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ABOUT THE POSSIBLE SHAPES OF THE EXPERIMENTAL VOLTAMMOGRAMS OBTAINED BY APPLYING THE VOLTAMMETRY WITH LINEAR SCANNING OF THE POTENTIAL TO REDOX UNIELECTRODES

N. BONCIOCAT

National Institute for Electrochemistry and Condensed Matter, Electrochemical Research Center, Spl. Independenței 202, 77208 Bucharest

ABSTRACT. In this paper, a theoretical analysis of the shapes that the experimental voltammograms obtained by applying the direct linear voltammetry to redox unielectrodes may have, has been carried out. The analysis is based on a recently deduced ordinary differential equation describing, by its solutions, the experimental voltammograms. From this analysis has resulted that in the case of quasireversible redox reactions, although at an unielectrode occurs only one redox reaction 0 + e ↔ R, the experimental voltammogram may present, excepting the normal peak (cathodic, or anodic), two additional peaks, one before, the second after, the normal one; such voltammograms may appear only if some restrictive conditions regarding the values of the symmetry factor β and of the ratio $r=(D_O/D_R)^{1/2}(c_O/c_R)$ are fulfilled. Thus, the appearance of a succeeding peak after the normal one doesn't mean that at interface occurs a second electrode reaction, or that the electrode redox reaction occurs in two steps, and in order to give a correct answer one must change the quasireversible kinetic behaviour of the electrode reaction in a reversible kinetic behaviour, by adequately changing the values of c_O, c_R (and thus of r), respective of the scanning rate v.

INTRODUCTION

In a series of recent papers [1-6] it has been shown that the faradaic current density $i_F(t)$ of an electrode redox reaction 0 + e ↔ R, occurring with combined overtension of charge transfer and nonstationary, linear, semiinfinite diffusion of the species 0, R is the solution of the following integral equation of Volterra type:

$$i_F(t) = \lambda \frac{i^0 N^*(t)}{\pi^{1/2}} \int_0^t \frac{i_F(u)}{(t-u)^{1/2}} du + f(t) \qquad (1)$$

where:

$$N^*(t) = \frac{\exp[-\beta f\eta(t)]}{F\sqrt{D_O}a_O} + \frac{\exp[(1-\beta)f\eta(t)]}{F\sqrt{D_R}a_R} \qquad (1')$$

$$f(t) = i^0\left(\exp[-\beta f\eta(t)] - \exp[(1-\beta)f\eta(t)]\right) \qquad (1'')$$

$$(\lambda = -1; \quad f = F/RT) \qquad (1''')$$

$\eta(t)$ represents the overtension at the moment of time t, and the other quantities have the usual meanings: β - symmetry factor, i^0 - exchange current density, D_O, D_R - diffusion coefficients, a_O, a_R - activities.

Further, eq. (1) has been applied to the voltammetry with linear scanning of the potential, when, considering the cathodic voltammetry, $N^*(t)$ and f(t) may be put in the forms:

$$N^*(t) = \bar{N}\left[1/r + \exp(-f|v|t)\right]\exp(\beta f|v|t) \qquad (2)$$

$$f(t) = i^0\left[1 - \exp(-f|v|t)\right]\exp(\beta f|v|t) \qquad (2')$$

where:

$$\bar{N} = 1/F\sqrt{D_R}a_R; \quad r = \sqrt{\frac{D_O}{D_R}} \cdot \frac{a_O}{a_R} \qquad (2'')$$

and |v| is the magnitude of the scanning rate. An important conclusion has come out, namely: although a rigorous description of the experimental voltammograms is given only by the solutions of the integral eq. (1), one may get a sufficient accurate description by solving the following ordinary differential equation of the first order [7]:

$$\frac{1}{S(i^0\bar{N})^2}\left\{\frac{dI(t)}{dt} - \left[\beta + \frac{\exp(-f|v|t)}{1-\exp(-f|v|t)}\right]f|v|I(t)\right\} = \left\{1 + 2\left[\beta - \frac{\exp(-f|v|t)}{1/r + \exp(-f|v|t)}\right]f|v|t\right\}$$
$$\left[\exp(2\beta f|v|t)\right]\left[1/r + \exp(-f|v|t)\right] \cdot \left\{\left[1/r + \exp(-f|v|t)\right]\frac{I(t)}{S} - \frac{1-\exp(-f|v|t)}{\pi^{1/2}\bar{N}t^{1/2}}\right\} \qquad (3)$$

