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A THEORETICAL STUDY OF FARADAIC RECTIFICATION POLAROGRAPHY

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INTRODUCTION

In kinetic studies of fast electrode reactions the faradaic rectification method appears to be full of promise[1-5]. The faradaic rectification effect was discovered and studied in a low-frequency range by Doss and Agarwal[6] and was applied to the determination of kinetic parameters at equilibrium potentials by Delahay and co-workers[3], who recognized the profits of the use of very high frequencies. The merits of the method, when the sinusoidal voltage was superimposed on a varying d.c. polarizing potential, were investigated by Barker[1,7]. In both treatments, however, the analysis procedures proposed were based on some simplifying assumptions which do not hold generally.

Recently, De Leeuwe *et al.*[4,8] have introduced, in an "amended treatment", analysis procedures without simplifications, especially for measurements at the equilibrium potential. The importance of incorporating the faradaic impedance in the basic equations was emphasized. In this treatment the theory was based on the absolute rate equation in its most simple form, *i.e.* expressing the relation between current and potential with the aid of the rate constant k_{sh} and the transfer coefficient α as the so-called kinetic parameters. However, both on theoretical and experimental grounds, evidence has been provided that for many systems a more complicated current–voltage relation holds, or at least should be supposed[9,10]. It is possible to account for such complications by admitting the possibility of k_{sh} and α being potential dependent, as has been done recently for the d.c. polarogram[11,12] (potential dependent α) and the a.c. impedance method[13] (potential dependent k_{sh}). It can be expected that also for the faradaic rectification method the implications of the potential dependency of k_{sh} and/or α have to be examined.

For example, in the simple case of a charge-transfer controlled electrode reaction with $\alpha = 0.5$ the classical i–E relationship near the equilibrium potential E_{eq} is linear in two orders, so that an alternating current does not produce a d.c. voltage shift. If, however, the rate constant is potential dependent, the faradaic rectification voltage is found to be

$$\Delta E_F = -\tfrac{1}{4}\frac{1}{k_{sh}}\left(\frac{dk_{sh}}{dE}\right) V_A \qquad (1)$$

where V_A is the amplitude of the a.c. voltage across the electrode–solution interface. This result is easily obtained by combining $i \sim k_{sh}(E - E_{eq})$ with the general expression

for the rectification voltage shift derived by Delahay *et al*[2]., for this case simplified to

$$\Delta E_F = -\tfrac{1}{4}\left(\frac{d^2i/dE^2}{di/dE}\right) V_A^2 \tag{2}$$

In this paper we intend to study the applicability of the faradaic rectification method, carried out with d.c. polarization. This may be fruitful for two reasons. First, it is advantageous to generate the less stable component of a redox couple *in situ*. Secondly, a wider potential range than with equilibrium measurements can be covered; this is especially important if one wishes to make a detailed study of a system with a view to the possible potential dependency of k_{sh} and/or α.

A general expression for the faradaic rectification voltage, not liable to approximations with respect to reversibility, will be derived, taking into account potential dependency of the kinetic parameters. For this purpose we will make use of the parameter g, defined by Sluyters and coworkers[13], in our notation

$$g_k \equiv d \ln k_{sh}/d\varphi \tag{3}$$

with

$$\varphi = (nF/RT)(E-E^0) \tag{4}$$

Thus, the rate constant at a small excursion from the mean potential can be written as

$$k_{sh,\bar{\varphi}+\Delta\varphi} = k_{sh,\varphi}(1+g_k\Delta\varphi) \tag{5}$$

which can be applied also in the theory for a second-order effect, if $dg_k/d\varphi \ll 1$ and $g_k^2 \ll 1$.

For the case of a potential dependent α a similar parameter g_α can be used if it is defined by

$$g_\alpha \equiv \bar{\varphi}\, d\alpha/d\varphi \tag{6}$$

Therefore, if $d\alpha/d\varphi$ and $d^2\alpha/d\varphi^2 \ll 1$,

$$\exp[\alpha_{\bar{\varphi}+\Delta\varphi}(\bar{\varphi}+\Delta\varphi)] = (1+g_\alpha\Delta\varphi)\exp[\alpha_{\bar{\varphi}}(\bar{\varphi}+\Delta\varphi)] \tag{7}$$

If both k_{sh} and α are supposed to be potential dependent, we define the parameter g as

$$g \equiv d \ln k_{sh}/d\varphi + \bar{\varphi}\, d\alpha/d\varphi = g_k + g_\alpha \tag{8}$$

The general expressions derived will be used to calculate rectification polarograms under different circumstances. They will be compared with rectification polarograms based on approximations for d.c. reversible and d.c. irreversible systems.

