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Theory of A.c. Polarization and A.c. Polarography and Voltammetry of Two-step Surface Redox Reactions

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Theoretical expressions are presented of the a.c. polarization and of the a.c. polarography and voltammetry for a two-step surface redox reaction ($O_{ad}+n_1e\rightleftharpoons S_{ad}$, $S_{ad}+n_2e\rightleftharpoons R_{ad}$) in which the charge transfer reactions take place exclusively between the adsorbed reactants O_{ad}, S_{ad}, and R_{ad}, and all the reactants are adsorbed so strongly that the amount of O, S, or R brought to or removed from the electrode surface can be neglected. The interaction between the adsorbed reactants is assumed to be expressed by Frumkin's *a*-parameters. The effect of the double layer impedance is taken into account. Several simplified cases are discussed in detail.

There have been recently increasing studies on redox modified electrodes, which are prepared by attaching irreversibly redox species to the surface of an electrode material (*via* irreversible adsorption, coating, or chemical binding *etc.*), in prospect of their applications to electroanalysis and electrocatalysis (for reviews, see Refs. 1 and 2). Information on the electrochemical characteristics of surface redox reactions is very important in the applications of the redox modified electrodes. For this purpose cyclic voltammetry has been widely used. In a previous paper[3] we have presented a theory of the faradaic impedance and of a.c. polarography and voltammetry for surface redox reaction ($O_{ad}+ne\rightleftharpoons R_{ad}$) in which the interaction between the adsorbed reactants and the correction for the double layer impedance are taken into account. This theory has been applied to the electrode processes of ferredoxins irreversibly adsorbed on the mercury electrode surface.[4,5] The results indicated that a.c. polarography and voltammetry are powerful techniques, in particular, for elucidating the kinetic aspect of the electrode processes.

Two-step charge transfer mechanism is an important mechanistic category in biochemical as well as chemical redox reactions. Numerous studies have been devoted to this type of electrode reaction (EE mechanism) and theoretical treatments of the EE mechanism have been presented for d.c.[6-13] and a.c.[14-18] polarography and other electrochemical techniques.[19-25] To our knowledge, however, no theoretical treatment of a.c. polarization has been presented for the two-step surface redox reaction (*surface EE mechanism*).

In this study we present a theory of the faradaic impedance and of a.c. polarography and voltammetry for the two-step surface redox reaction. In this theory the interaction between the adsorbed reactants is taken into account. Also the effect of the double layer impedance is considered.

Derivation of the General Expressions

Let us consider a two-step surface redox reaction,

$$\text{1st Step: } O_{ad} + n_1e \rightleftharpoons S_{ad} \tag{1a}$$

$$\text{2nd Step: } S_{ad} + n_2e \rightleftharpoons R_{ad}. \tag{1b}$$

In the following we shall make the same assumptions as made in the previous work:[3] (a) the charge transfer reactions take place exclusively between the adsorbed reactants, (b) all the electroactive species (O, S, and R) are adsorbed so strongly (irreversibly) that the amount of O, S, or R brought to or removed from the electrode surface by mass transfer can be neglected in comparison with the amount which remains adsorbed, and (c) the interaction between the adsorbed reactants can be expressed by Frumkin's *a*-parameters.[26]

Since the surface redox reaction proceeds exclusively between the adsorbed reactants (assumption (a)), the faradaic current-density, I_F, is a function of the electrode potential, E, and the surface concentration of the reactants, Γ_O, Γ_S, and Γ_R;

$$I_F = I_F(1) + I_F(2) \tag{2a}$$

$$I_F(1) = g_1(E, \Gamma_O, \Gamma_S) \tag{2b}$$

$$I_F(2) = g_2(E, \Gamma_S, \Gamma_R), \tag{2c}$$

where Γ_i (i=O, S, or R) is the amount of the adsorbed reactant i per unit electrode surface area, $I_F(1)$ and $I_F(2)$ are the faradaic current-densities of the first and second step, respectively.

