reacting species and/or composition of the electrolyte solution, not only one but two or three isopoints sometimes appear in the same presentation[1,2,6,12]. According to Fitch and Edens[6], unperturbed, perturbed and quasi-

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isopotential points could appear when two distinguishable electroactive species are present in the same solution, depending on the electron transfer rate and importance of the homogeneous cross reaction. Another type of isopoints (so-called isoalpha points[14]) appears in CV when, under otherwise identical conditions, transfer coefficient (α) is gradually increased. The effect can be demonstrated by model calculations, but in real systems its confirmation becomes a problem, because changes in α are usually coupled to changes in the electrochemical rate constant and the resulting peak shift.

Interpretation of isopotential points was not completely solved. Starting from visual similarity between the voltammograms with a common intersection and absorption spectra with an isobestic point, the way in which the spectroscopic results are usually treated was modified for application in voltammetry[1]. In the case of adsorption/deposition reactions some valuable results have been obtained in such a way. However, it could not be said that this approach was generally accepted[8]. On the other hand, it was found that the isopoint that appears when a series of cyclic voltammograms (recorded at different scan rates) is presented on the same plot, could be used for calculation of the corresponding transfer coefficient[9,10]. On planar electrodes the curves intersect at zero current[9,10], while on spherical electrodes the current of intersection depends on the electrode radius[12].

As far as we know, isopoints in square wave voltammetry (SWV) have never been described. In this communication, their existence in different sets of current–potential curves, which reflect a reversible electrode reaction (and their disappearance at a decreased electrode reaction rate) is demonstrated by model calculations and real measurements. In practice, this type of experimental results is readily identifiable and could serve to characterize electrode processes.

EXPERIMENTAL

Apparatus and Methods

All electrolyte solutions were prepared from reagent-grade chemicals and deionized water obtained in a Millipore Milli-Q system. For preparation of the uranyl(VI) stock solution, the classical procedure given in the Gmelins handbook[15] was applied. The starting salt for all solutions of Eu^{3+} was $Eu(NO_3)_3 \cdot 5H_2O$ (Fluka puriss., >98.5%).

Voltammetric measurements on a static mercury drop electrode were performed using μAutolab (Eco Chemie, The Netherlands) connected to a 663 VA stand (Metrohm) and a computer with the corresponding software (GPES, version 4.9). A glassy carbon rod served as a counter-electrode. All electrode potentials are given versus the Ag|AgCl (3 M KCl) reference electrode. For measurements in the perchlorate medium, the electrolyte bridge was filled with 3 M NaCl in order to prevent formation of sparingly soluble $KClO_4$ in the frit. Prior to

every new series of scans, the solution in the cell was deaerated by high purity (99.999%) nitrogen for 15 min. The room temperature was maintained at 24 ± 1 °C.

Model

A simple, fast and reversible electrode reaction is considered:

$$\mathrm{Ox}^{m+} + n\mathrm{e} \leftrightarrow \mathrm{Red}^{m-n}. \qquad (1)$$

It is assumed that both the oxidized and reduced forms of this redox couple are soluble in the electrolyte medium, and that only the oxidized form is initially present in the solution at concentration c_{ox}. Differential equations for the mass transfer towards the stationary planar and spherical electrodes under the conditions of SWV are solved using the numerical integration method described previously[16].

RESULTS AND DISCUSSION

Stationary Planar Electrode

Figure 1 shows theoretical square-wave voltammograms of a reversible electrode reaction (*1*) at a stationary planar electrode with clearly visible common intersection of all backward currents. The net current is a difference between the backward and forward components: $\Delta I = I_b - I_f$. The SWV components are similar to the forward and reverse branches of a cyclic voltammogram. Every net current is proportional to the bulk concentration of the reactant (c_{ox}) and to the square-root of square-wave frequency (f).