THEORY

When current and potential are related by:

$$i = nFk_{sh}\{c_R \exp(\alpha\varphi) - c_O \exp(-\beta\varphi)\} \tag{9}$$

the relationship for an a.c. current $i_m \sin \omega t$ superimposed on a d.c. current $\bar{i}$ is, following eqns. (3)–(8), given by

$$\bar{i} + i_m \sin \omega t = nFk_{sh,\bar{\varphi}}(1+g\Delta\varphi) \times \{(\bar{c}_R+\Delta c_R)\exp[\alpha_{\bar{\varphi}}(\bar{\varphi}+\Delta\varphi)] - (\bar{c}_O+\Delta c_O)\exp[-\beta_{\bar{\varphi}}(\bar{\varphi}+\Delta\varphi)]\} \tag{10}$$

in which $\bar{c}_R$ and $\bar{c}_O$ are the mean surface concentrations, in the absence of double layer effects, and Δc_R and Δc_O are the sinusoïdal deviations from the mean concentrations; $\bar{\varphi}$ is the mean value of φ and $\Delta\varphi$ is the deviation from $\bar{\varphi}$ due to the alternating current.

After three-term expansion of $\exp(\alpha\Delta\varphi)$ and $\exp(-\beta\Delta\varphi)$ and subtraction of the d.c. components, *cf.* eqn. (9), the resulting equation for the alternating current is rearranged to:

$$\Delta\varphi = \left\{\frac{i_m \sin\omega t}{nFk_{sh}} - \Delta c_R \exp(\alpha\varphi) + \Delta c_O \exp(-\beta\varphi)\right\}\frac{1}{N}$$
$$-\{(\alpha+g)\Delta c_R \exp(\alpha\varphi) + (\beta-g)\Delta c_O \exp(-\beta\varphi)\}\frac{\Delta\varphi}{N}$$
$$-\tfrac{1}{2}\{\alpha(\alpha+2g)\bar{c}_R \exp(\alpha\varphi) - \beta(\beta-2g)\bar{c}_O \exp(-\beta\varphi)\}\frac{(\Delta\varphi)^2}{N} \quad (11)$$

with

$$N = (\alpha+g)\bar{c}_R \exp(\alpha\varphi) + (\beta-g)\bar{c}_O \exp(-\beta\varphi) \quad (12)$$

$\Delta\varphi$ can be written explicitly by introduction of the first-order term (the fundamental) into the second-order terms. With the Warburg relations[14],

$$\Delta c_i = \pm(i_m/nF)(2D_i\omega)^{-\frac{1}{2}}(\sin\omega t - \cos\omega t)$$

where the plus and minus signs refer to Ox and Red respectively, it is now possible to calculate the faradaic rectification voltage-shift as

$$\Delta E_F = (nF/RT)(2\pi)^{-1}\int_0^{2\pi}\Delta\varphi\, d(\omega t) \quad (13)$$

The result is conveniently written in terms of the charge transfer resistance[13]

$$\theta = RT/n^2F^2k_{sh}N \quad (14)$$

and the irreversibility quotient

$$p = (\sqrt{2\omega}/k_{sh})[D_R^{-\frac{1}{2}}\exp(\alpha\varphi) + D_O^{-\frac{1}{2}}\exp(-\beta\varphi)]^{-1} \quad (15)$$

namely

$$\Delta E_F = -\frac{i_m^2\theta}{2N}\left\{\frac{1}{nF\sqrt{2\omega}}\left(\frac{p+2}{2}\right)\left[\frac{-(\alpha+g)\exp(\alpha\varphi)}{D_R^{\frac{1}{2}}} + \frac{(\beta-g)\exp(-\beta\varphi)}{D_O^{\frac{1}{2}}}\right]\right.$$
$$+\frac{\theta}{2}\cdot\frac{nF}{RT}\left(\frac{p^2+2p+2}{p^2}\right)[\alpha(\alpha+2g)\bar{c}_R\exp(\alpha\varphi) - \beta(\beta-2g)\bar{c}_O\exp(-\beta\varphi)] \quad (16)$$