For a small variation of the potential, δE, superimposed on the "d.c." potential, E_{dc}, ($E=E_{dc}+\delta E$), the surface concentration Γ_i will change around the mean ("d.c.") value, $\overline{\Gamma_i}$, with a small variation, $\delta\Gamma_i$, ($\Gamma_i=\overline{\Gamma}_i+\delta\Gamma_i$) and the faradaic current-density will be given by

$$I_F = I_{dc} + \delta I_F. \tag{3}$$

Thus we have for the first harmonic of faradaic current,[27] $\delta_1 I_F$,

$$\delta_1 I_F = \delta_1 I_F(1) + \delta_1 I_F(2), \tag{4a}$$

$$\delta_1 I_F(1) = (\partial I(1)/\delta E)\delta_1 E + (\partial I(1)/\partial\Gamma_O)\delta_1\Gamma_O + (\partial I(1)/\partial\Gamma_S)\delta_1\Gamma_S, \tag{4b}$$

$$\delta_1 I_F(2) = (\partial I(2)/\partial E)\delta_1 E + (\partial I(2)/\partial\Gamma_S)\delta_1\Gamma_S + (\partial I(2)/\partial\Gamma_R)\delta_1\Gamma_R, \tag{4c}$$

where $\delta_1 E$ and $\delta_1\Gamma_i$'s are the first harmonic variations of E and Γ_i's, respectively. From assumption (b) we further have

$$d(\delta_1\Gamma_O)/dt = j\omega\delta_1\Gamma_O = \delta_1 I_F(1)/n_1F, \tag{5a}$$

$$d(\delta_1\Gamma_S)/dt = j\omega\delta_1\Gamma_S = -(\delta_1 I_F(1)/n_1F) + (\delta_1 I_F(2)/n_2F), \tag{5b}$$

$$d(\delta_1\Gamma_R)/dt = j\omega\delta_1\Gamma_R = -\delta_1 I_F(2)/n_2F, \tag{5c}$$

where j is the operator $(-1)^{1/2}$, and ω the angular frequency of sinusoidal variations.

By combining Eqs. 4a to 5c we obtain the *I-E* characteristic for sinusoidal variation of small amplitude,

$$\delta_1 I_F = \delta_1 I_F^{real} + j\delta_1 I_F^{imag} = \frac{(r_1+r_2) - j[y_1+y_2+(n_1/n_2)x_1-(n_2/n_1)x_2]}{(r_1r_2-y_1y_2-x_1x_2)-j(r_2y_1+r_1y_2)}\delta_1 E, \tag{6a}$$

$$\delta_1 I_F^{real} = \frac{(r_1+r_2)(r_1r_2-y_1y_2-x_1x_2)+(r_1y_2+r_2y_1)[y_1+y_2+(n_1/n_2)x_1-(n_2/n_1)x_2]}{(r_1r_2-y_1y_2-x_1x_2)^2+(r_1y_2+r_2y_1)^2}\delta_1 E, \tag{6b}$$

$$\delta_1 I_F^{imag} = \frac{(r_1+r_2)(r_1y_2+r_2y_1)-(r_1r_2-y_1y_2-x_1x_2)[y_1+y_2+(n_1/n_2)x_1-(n_2/n_1)x_2]}{(r_1r_2-y_1y_2-x_1x_2)^2+(r_1y_2+r_2y_1)^2}\delta_1 E, \tag{6c}$$

where $\delta_1 I_F^{real}$ and $\delta_1 I_F^{imag}$ are the real and imaginary component of the faradaic a.c. current-density, respectively, and r_1, r_2, y_1, y_2, x_1, and x_2 are given by

$$r_1 = 1/(\partial I(1)/\partial E), \tag{7a}$$

$$r_2 = 1/(\partial I(2)/\partial E), \tag{7b}$$

$$y_1 = (1/\omega n_1 F)[-(\partial I(1)/\partial \Gamma_O) + (\partial I(1)/\partial \Gamma_S)]/(\partial I(1)/\partial E), \tag{7c}$$

$$y_2 = (1/\omega n_2 F)[-(\partial I(2)/\partial \Gamma_S) + (\partial I(2)/\partial \Gamma_R)]/(\partial I(2)/\partial E), \tag{7d}$$

$$x_1 = (1/\omega n_1 F)(\partial I(1)/\partial \Gamma_S)/(\partial I(1)/\partial E), \tag{7e}$$

$$x_2 = (1/\omega n_2 F)(\partial I(2)/\partial \Gamma_S)/(\partial I(2)/\partial E). \tag{7f}$$