$$\Delta I = nFSD^{1/2} c_{ox} f^{1/2} \Delta\Phi \qquad (2)$$

In this equation, S is the electrode surface area, D is the diffusion coefficient, n is the number of electrons, F is the Faraday constant and $\Delta\Phi$ is the dimensionless current ($\Delta\Phi = \Phi_b - \Phi_f$) which depends on the signal parameters, i.e., square-wave amplitude (E_{SW}) and step potential (ΔE). The dimensionless backward component of the SWV response (Φ_b) is equal to zero at a certain potential E_0. At this potential, the real backward components of voltammograms recorded either at various reactant concentrations or at various frequencies are all equal to zero as well. The potential of intersection E_0 depends on the number of electrons in the electrode reaction (*1*). For the products $n\Delta E$ = –2 mV, nE_{SW} = 50 mV and nE_{st} = 0.3 V vs E^o (where E_{st} denotes the starting potential), the isopoint potential is $E_0 = -0.086/n$ V vs E^o. This result obtained by model calculation was (nearly) confirmed experimentally, taking UO_2^{2+}/UO_2^{+} in 3 M $NaClO_4$ as a model system[17] (Fig. 2). Backward currents intersect at the potential –90 ± 2 mV vs E_p, which is in

SWV equal to E^o. At increasing concentrations of dissolved uranium(VI), the isopoint is nearly perfect, i.e., it remains undisturbed (at –88 mV vs E_p) even on a highly expanded scale. When, however, the chosen solution is

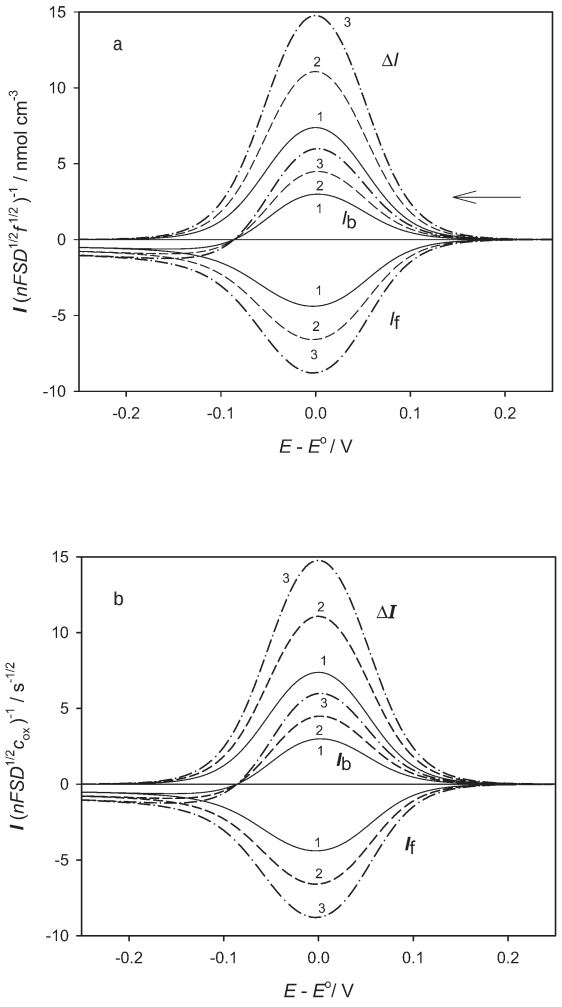

FIG. 1

Theoretical square-wave voltammograms of reversible electrode reaction (*1*) on stationary planar electrode. The net current (ΔI) and its forward (I_f) and backward (I_b) components. $D_{ox} = D_{red}$, $n = 1$, $E_{SW} = 50$ mV, $\Delta E = -2$ mV, $E_{st} = 0.3$ V vs E^o. a c_{ox} (mol ml^{-1}): 1×10^{-8} (*1*), 1.5×10^{-8} (*2*), 2×10^{-8} (*3*); b f (s^{-1}): 100 (*1*), 225 (*2*), 400 (*3*). Scan direction is indicated by the arrow

measured at different frequencies, basic current changes its value together with the signal of interest. Consequently, a real isopoint appears only after corrections of the recorded curves.