Equation (16) contains the surface concentrations $\bar{c}_O$ and $\bar{c}_R$, given by[14]

$$\bar{c}_O = c_O^* \cdot \frac{a_O + (a_O/a_R + c_R^*/c_O^*)\exp(\alpha\varphi)}{a_O + (a_O/a_R)\exp(\alpha\varphi) + \exp(-\beta\varphi)} \quad (17a)$$

$$\bar{c}_R = c_R^* \frac{a_O + [(a_O/a_R)(c_O^*/c_R^*) + 1]\exp(-\beta\varphi)}{a_O + (a_O/a_R)\exp(\alpha\varphi) + \exp(-\beta\varphi)} \quad (17b)$$

where c_O^* and c_R^* are the bulk concentrations and

$$a_i = D_i/\delta_i k_{sh} \tag{18}$$

in which δ_i is the thickness of the diffusion layer. Finally the unknown amplitude i_m of the faradaic current should be related to the known amplitude i_A of the total current passing the cell, by

$$i_m^2 = a^2 i_A^2/[(p+1)^2+(a+1)^2] \tag{19}$$

where[15]

$$a = p/\theta\omega C_d \tag{20}$$

and C_d is the double layer capacity.

In practice the measured rectification signal ΔE_m equals ΔE_F only at a certain time after the start of the a.c. electrolysis, sufficiently long to charge the double layer capacity correspondingly to the new d.c. potential. This charging process is slower when the faradaic impedance is large, *i.e.* at potentials more remote from the half-wave potential. Therefore it is better to consider the rectification signal measured a definite time t after the start of the a.c. electrolysis, instead of ΔE_F, the two being related by[2]

$$\Delta E_m = \Delta E_F \left\{1 - \frac{1}{\theta C_d(H-G)} \left[\frac{1}{G}\exp(G^2t)\,\mathrm{erfc}(Gt^{\frac{1}{2}}) - \frac{1}{H}\exp(H^2t)\,\mathrm{erfc}(Ht^{\frac{1}{2}})\right]\right\} \tag{21}$$

with

$$G, H = \tfrac{1}{2}\left\{\frac{\sqrt{2\omega}}{p} \pm \left[\frac{2\omega}{p^2} - \frac{4}{\theta C_d}\right]^{\frac{1}{2}}\right\} \tag{22}$$

With eqns. (14)–(22) theoretical faradaic rectification polarograms can be calculated for various circumstances, which are mainly dictated by the parameters k_{sh}, α and g and the angular frequency ω of the applied sinusoïdal signal.

For δ_i, the obvious choice is the value $\delta_i = (3\pi T D_i/7)^{\frac{1}{2}}$, which holds to a good approximation for the dropping mercury electrode where T is the time elapsed since the preceding drop was dislodged. If necessary, a correction for spherical diffusion may be applied. We have carried out a variety of calculations in this way. Some of these calculated faradaic rectification polarograms are shown in Figs. 1 and 2.

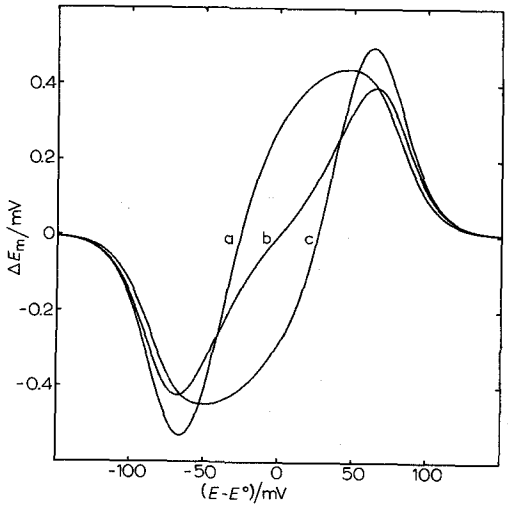
DISCUSSION

First, we will consider some particular cases in which the general expression may be simplified.