Because of the specific adsorption of the reactants, the non-faradaic impedance may differ from that observed in the absence of the electroactive species. In this case we can assume that the surface charge density on the electrode, q, is a function of E, Γ_O, Γ_S, and Γ_R only. Thus for sinusoidal variation of the nonfaradaic current-density we have for the first harmonic,[27]

$$\begin{aligned}\delta_1 I_{NF} &= (dq/dt)_{ac} \\ &= j\omega[(\partial q/\partial E)\delta_1 E + (\partial q/\partial \Gamma_O)\delta_1\Gamma_O + (\partial q/\partial \Gamma_S)\delta_1\Gamma_S \\ &\quad + (\partial q/\partial \Gamma_R)\delta_1\Gamma_R].\end{aligned} \tag{8}$$

From Eqs. 5a, 5b, 5c, and 8 we obtain for the nonfaradaic a.c. current-density,

$$\begin{aligned}\delta_1 I_{NF} &= [(m_1-n_1)/n_1]\delta_1 I_F(1) + [(m_2-n_2)/n_2]\delta_1 I_F(2) \\ &\quad + j\omega(\partial q/\partial E)\delta_1 E\end{aligned} \tag{9}$$

where $(m_1-n_1)/n_1$ and $(m_2-n_2)/n_2$ are given by

$$(m_1-n_1)/n_1 = (1/n_1F)[(\partial q/\partial \Gamma_O)-(\partial q/\partial \Gamma_S)], \tag{10a}$$

$$(m_2-n_2)/n_2 = (1/n_2F)[(\partial q/\partial \Gamma_S)-(\partial q/\partial \Gamma_R)], \tag{10b}$$

Thus for the total (faradaic and non-faradaic) a.c. current-density we obtain

$$\begin{aligned}\delta_1 I_t &= \delta_1 I_F + \delta_1 I_{NF} \\ &= (m_1/n_1)\delta_1 I_F(1) + (m_2/n_2)\delta_1 I_F(2) + j\omega(\partial q/\partial E)\delta_1 E,\end{aligned} \tag{11}$$

and the real and imaginary component of the total a.c. current are

$$\delta_1 I_t^{real} = (m_1/n_1)\delta_1 I_F^{real}(1) + (m_2/n_2)\delta_1 I_F^{real}(2), \tag{12a}$$

$$\begin{aligned}\delta_1 I_t^{imag} &= (m_1/n_1)\delta_1 I_t^{imag}(1) + (m_2/n_2)\delta_1 I_F^{imag}(2) \\ &\quad + \omega(\partial q/\partial E)\delta_1 E,\end{aligned} \tag{12b}$$

where $\delta_1 I_F^{real}(i)$ and $\delta_1 I_F^{imag}(i)$ are the real and imaginary component of $\delta_1 I_F(i)$, respectively, and are given by

$$\begin{aligned}&\delta_1 I_F^{real}(1) \\ &= \frac{r_2(r_1r_2-y_1y_2-x_1x_2)+(r_1y_2+r_2y_1)[y_2+(n_1/n_2)x_1]}{(r_1r_2-y_1y_2-x_1x_2)^2+(r_1y_2+r_2y_1)^2} \\ &\quad \times \delta_1 E,\end{aligned} \tag{13a}$$

$$\begin{aligned}&\delta_1 I_F^{real}(2) \\ &= \frac{r_1(r_1r_2-y_1y_2-x_1x_2)+(r_1y_2+r_2y_1)[y_1-(n_2/n_1)x_2]}{(r_1r_2-y_1y_2-x_1x_2)^2+(r_1y_2+r_2y_1)^2} \\ &\quad \times \delta_1 E,\end{aligned} \tag{13b}$$

$$\begin{aligned}&\delta_1 I_F^{imag}(1) \\ &= \frac{r_2(r_1y_2+r_2y_1)-(r_1r_2-y_1y_2-x_1x_2)[y_2+(n_1/n_2)x_1]}{(r_1r_2-y_1y_2-x_1x_2)^2+(r_1y_2+r_2y_1)^2} \\ &\quad \times \delta_1 E,\end{aligned} \tag{13c}$$

$$\begin{aligned}&\delta_1 I_F^{imag}(2) \\ &= \frac{r_1(r_1y_2+r_2y_1)-(r_1r_2-y_1y_2-x_1x_2)[y_1-(n_2/n_1)x_2]}{(r_1r_2-y_1y_2-x_1x_2)^2+(r_1y_2+r_2y_1)^2} \\ &\quad \times \delta_1 E.\end{aligned} \tag{13d}$$