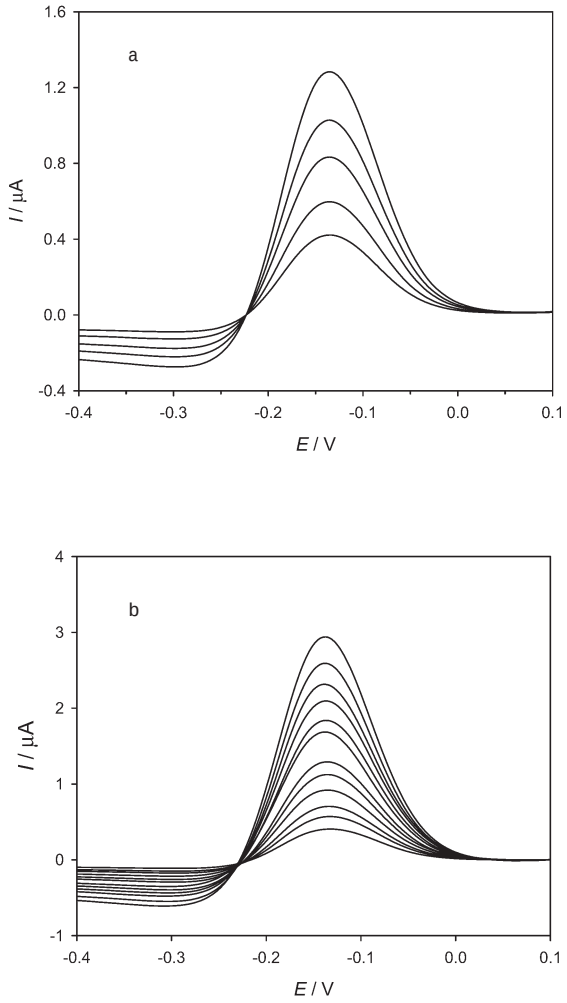

FIG. 2
Real backward components of the net SWV response obtained at increasing concentration of UO_2^{2+} (a) and SWV frequency (10–500 s^{-1}) (b). Electrolyte: 3 M $NaClO_4$, 2 mM $HClO_4$; metal concentration (mol l^{-1}): 9.9×10^{-5}–3.1×10^{-4} (a), 3.1×10^{-4} (b); amplitude 50 mV, step potential 2 mV, frequency (a) 100 s^{-1}

The relationships between E_0 and the E_{SW} parameter is shown in Fig. 3, where the full points indicate the calculated values whereas the empty points reflect experimental measurements. Real backward currents measured in uranium(VI)/uranium(V) system at the lowest amplitude applied (10 mV) are also given in the inset. In comparison with the results obtained at E_{SW} = 50 mV (Fig. 2b), the peak shape is changed whereas the isopoint is obviously shifted. The dashed line in Fig. 3 shows that for square-wave amplitudes higher than 50/n mV a linear relationship exists: $E_0 - E^o = -E_{SW} - 0.040/n$ V. The experimental values are only slightly more negative, but it should be taken into account that they were obtained with a spherical electrode.

Another parameter that changes the isopoint potential is the step potential. From model calculations it follows that there is a linear relationship $E_0 - E^o = 3.5\Delta E - 0.089/n$ V if $\Delta E > 3/n$ mV. The value of starting potential is not very important. For the reduction peaks that appear at relatively positive potentials, meaningful results could be obtained even if E_{st} is not much more positive than the peak potential, assuming that a horizontal part of the basic current appears before the signal starts to rise. All the above-mentioned relationships were calculated assuming $D_{ox} = D_{red}$. The influence of the difference between D_{ox} and D_{red} on E_0 is neglected at this point.