(*i*) *Zero d.c. current*

At the equilibrium potential the surface concentrations are equal to the bulk concentrations and the potential is related to them by Nernst's law, $\exp(\varphi) = c_O/c_R$. Substituting this in eqn. (16) one finds

$$\Delta E_F = -\tfrac{1}{4}\frac{nF}{RT}\left\{(\alpha+g)-(\beta-g) + \frac{2(p+2)}{p^2+2p+2}\left[(\beta-g) - \frac{c_O D_O^{\frac{1}{2}}}{c_O D_O^{\frac{1}{2}} + c_R D_R^{\frac{1}{2}}}\right]\right\} V_A^2 \tag{23}$$



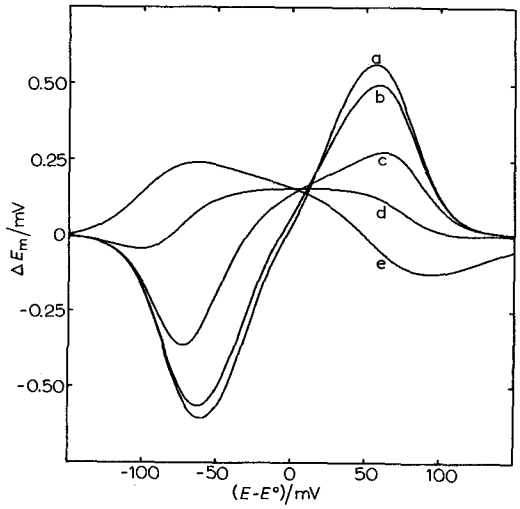


Fig. 1. Theoretical rectification polarograms for varying α at temp. 25°C. $n=2$; $D_O^{\frac{1}{2}}=D_R^{\frac{1}{2}}=3\times10^{-3}$; $c_{Ox}^*=c_{Red}^*$ (in mercury) $=3$ mmol l^{-1}; modulation time: 2 ms; $i_A=1$ A cm^{-2}; droptime 3.2 s; drop radius $=0.5$ mm; $c_d=25$ μF cm^{-2}; frequency $=1$ MHz; $g=0$; $k_{sh}=1$ cm s^{-1}, α: (a) 0.25, (b) 0.50, (c) 0.75.

Fig. 2. Theoretical rectification polarograms for varying k_{sh}. Data as in Fig. 1. $\alpha=0.4$. k_{sh}: (a) 5, (b) 2.5, (c) 0.5, (d) 0.05, (e) 0.005 cm s^{-1}.

This result is similar to the equations derived by Doss and Agarwal[6], Barker[1] and Delahay *et al.*[2], containing only apparent transfer coefficients $(\alpha+g)$ and $(\beta-g)$. For this case an analysis method is given by De Leeuwe[8].

(ii) D.c. reversible reaction

In the case of a reversible reaction the surface concentrations obey Nernst's law, which with eqn. (16) becomes

$$\Delta E_F=\tfrac{1}{8}\frac{nF}{RT}\left\{(p+2)\frac{\exp(\varphi)-(D_O/D_R)^{\frac{1}{2}}}{\exp(\varphi)+(D_O/D_R)^{\frac{1}{2}}}-[(\alpha+g)-(\beta-g)](p^2+p)\right\}V_A^2 \quad (24)$$

This equation, with $g=0$ and $D_R=D_O$, was used by De Leeuwe in his thesis to compute theoretical rectification polarograms[15].

It is of interest to consider the usefulness of a d.c. polarizing circuit. From eqn. (24) it follows that for small values of $p(p\ll 1)$ and potentials more remote from E^0 $([\exp(\varphi)-1]/[\exp(\varphi)+1]\gg p)$ the faradaic rectification voltage becomes independent of α and k_{sh}. This can also be concluded from Figs. 1 and 2. Thus there will be a limited potential region around E^0 where α and k_{sh} can be determined with sufficient accuracy. Since p increases with frequency, this range is larger for higher frequencies.