As pointed out previously,[3] the term $\omega(\partial q/\partial E)\delta_1 E$ on the right-hand side of Eq. 12b can be estimated from double-layer capacity measurements employing very high frequencies and for practical purpose can be eliminated approximately by the conventional method of correction for a.c. base current as usually used in a.c. polarographic technique:

$$\begin{aligned}\delta_1 I_{corr}^{imag} &= \delta_1 I_t^{imag} - \omega(\partial q/\partial E)\delta_1 E \\ &= (m_1/n_1)\delta_1 I_F^{imag}(1) + (m_2/n_2)\delta_1 I_F^{imag}(2).\end{aligned} \tag{12c}$$

On the other hand it is very difficult to estimate the terms (m_1/n_1) and (m_2/n_2) experimentally. However, since the potential range in which the faradaic current of each step appears does not exceed a few tenths of a volt, it would be reasonable to assume that these terms are practically constant within the range studied.

In a similar manner as has been done in the previous work,[3] we assume that the current-potential-concentration characteristic can be expressed as

$$I_F = I_F(1) + I_F(2) \tag{14a}$$

$$I_F(1) = n_1F(\overleftarrow{V}(1) - \overrightarrow{V}(1)) \tag{14b}$$

$$I_F(2) = n_2F(\overleftarrow{V}(2) - \overrightarrow{V}(2)) \tag{14c}$$

$$\begin{aligned}\overleftarrow{V}(1) &= k_s'(1)f_2\theta_t B_s(1)^{-1}\exp[\beta_1(n_1F/RT)(E-E_{o1})] \\ &\quad \times \exp[-a_{SS}f_2\theta_t - a_{SO}f_1\theta_t - a_{SR}(1-f_1-f_2)\theta_t]\end{aligned} \tag{14d}$$

$$\begin{aligned}\overrightarrow{V}(1) &= k_s'(1)f_1\theta_t B_O(1)^{-1}\exp[-\alpha_1(n_1F/RT)(E-E_{o1})] \\ &\quad \times \exp[-a_{OO}f_1\theta_t - a_{OS}f_2\theta_t - a_{OR}(1-f_1-f_2)\theta_t]\end{aligned} \tag{14e}$$

$$\begin{aligned}\overleftarrow{V}(2) &= k_s'(2)(1-f_1-f_2)\theta_t B_R(2)^{-1}\exp[\beta_2(n_2F/RT)(E-E_{o2})] \\ &\quad \times \exp[-a_{RR}(1-f_1-f_2)\theta_t - a_{RO}f_1\theta_t - a_{RS}f_2\theta_t]\end{aligned} \tag{14f}$$

$$\begin{aligned}\overrightarrow{V}(2) &= k_s'(2)f_2\theta_t B_S(2)^{-1}\exp[-\alpha_2(n_2F/RT)(E-E_{o2})] \\ &\quad \times \exp[-a_{SS}f_2\theta_t - a_{SO}f_1\theta_t - a_{SR}(1-f_1-f_2)\theta_t].\end{aligned} \tag{14g}$$