where S is the electrode area and I the current intensity as measured in the external circuit (i.e., one supposes that the capacity current may be neglected). In a succeeding paper [8], it has been shown that the solutions of eq. (3) are, abstraction of some constant factors in perfect agreement with- the prediction given in the literature (but using totally different mathematical approach and, also, numerical methods). More, on the basis of eq. (3) it was possible to elaborate new direct-voltammetry methods for determining the diffusion coefficients D_O, D_R (or the concentrations c_O, c_R) [9, 10], the standard exchange current densities i^{00} [11] and the symmetry factors β [12] of the electrode redox reactions, as well as for studying the high temperature superconductor/redox electrolyte interface [13, 14].

The above mentioned applications of the differential eq. (3), successfully verified experimentally, prove that the solutions of eq. (3) give correctly the explicit dependencies of the current intensity on all other quantities and, consequently, eq. (3) may be used to discuss the possible shapes of the experimental voltammograms obtained by applying the direct voltammetry technique to the redox unielectrodes. In the following, we shall discuss the general case of quasireversible electrode redox reactions, when i^0 has a finite value.

IN WHAT CONDITIONS THE FIRST MEMBER OF THE DIFFRENTIAL EQUATION (3) CANCELS?

From eq. (3) one sees that its second member is the product of four factors, the second and the third being always different of zero. It follows that the first member of eq. (3) may cancel, either when:

$$1+2\left[\beta-\frac{\exp(-f|\eta|)}{1/r+\exp(-f|\eta|)}\right]f|\eta|=0 \tag{4}$$

or:

$$I(|\eta|)=\frac{1-\exp(-f|\eta|)}{|\eta|^{1/2}\left[1+r\exp(-f|\eta|)\right]}\cdot\frac{SF\sqrt{D_O|v|}a_O}{\pi^{1/2}} \tag{5}$$

where we have introduced the magnitude of the cathodic overtension $|\eta|=|v|t$.

Let's start with equation (4). It shows that the relation between r and $|\eta|$, for which eq. (4) holds true, depends on the value of the symmetry factor β, which plays the role of a parameter. Indeed, eq. (4) may be written:

$$r(|\eta|;\beta)=e^{f|\eta|}\,\frac{\beta+1/2f|\eta|}{1-\beta-1/2f|\eta|} \tag{4'}$$

and some values of the function $r(|\eta|;\beta)$ are given in table 1.

Table 1.

Examples of values r(|η|; β) for which, eq. (4) being satisfied, the first member of eq. (3) cancels

10^2|η| (V)	10^{-2}r(|η|; β)						
	β=0.0	β=0.2	β=0.4	β=0.5	β=0.6	β=0.8	β=1.0
1.00	<0	<0	<0	<0	<0	<0	<0
1.25	∞	"	"	"	"	"	"
1.60	.076	∞	"	"	"	"	"
2.00	.038	.109	"	"	"	"	"
2.10	.034	.093	∞	"	"	"	"
2.50	.027	.064	.245	∞	"	"	"
2.60	.026	.060	.206	1.390	"	"	"
2.70	.026	.060	.197	.810	"	"	"
2.80	.025	.057	.174	.525	"	"	"
2.90	.024	.054	.156	.424	"	"	"
3.00	.024	.054	.152	.357	"	"	"
3.10	.023	.052	.138	.328	∞	"	"
3.50	.023	.052	.128	.240	.975	"	"
4.00	.022	.052	.122	.214	.495	"	"
4.50	.024	.057	.128	.217	.442	"	"
5.00	.024	.063	.137	.222	.422	"	"
6.00	.029	.078	.172	.268	.470	"	"
6.30	.031	.083	.187	.187	.497	∞	"
7.00	.036	.101	.226	.236	.583	8.060	"
8.00	.047	.138	.312	.468	.775	5.860	"
10.00	.074	.257	.465	.912	1.480	7.270	"
12.00	.135	.522	1.215	1.850	2.820	10.090	"
14.00	.268	1.100	2.600	3.900	6.000	24.000	"
16.00	.521	2.340	5.550	8.340	12.700	44.200	"
18.00	.937	4.946	11.600	17.800	27.200	93.000	"
20.00	1.900	10.500	22.600	39.000	57.800	180.000	"
30.00	65.000	510.000	1170.000	1790.000	2900.000	8550.000	"