With eqns. (14)–(22) the extent of such regions is calculated for different frequencies (Table 1). The accuracy of the method was considered satisfactory when a change of 0.05 in α or 35% in k_{sh} caused a deviation in the rectification signal of at least 5%, which is about the accuracy in the measurements. In practice the upper limit of the applicable frequencies is determined by the power of the sinewave generator, because at higher frequencies a larger total current is required in order to obtain a certain current through the faradaic process. With a supposed maximum total

TABLE 1

THEORETICAL POTENTIAL RANGES (mV), IN WHICH α AND k_{sh} ARE OBTAINED FROM FARADAIC RECTIFICATION SIGNALS WITH A CHOSEN ACCURACY (± 0.05 FOR α AND $\pm 35\%$ FOR k_{sh})

α	k_{sh}/cm s^{-1}	*Concerning k_{sh} determination*					*Concerning α determination*				
		100 *KHz*	1 *MHz*	5 *MHz*	10 *MHz*	100 *MHz*	100 *KHz*	1 *MHz*	5 *MHz*	10 *MHz*	100 *MHz*
0.5	10	< 10	< 10	80	100	150	10	25	50	50	80
	5	< 10	10	100	150	200	20	50	60	70	200
	2	20	110	150	200	200	50	60	90	120	200
	0.5	80	200	200	200	> 200	75	200	200	> 200	> 200
0.75	10	25	40	60	60	70	10	40	50	70	150
	5	30	60	100	125	125	40	60	75	80	> 200
	2	50	130	130	130	130	60	80	125	125	> 200
	0.5	100	130	130	140	140	100	150	200	> 200	> 200

TABLE 2

α	k_{sh}/cm s^{-1}	*Concerning k_{sh} determination*					*Concerning α determination*				
		100 *KHz*	1 *MHz*	5 *MHz*	10 *MHz*	100 *MHz*	100 *KHz*	1 *MHz*	5 *MHz*	10 *MHz*	100 *MHz*
0.5	10	< 10	< 10	50	30	< 10	10	25	50	20	< 10
	5	< 10	10	90	50	< 10	20	50	60	50	< 10
	2	20	110	150	100	< 10	50	60	90	60	< 10
	0.5	80	200	180	< 10	< 10	75	200	170	100	< 10
0.75	10	25	40	60	45	< 10	10	40	50	35	< 10
	5	30	60	70	50	< 10	40	60	75	75	< 10
	2	50	70	65	30	< 10	60	80	125	80	< 10
	0.5	90	80	70	45	< 10	100	150	200	150	< 10

Data as in Table 1, with a maximum a.c. current density of 10 A cm^{-2} peak-to-peak as an additional condition.

current density of 10 A cm^{-2} peak-to-peak and an inaccuracy in the measurements of 5% or 10 μV, whichever of the two is the largest, the extent of the potential ranges in Table 1 is recalculated (Table 2).

(iii) D.c. irreversible electrode reaction

In those potential regions where the change of surface concentrations with potential is negligible, the faradaic rectification signal is most easily given by a combination of eqns. (2) and (9). The result,

$$\Delta E_F = -\tfrac{1}{4}\frac{nF}{RT}\cdot\frac{\alpha(\alpha+2g)\bar{c}_R\exp(\alpha\varphi)-\beta(\beta-2g)\bar{c}_O\exp(-\beta\varphi)}{N}\cdot V_A^2 \qquad (25)$$

is also obtained by neglecting the first term in eqn. (16) with respect to the second.

In Fig. 3 the relative contribution of the second term in eqn. (16) to ΔE_F at an arbitrarily chosen potential is plotted against $\log_{10}k_{sh}$. It can be seen that for small k_{sh} the first term is negligible.

At sufficiently positive potentials eqn. (25) becomes

$$\Delta E_F = -(\alpha+g)(nF/4RT)V_A^2$$

and at sufficiently negative potentials

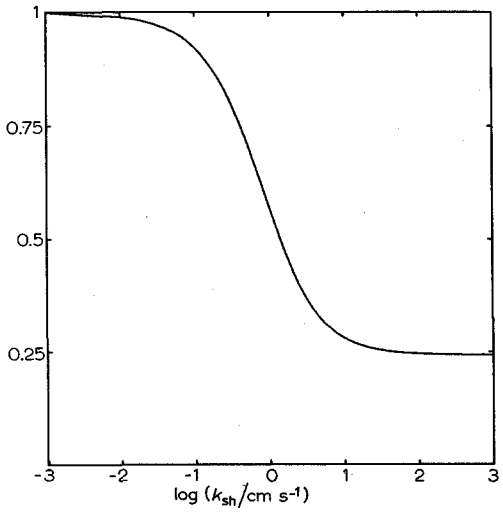
$$\Delta E_F = (\beta-g)(nF/4RT)V_A^2$$

If $c_R\exp(\alpha\varphi)=c_O\exp(-\beta\varphi)$, *i.e.* at the equilibrium potential, eqn. (25) becomes

$$\Delta E_F = -[(\alpha+g)-(\beta+g)](nF/4RT)V_A^2$$

Only in the three last mentioned cases does the faradaic rectification signal contain no information about k_{sh}.