In these equations $B_i(1)$ and $B_i(2)$ are constants related to the molar adsorption energies of species i on the electrode surface at $E=E_{o1}$ and $E=E_{o2}$, respectively; a_{ij} is the Frumkin's a-parameter of interaction between the adsorbed molecules i and j (a_{ij} is positive for attraction and negative for repulsion); θ_t is the total coverage defined by $\theta_t=\Gamma_t/\Gamma_m=\theta_O+\theta_S+\theta_R$ with $\theta_O=\Gamma_O/\Gamma_m$, $\theta_S=\Gamma_S/\Gamma_m$, $\theta_R=\Gamma_R/\Gamma_m$, and $\Gamma_t=\Gamma_O+\Gamma_S+\Gamma_R=\overline{\Gamma}_O+\overline{\Gamma}_S+\overline{\Gamma}_R$, Γ_m being the maximum value of the total surface concentration; $f_1=\theta_O/\theta_t$, $f_2=\theta_S/\theta_t$; $k'_s(1)=k_s(1)\Gamma_m$; $k'_s(2)=k_s(2)\Gamma_m$; $k_s(1)$ and $k_s(2)$ are respectively the rate constants of the first and second charge transfer step at the formal standard potentials of the surface redox reactions, E'_{o1} and E'_{o2}, which are defined by

$$E'_{o1} = E_{o1} + [RT/(\alpha_1+\beta_1)n_1F][\ln(B_S(1)/B_O(1)) - (1/3)(a_{OO}-a_{SS}+a_{OS}-a_{SO}+a_{OR}-a_{RS})\theta_t] \tag{15a}$$

$$E'_{o2} = E_{o2} + [RT/(\alpha_2+\beta_2)n_1F][\ln(B_R(2)/(B_S(2)) - (1/3)(a_{SS}-a_{RR}+a_{SR}-a_{RS}+a_{SO}-a_{RO})\theta_t] \tag{15b}$$

α_i and β_i (i=1 and 2) are the transfer coefficients for cathodic and anodic charge transfer of the i-th redox step, respectively. E_{o1} and E_{o2} correspond to the standard potentials of the redox couples O/S and S/R in the bulk of solution, respectively. Here we shall make the following two assumptions: (1) α_i's and β_i's are independent of the potential, and (2) the a_{ij}-parameters are independent of the potential. These assumptions will be reasonable as the first approximation, because the potential range in which the faradaic a.c. current appears does not exceed a few tenths of a volt.

From Eqs. 7a to 7f and 14a to 14g we obtain

$$r_1 = (1/n_1F)[\beta_1(n_1F/RT)\overleftarrow{V}_{dc}(1)+\alpha_1(n_1F/RT)\overrightarrow{V}_{dc}(1)]^{-1} \tag{16a}$$

$$r_2 = (1/n_2F)[\beta_2(n_2F/RT)\overleftarrow{V}_{dc}(2)+\alpha_2(n_2F/RT)\overrightarrow{V}_{dc}(2)]^{-1} \tag{16b}$$

$$y_1 = (r_1/\omega)\{\overrightarrow{V}_{dc}(1)[(1/\overline{\Gamma}_O)-(a_{OO}-a_{OS})(\theta_t/\Gamma_t)] + \overleftarrow{V}_{dc}(1)[(1/\overline{\Gamma}_S)-(a_{SS}-a_{SO})(\theta_t/\Gamma_t)]\} \tag{16c}$$

$$y_2 = (r_2/\omega)\{\overrightarrow{V}_{dc}(2)[(1/\overline{\Gamma}_S)-(a_{SS}-a_{SR})(\theta_t/\Gamma_t)] + \overleftarrow{V}_{dc}(2)[(1/\overline{\Gamma}_R)-(a_{RR}-a_{RS})(\theta_t/\Gamma_t)]\} \tag{16d}$$

$$x_1 = (r_1/\omega)[\overleftarrow{V}_{dc}(1)(1/\overline{\Gamma}_S)-(\overleftarrow{V}_{dc}(1)a_{SS}-\overrightarrow{V}_{dc}(1)a_{OS})(\theta_t/\Gamma_t)] \tag{16e}$$

$$x_2 = -(r_2/\omega)[\overrightarrow{V}_{dc}(2)(1/\overline{\Gamma}_S)-(\overrightarrow{V}_{dc}(2)a_{SS}-\overleftarrow{V}_{dc}(2)a_{RS})(\theta_t/\Gamma_t)]. \tag{16f}$$