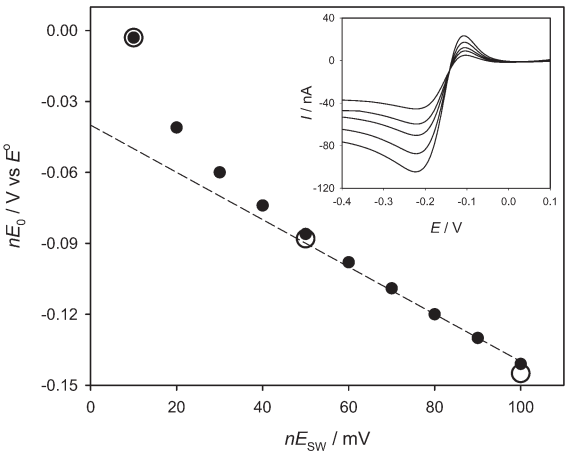

FIG. 3

Dependence of the isopoint potential on the square-wave amplitude. $n\Delta E$ = –2 mV, nE_{st} = 0.3 V vs E^o. ●, obtained by model calculation; ○, experimental values in 3.1 × 10^{-4} M solution of uranium(VI). Inset: real backward currents obtained at E_{SW} = 10 mV, ΔE = –2 mV; f (s^{-1}): 10, 20, 30, 50, 70

Generally, the SWV response of any electrode reaction depends on the dimensionless kinetic parameter $\kappa = k_s(Df)^{-1/2}$, where k_s is the standard reaction rate constant[16]. Figure 4 shows the calculated dependence of the potential E_0 on the logarithm of the kinetic parameter κ together with the experimentally obtained shift of E_0 on log $f^{-1/2}$ in 5 M bromide solution of Eu^{3+}, whose reduction to Eu^{2+} was taken as a model for the electrode reaction which is not fully reversible[18]. The two dependences are analogous, as follows from the definition of κ. The consequence of this relationship is that the potential at which the dimensionless backward component is equal to zero, depends on the applied frequency. So, if the frequency is constant and the reactant concentration is varied, the real backward components of all SWV responses intersect at the potential E_0, as shown in Fig. 1a. In bromide solution of Eu^{3+}, this relationship was confirmed without difficulties. However, variation of frequency may cause a change in the potential E_0 and real backward components corresponding to various frequencies do not necessarily intersect in the same point. A theoretical example is shown in Fig. 5. These responses were calculated for three frequencies with the parameter κ decreasing from 1 to 0.3 and 0.1. The potentials E_0 corresponding to κ = 1 and 0.3 are similar: –0.0955 and –0.095 V vs E^o, respectively. So, the current of intersection of backward components *1* and

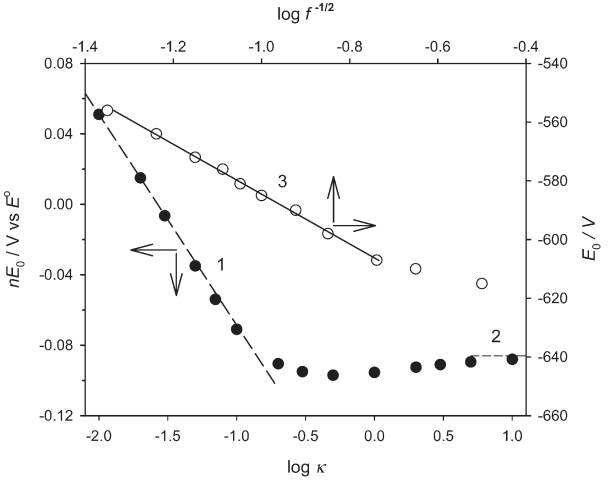

FIG. 4

Theoretical dependence of the E_0 potential on the logarithm of the kinetic parameter κ (●). $D_{ox} = D_{red}$, $n = 1$, $\alpha = 0.5$, $E_{SW} = 50$ mV, $\Delta E = -2$ mV, $E_{st} = 0.3$ V vs E^o. Experimental dependence of E_0 on log $f^{-1/2}$ (○) in 5.7×10^{-4} M Eu^{3+} solution. Electrolyte: 5 M NaBr, 2 mM $HClO_4$