In Fig. 4 $\Delta E_F/(-nF/4RT)V_A^2)$ is plotted against $E-E_0$.



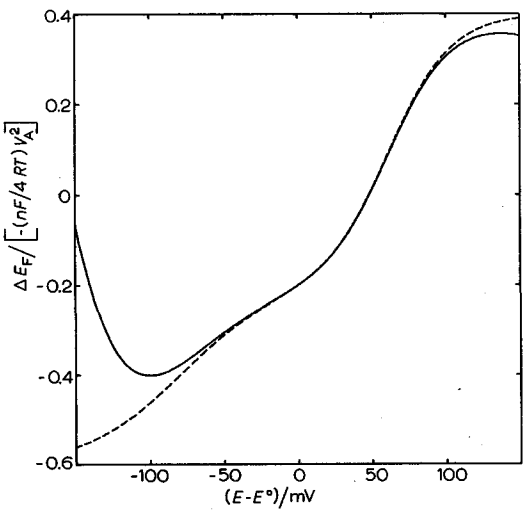


Fig. 3. Relative contribution of second term in eqn. (16) *vs.* log k_{sh}. Data as in Fig. 1. $\alpha=0.4$; $E-E_0=30$ mV.

Fig. 4. ΔE_F *vs.* $E-E_0$ for irreversible reactions. Data as in Fig. 1. $\alpha=0.4$; $k_{sh}=0.005$ cm s^{-1}. (——) ΔE_F (eqn. (16))/$-(nF/4RT)V_A^2$; (------) ΔE_F (eqn. (25))/$-(nF/4RT)V_A^2$.

ANALYSIS PROCEDURE

The three parameters α, k_{sh} and g are not independent, as follows from eqn. (9) which can, with $\alpha+\beta=1$, be written as

$$i = nFk_{sh} \exp(\alpha\varphi)\{c_R - c_O \exp(-\varphi)\} \tag{26}$$

Thus in all equations there will be one independent parameter $k_f = k_{sh} \exp(\alpha\varphi)$. The second parameter occurring in the derived equations, $(\alpha+g)$, is related to k_f by the definition of g:

$$\mathrm{d} \ln k_f/\mathrm{d}\varphi = \alpha + g = \alpha^{app}. \tag{27}$$

This approach is analogous to that given by Barker[7]. Of course eqns. (10)–(24), written in terms of k_f and $\mathrm{d} \ln k_f/\mathrm{d}\varphi$, can be derived directly from eqn. (26). However, since there is some confusion as to the meaning of Sluyter's parameter g[16], which is, in our opinion, just a formal parameter expressing the deviation of a measured system from the absolute rate theory, it seemed to be useful to reintroduce this parameter with a more complete set of definitions.

Values for k_f and α^{app} at each potential can be obtained from measurements with different frequencies. They should then be inspected with respect to relation (27). Based on the behaviour of k_f with potential, a model can be chosen; for instance the absolute rate theory if a plot of log k_f *vs.* φ delivers a straight line. After expressing k_f and α^{app} in terms of the model parameters—for the absolute rate theory α, k_{sh} and φ – the values of these parameters are solved more accurately with a best fit procedure for a matrix of measurements, varying both frequency and potential. This feature of faradaic rectification polarography: the possibility of varying both frequency and d.c. potential, is an important advantage of the method which it shares with the a.c. impedance method. The application of high frequencies, however, enables the kinetic study of very fast electrode reactions, or a more detailed inspection of the transfer coefficient of slower reactions.

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SUMMARY

The shape of faradaic rectification polarograms is calculated on the assumption of a single step charge transfer, allowing deviations from the absolute rate theory. As a result, the conditions necessary for obtaining significant information about the kinetic parameters from measured rectification signals, are reported. Also, the conditions for which simplifications are allowed, are given.

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