Here $\overleftarrow{V}_{dc}(1)=\overleftarrow{V}(1)[E=E_{dc},\ f_1=\overline{f}_1,\ f_2=\overline{f}_2]$, $\overrightarrow{V}_{dc}(1)=\overrightarrow{V}(1)[E=E_{dc},\ f_1=\overline{f}_1,\ f_2=\overline{f}_2]$, $\overleftarrow{V}_{dc}(2)=\overleftarrow{V}(2)[E=E_{dc},\ f_1=\overline{f}_1,\ f_2=\overline{f}_2]$, and $\overrightarrow{V}_{dc}(2)=\overrightarrow{V}(2)[E=E_{dc},\ f_1=\overline{f}_1,\ f_2=\overline{f}_2]$ with $\overline{f}_1=\overline{\Gamma}_O/\Gamma_t$ and $\overline{f}_2=\overline{\Gamma}_S/\Gamma_t$, and these are related to the faradaic d.c. current-densities by

$$(I_F(1))_{dc}/n_1F = \overleftarrow{V}_{dc}(1) - \overrightarrow{V}_{dc}(1), \tag{17a}$$

$$(I_F(2))_{dc}/n_2F = \overleftarrow{V}_{dc}(2) - \overrightarrow{V}_{dc}(2). \tag{17b}$$

(i) A.c. Polarization with Negligible Rectification[27] *at D.c. Equiliblium Potential*: In this case

$$(\overleftarrow{V}_{dc}(1) - \overrightarrow{V}_{dc}(1))_{\text{equilibrium}} = 0 \tag{18a}$$

$$(\overleftarrow{V}_{dc}(2) - \overrightarrow{V}_{dc}(2))_{\text{equilibrium}} = 0 \tag{18b}$$

and the mean surface-coverage fractions $\overline{f}_1=\overline{\Gamma}_O/\Gamma_t$ and $\overline{f}_2=\overline{\Gamma}_S/\Gamma_t$ are given by

$$E_{dc} = E_{o1} + [RT/(\alpha_1+\beta_1)n_1F][\ln(B_S(1)/B_O(1)) - (1/3)(a_{OO}-a_{SS}+a_{OS}-a_{SO}+a_{OR}-a_{SR})\theta_t + \ln(\bar{f}_1/\bar{f}_2)+(1/3)(1-3\bar{f}_1)G_1\theta_t+(1/3)(1-3\bar{f}_2)H_1\theta_t] \tag{19a}$$

$$E_{dc} = E_{o2} + [RT/(\alpha_2+\beta_2)n_2F][\ln(B_R(2)/B_S(2)) - (1/3)(a_{SS}-a_{RR}+a_{SR}-a_{RS}+a_{SO}-a_{RO})\theta_t + \ln(\bar{f}_2/(1-\bar{f}_1-\bar{f}_2))+(1/3)(1-3\bar{f}_1)G_2\theta_t + (1/3)(1-3\bar{f}_2)H_2\theta_t] \tag{19b}$$

with

$$G_1 = a_{OO} - a_{OR} - a_{SO} + a_{SR} \tag{20a}$$

$$H_1 = a_{OS} - a_{OR} - a_{SS} + a_{SR} \tag{20b}$$

$$G_2 = a_{SO} - a_{SR} - a_{RO} + a_{RR} \tag{20c}$$

$$H_2 = a_{SS} - a_{SR} - a_{RS} + a_{RR} \tag{20d}$$

In this case r_1, r_2, y_1, y_2, x_1, and x_2 are given by

$$r_1 = [(\alpha_1+\beta_1)(n_1F/RT)I_o(1)]^{-1} \tag{21a}$$

$$r_2 = [(\alpha_2+\beta_2)(n_2F/RT)I_o(2)]^{-1} \tag{21b}$$

$$y_1 = [(\alpha_1+\beta_1)(n_1^2F^2/RT)\omega\Gamma_t]^{-1} \times [(1/\bar{f}_1)+(1/\bar{f}_2)-(G_1-H_1)\theta_t] \tag{21c}$$

$$y_2 = [(\alpha_2+\beta_2)(n_2^2F^2/RT)\omega\Gamma_t]^{-1} \times [(1/\bar{f}_2)+(1/(1-\bar{f}_1-\bar{f}_2))-H_2\theta_t] \tag{21d}$$