2 in Fig. 5 is close to zero. If κ is diminished to 0.1, the potential E_0 is changed to –0.071 V vs E^o. Consequently, the backward component *3* in Fig. 5 intersects components *1* and *2* at two different potentials and the isopoint disappears. This phenomenon is an indication of a quasireversible electrode reaction. Additional criteria are marked by straight lines *1* and *2* in Fig. 4. The first line shows the property of irreversible electrode reaction

$$E_0 - E^o = -(0.0595/\alpha n) \log \kappa - (0.188/n) \text{ V} . \qquad (3)$$

This relationship applies if log κ < –1.5. Line *2* in Fig. 4 is the result of fast and reversible electrode reactions for the given signal parameters: $E_0 - E^o = -0.086/n$ V. Figure 4 shows that an electrode reaction appears reversible if κ > 1 at the highest frequency applied. This means that the appearance of an isopotential point as shown in Fig. 1b, indicates that the electrode reaction is reversible within the investigated frequency range.

Experimental backward currents obtained with Eu^{3+} in 5 M NaBr at increasing SW frequency are given in Fig. 6a. At first glance it seems that some (if not all) signals intersect but the current of intersection is much higher than zero. After correction of each curve for the value of its own capacitive current (measured at a horizontal part of the basic current, before the peak) it becomes clear that the signal shifts positively with increasing

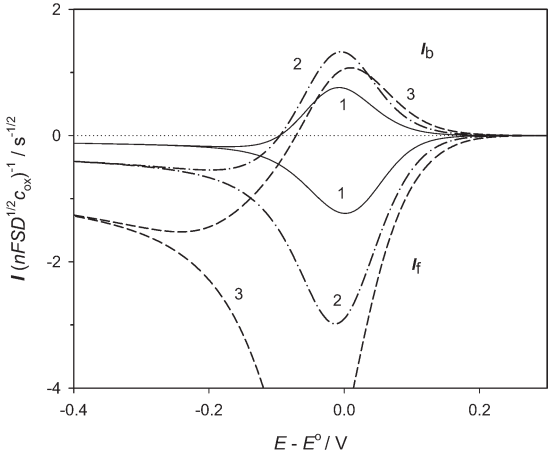

FIG. 5

The forward and backward components of theoretical square-wave voltammograms on stationary planar electrode. $D = 9 \times 10^{-6}$ cm^2 s^{-1}, $n = 1$, $\alpha = 0.5$, $k_s = 9 \times 10^{-3}$ cm s^{-1}, $E_{SW} = 50$ mV, $\Delta E = -2$ mV, $E_{st} = 0.3$ V vs E^o; f (s^{-1}): 9 (*1*), 100 (*2*), 900 (*3*)

frequency and the isopotential point does not exist any longer (Fig. 6b) in agreement with the theoretical prediction.