Suppose β=0.5. Then, the values given in table 1 show that for r(|η|; β=0.05)>21.40 there are two values of |η| satisfying eq. (4). For instance, if r=47, the first value is about $|\eta_1|$=0.0285 V and the second one about $|\eta_2|$=0.08 V. For r very great, $|\eta_1|$ tends to 0.025 V and $|\eta_2|$ to infinity, while for $r=r_m$=21.40 (the minimum permitted value) the values of the two overtensions become equal to $|\eta_1|=|\eta_2|=0.04$ V. The values in the other five columns must be interpreted in the same manner. One must not forget that eq. (3) refers to the cathodic voltammograms. For the anodic voltammograms it has been shown that suffice to change in eq. (3) β in $1-\beta$, r in 1/r, and to write |I(t)| and d|I(t)|/dt instead of I(t) and dI(t)/dt (because in our convention the anodic current is negative) [7]. Of course, the same changes must be made in condition (4) and table 1, for becoming valid for the anodic voltammograms, but, for sake of simplicity, we don't give these transcriptions. However, the principal conclusions that may be drawn from the table 1 (and its transcription) concern the inequalities that the value $r(\beta)$ must satisfy in order to exist (for the values β given in the table) pairs of overtensions ($|\eta_1|$, $|\eta_2|$) satisfying eq. (4) (and its transcription), and they are given in table 2.

Table 2.

Domains of $r(\beta)$ values for which eq. (4), respective its anodic transcription, have solutions (i.e., each equation a pair of values $|\eta|$ satisfying it).

β	Domains of $r(\beta)$ values	
	Cathodic voltammograms	Anodic voltammograms
0.0	r>2.22	-
0.2	r>5.15	r<1/586.00
0.4	r>12.20	r<1/42.20
0.5	r>22.17	r<1/22.17
0.6	r>42.20	r<1/12.20
0.8	r>586.00	r<1/5.15
1.0	-	r<1/2.22
By "-" one indicates that there is no such a domain		

As one sees, if, for a given β, the necessary condition holds true for the cathodic voltammograms, it doesn't hold for the anodic voltammograms, and inversely. As we shall see in the next paragraph, this conclusion is very important from the point of view of the possible shapes of the voltammograms.

Let's pass now to eq. (5) which gives an other situation when the *second* member of eq. (3) cancels and, consequently, the *first* member of eq. (3) cancels too. Let's observe that for reversible electrode reactions, when $i^0 \to \infty$, the first member of eq. (3) is equal to zero, *whatever the value* $|\eta|$ *would be*. But this means that also the second member of eq. (3) must be equal to zero, *whatever* $|\eta|$ *would be*, condition that is fulfilled only if eq. (5) holds true. In other words, eq. (5) describes the experimental voltammograms when the electrode redox reactions $0 + e \leftrightarrow R$ have a reversible kinetic behaviour [7]. It thus results that it is possible to exist also other overtensions for which the first member of eq. (3) cancels, namely that corresponding to certain intersection points of the *real experimental* voltammogram with the *theoretic* voltammogram described by eq. (5) (valid for reversible electrode reactions). Denoting by $|\eta_3|$ the magnitude of such an overtension, it must be less than $|\eta_P|$ (corresponding to the cathodic peak current on the real voltammogram, I_P), because the first member of eq. (3) may cancel only if both I and dI/dt are positive; generally, such an overtension, either doesn't exist, or there is only one.

Concerning the values $|\eta_1|$, $|\eta_2|$, as we have seen, they may be equal (if $r=r_m$), when, generally, $|\eta_1|=|\eta_2|<|\eta_P|$, but for sufficient great values of the ratio r/r_m, $|\eta_1|$ is less than $|\eta_P|$, while $|\eta_2|>|\eta_P|$ (because $|\eta_1|$ gets smaller, and $|\eta_2|$ tends to infinity, when $r/r_m \rightarrow \infty$).