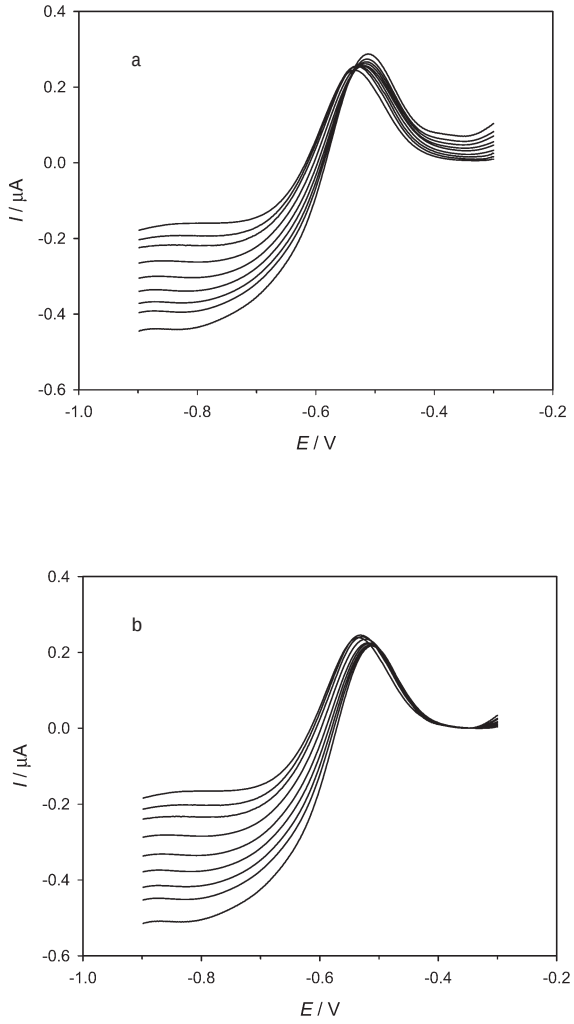

FIG. 6
Experimental backward currents from 5.7×10^{-4} M Eu^{3+} in 5 M NaBr–0.01 M $HClO_4$; signals uncorrected (a) and corrected (b) for the capacitive currents. Frequency range 10–200 s^{-1}, E_{SW} = 50 mV, ΔE = –2 mV

Stationary Spherical Electrode

On stationary spherical electrodes, square-wave voltammograms of reversible electrode reactions exhibit two isopotential points. The response depends on the dimensionless sphericity parameter $\rho = D^{1/2} r_0^{-1} f^{-1/2}$, where r_0 is electrode radius. Figure 7 (inset) shows dimensionless voltammograms recorded on macroelectrode (curve *1*) and microelectrode (curve 2). It can be noted that the dimensionless backward component Φ_b is equal to zero at a lower potential on the macroelectrode than on the microelectrode. The relationship of the potential E_0 and the logarithm of the parameter ρ is shown in Fig. 7. For the given signal parameters, the E_0 potential is equal to –0.0717 V vs E^o and independent of ρ if $\rho < 3 \times 10^{-3}$. (The difference in comparison with the previously mentioned value of –0.086 V is a consequence of a higher step potential.) So, if at the lowest frequency the parameter ρ is not higher than 2×10^{-3}, the isopotential points on spherical and planar electrodes are identical. Also, if the frequency is constant and only the reactant concentration is varied, all real backward components intersect at the isopotential point defined by zero current and the E_0 potential, which is the function of parameters ρ, E_{SW} and ΔE. Variation of frequency results in the appearance of the second isopotential point, which is shown

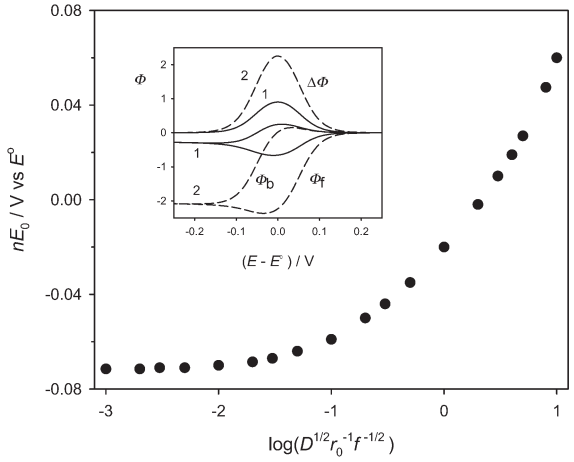

FIG. 7

Dependence of the E_0 potential on the logarithm of the sphericity parameter. Inset: dimensionless square-wave voltammograms of reversible electrode reaction (*1*) on a stationary spherical electrode. $D_{ox} = D_{red}$, $n = 1$, $E_{SW} = 50$ mV, $\Delta E = -5$ mV, $E_{st} = 0.3$ V vs E^o; ρ: 0.2 (*1*), 2 (*2*)