POSSIBLE SHAPES OF THE EXPERIMENTAL VOLTAMMOGRAMS IN THE CASE OF QUASIREVERSIBLE ELECTRODE REDOX REACTIONS

Let's analyse the sign of the first member of eq. (3). It is easy to observe that for very small values of t, the great bracket in the first member of eq. (3) tends to the function dI(t)/dt-I(t)/t, whose sign depends on the shape of the curve I vs t very close to t=0. In our recent papers [11, 12] the experimental cathodic voltammograms, obtained by applying the voltammetry with linear scanning of the potential to the redox unielectrodes $Pt/[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, KCl(1M), using for r the values 10, 20 and 100, had a convex shape (i.e., a negative second derivative) immediately after t=0, followed (after a change of concavity) by a linear increase of I with t and, afterwards, by a nonlinear increase of I towards the peak value I_P. This is the type of voltammograms which we are interested in, because, as we shall see, they may have an unusual shape.

In the first interval, where I(t) is convex, the derivative dI(t)/dt is smaller than I(t)/t and, therefore, the difference dI(t)/dt-I(t)/t being negative, so is also the first member of eq. (3). In the interval, where I increases linearly with t, it has been shown [11] that the great bracket of the first member of eq. (3) gets the expression:

$$\left[\frac{1}{1-\exp(-fvt_0)}-\beta\right]f|v|I_0$$

where $I_0=I(t_0)$, t_0 being a time within this interval. It is obvious that this expression is positive, and thus the first member of eq. (3) passes from a negative sign to a positive one, existing an intermediate time τ_1, in-between the two intervals, when the first member of eq. (3) cancels. Of course, because both dI/dt and I must be positive, the point $P_1(\tau_1, I(\tau_1))$ must be before the point where begins the linear increase of I with t, but where I already increases with t. It follows that before the point $P_1(\tau_1, I(\tau_1))$, the curve I(t) presents, if not a veritable "hump" (i.e., local maximum, followed by a local minimum), at least a "shoulder". Of course, the overtension corresponding to the time τ_1 is that denoted in the preceding paragraph by η_1, and its magnitude $|\eta_1|=|v|\tau_1$ satisfies eq. (4). But, in the same paragraph it has been shown that, if eq. (4) (which refers to cathodic voltammograms) has solutions for a given voltammogram (i.e., given r and β), then it has two solutions, η_1 and η_2, satisfying the inequalities $|\eta_1|<|\eta_P|<|\eta_2|$.

On such a voltammogram there is a second point $P_2(\tau_2,I(\tau_2))$; $|\eta_2|=|v|\tau_2$ situated on an other increasing part of the voltammogram (because of the necessary conditions dI/dt>0, I>0). Consequently, it results that the curve I vs t decreases after the cathodic peak up to a moment $\tau<\tau_2$, and afterwards it starts to increase again. Of course, the voltammetry being made without stirring the solution, the thickness of the diffusion layer increases in time and, the electrode reaction getting more and more a reversible kinetic behaviour, the curve I vs t approaches more and more the curve described by eq. (5). Therefore, there is a time $t>\tau_2$ when the curve I vs. t passes through an other local maximum and afterwards it decreases monotonously towards I=0 (for $t \to \infty$).

Of course, similar conclusions apply to anodic voltammograms, for which the role of eq. (4) is played by the equation:

$$1+2\left[1-\beta-\frac{\exp\left(-f|\eta|\right)}{r+\exp\left(-f|\eta|\right)}\right]f|\eta|=0 \qquad (6)$$

representing the transcription of eq. (4) by making the changes $\beta \to 1-\beta$; $r \to 1/r$. Therefore, if eq. (6) has solutions for a given anodic voltammogram, then, in fact it has two solutions satisfying the inequalities $\eta_1<\eta_P<\eta_2$, and on the curve I vs. t appears a "hump", or at least a "shoulder", followed by the anodic peak and afterwards, by a local maximum which precedes the monotonously decrease of I towards I=0 (for $t \to \infty$). The important difference consists in the fact that, now, the values r(β) must be smaller than certain upper limits (given in table 2) and, consequently there are three possibilities: both voltammograms have usual shapes (i.e., only with a cathodic, (respective anodic), peak), the cathodic voltammogram has an unusual shape (when the anodic one is normal), respective inversely, the shape of the cathodic voltammogram is normal (when the anodic one has an unusual shape).