in Fig. 8. The potential of intersection is independent of the parameter ρ and equal to –0.0717 V vs E^o, which is the potential of the isopoint on the planar electrode for the given experimental parameters nE_{SW} and $n\Delta E$. The normalized current of the intersection is equal to $-0.7D^{1/2}r_0^{-1}$. The propor-

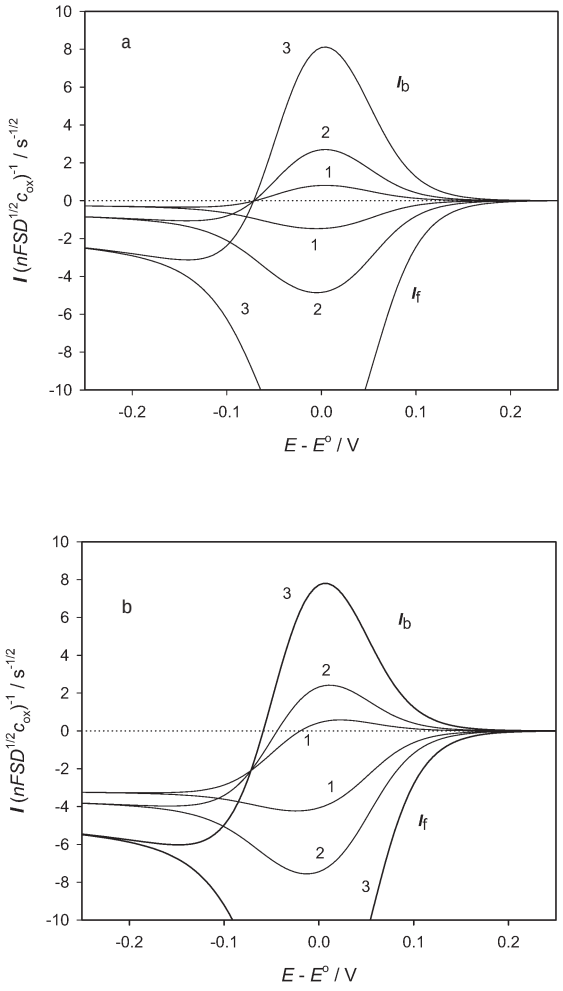

FIG. 8

The forward and backward components of theoretical square-wave voltammograms of reversible electrode reaction (*1*) on a spherical electrode. $D = 9 \times 10^{-6}$ cm^2 s^{-1}, $n = 1$, $E_{SW} = 50$ mV, $\Delta E = -5$ mV, $E_{st} = 0.3$ V vs E^o; r_0 (cm): 10^{-1} (a), 10^{-3} (b); f (s^{-1}): 9 (*1*), 100 (*2*), 900 (*3*)

tionality factor –0.7 depends on the signal parameters E_{SW} and ΔE. Considering the surface area of spherical electrode $S = 4r_0^2\pi$, the current of the second isopotential point is $I_{iso} = -8.8nFDr_0c_{ox}$. The condition for the second isopotential point is that the frequency variation does not change apparent reversibility of the electrode reaction.

CONCLUSION

The criteria of reversibility of an electrode reaction in SWV include the net peak potential, the half-peak width of the net response, the peak potentials of both components and the ratio of peak currents of the components. The reaction is reversible if all these characteristics do not depend on the frequency. The criteria are tabulated for the standard SW amplitude and the potential increment[16]. In this communication the isopotential point caused by the variation of frequency is proposed as an additional criterion. Its advantage is that it exists if the reaction is fast and reversible, and disappears if the reaction is quasireversible or slower.

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