The two unusual possibilities concerning the shapes of the experimental voltammograms in the case of quasireversible electrode redox reactions are shown in fig. 1, considering that in the vicinity of the first solution (i.e., overtension) of eq. (4) (respective of its anodic transcription) appears a “shoulder”, while in that of the second solution appears a local minimum followed by a local maximum.

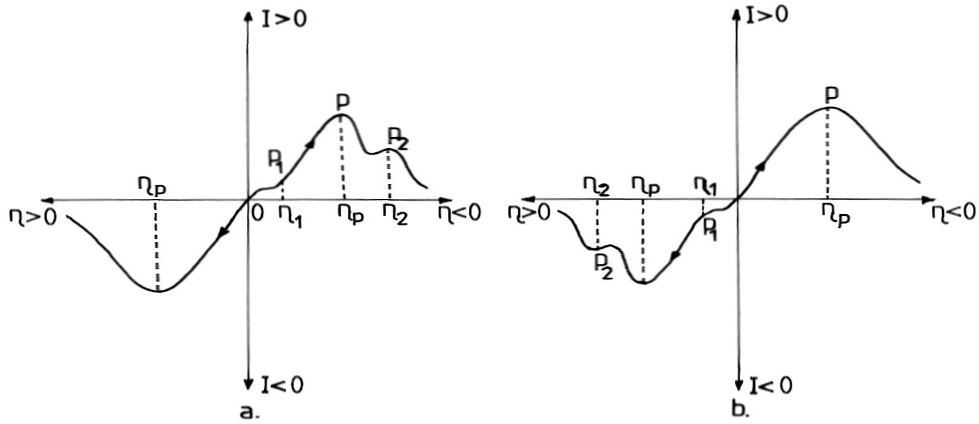

Figure 1. Unusual shapes that the experimental voltammograms may have, although at the interface takes place only one electrode redox reaction (which, of course, must have a quasireversible kinetic behaviour); a. if the shape of the cathodic voltammogram is unusual, then, that of the anodic one is normal; b. if the shape of the anodic voltammogram is unusual, then, that of the cathodic one is normal. The arrows indicate that the voltammograms must be obtained separately.

CONCLUDING REMARKS

The theoretical developments made in this paper demonstrate that in the case of quasireversible electrode redox reactions the voltammetry with linear scanning of the potential, either in a cathodic, or in an anodic, sense, may led to experimental voltammograms which present, excepting the usual cathodic (or anodic) peak (i.e., that corresponding to an overtension of magnitude $|\eta_P|$), a preceding peak, or at least a “shoulder”, for $|\eta_1|<|\eta_P|$, and a succeeding peak for $|\eta_2|>|\eta_P|$, although at the interface occurs only one redox reaction, which, in addition, takes place in a single step (e.g., 0 + e $\leftrightarrow$ R). Of course, such unusual shapes of the experimental voltammograms may appear only if some restrictive conditions regarding the values of the symmetry factor β and of the ratio $r=(D_O/D_R)^{1/2}(a_O/a_R)$ are fulfilled (given in table 2).

Therefore, an important conclusion comes out from the theoretical analysis made in this paper: if on an experimental voltammogram obtained by direct voltammetry appears a succeeding peak after the normal one, it doesn't mean that at interface occurs a second electrode reaction, or that the electrode redox reaction occurs in two steps; it is possible that the shape of the voltammogram to be the consequence of the quasireversible kinetic behaviour of the redox reaction and of the values of β and r. To give an answer, a possibility would be the changing of the values $|v|$, c_O, c_R (making them smaller) and of the value r (to be sure that the conditions given in table 2 don't hold). In this way, the kinetic behaviour of the electrode reaction approaches that of a reversible electrode reaction, and on the experimental voltammogram must appear only the normal cathodic (or anodic) peak.

Finally, such unusual voltammograms, obtained by direct voltammetry, may have electroanalytical applications, for instance in estimating the value of r from the values $|\eta_1|$, or $|\eta_2|$, where appear the additional peaks.

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