$$x_1 = [(\alpha_1+\beta_1)(n_1^2F^2/RT)\omega\Gamma_t]^{-1}[(1/\bar{f}_2)-(a_{SS}-a_{OS})\theta_t] \tag{21e}$$

$$x_2 = -[(\alpha_2+\beta_2)(n_2^2F^2/RT)\omega\Gamma_t]^{-1}[(1/\bar{f}_2)-(a_{SS}-a_{RS})\theta_t] \tag{21f}$$

where $I_o(1)$ and $I_o(2)$ are respectively the exchange current densities of the first and second step at $E=E_{eq}$, and are given by

$$I_o(1) = n_1F\Gamma_t k_s(1)(\bar{f}_1B_O(1)^{-1}\gamma_O)^{\beta_1/(\alpha_1+\beta_1)} \times (\bar{f}_2B_S(1)^{-1}\gamma_S)^{\alpha_1/(\alpha_1+\beta_1)} \tag{22a}$$

$$I_o(2) = n_2F\Gamma_t k_s(2)(\bar{f}_2B_S(2)^{-1}\gamma_S)^{\beta_2/(\alpha_2+\beta_2)} \times ((1-\bar{f}_1-\bar{f}_2)B_R(2)^{-1}\gamma_R)^{\alpha_2/(\alpha_2+\beta_2)} \tag{22b}$$

with

$$\gamma_O = \exp\{-[a_{OO}\bar{f}_1+a_{OS}\bar{f}_2+a_{OR}(1-\bar{f}_1-\bar{f}_2)]\theta_t\} \tag{23a}$$

$$\gamma_S = \exp\{-[a_{SS}\bar{f}_2+a_{SO}\bar{f}_1+a_{SR}(1-\bar{f}_1-\bar{f}_2)]\theta_t\} \tag{23b}$$

$$\gamma_R = \exp\{-[a_{RR}(1-\bar{f}_1-\bar{f}_2)+a_{RO}\bar{f}_1+a_{RS}\bar{f}_2]\theta_t\} \tag{23c}$$

The phase angle, ψ, is given by

$$\cot\psi = (\delta_1 I_F^{\text{real}}/\delta_1 I_F^{\text{imag}}) = \frac{(r_1r_2-y_1y_2-x_1x_2)(r_1+r_2)+(r_1y_2+r_2y_1)[y_1+y_2+(n_1/n_2)x_1-(n_2/n_1)x_2]}{(r_1y_2+r_2y_1)(r_1+r_2)-(r_1r_2-y_1y_2-x_1x_2)[y_1+y_2+(n_1/n_2)x_1-(n_2/n_1)x_2]} \tag{24}$$

(ii) A.c. Polarography and Voltammetry for D.c. Reversible Steps: Equations 19a, 19b, 21a to 21f, and 24 are applicable without alteration to a.c. polarography and a.c. cyclic voltammetry of the two-step surface redox reaction, when both the steps (1a) and (1b) are d.c. reversible (d.c. Nernstian), that is, when $k_s(1)\tau\gg 1$ and $k_s(2)\tau\gg 1$ in a.c. polarography with a d.m.e. whose drop time is τ or when $4RTk_s(1)/n_1Fv\gg 1$ and

$4RTk_s(2)/n_2Fv \gg 1$ in a.c. voltammetry with the potential sweep rate of v;

$$(\overleftarrow{V}_{\mathrm{dc}}(1)-\overrightarrow{V}_{\mathrm{dc}}(1))_{\mathrm{dc\ reversible}} \approx 0 \tag{25a}$$

and

$$(\overleftarrow{V}_{\mathrm{dc}}(2)-\overrightarrow{V}_{\mathrm{dc}}(2))_{\mathrm{dc\ reversible}} \approx 0. \tag{25b}$$

Simplified Cases

In the following we shall consider several simplified cases, in which both the redox steps (1a) and (1b) are d.c. reversible, and $n_1=n_2=n$, $\alpha_1=\alpha_2=\alpha$, and $\beta_1=\beta_2=\beta$.

Case (I): $a=a_{OO}=a_{OS}=a_{OR}=a_{SS}=a_{SO}=a_{SR}=a_{RR}=a_{RO}=a_{RS}$. When all the interaction parameters a_{ij}'s are of the same value, a, the effect of the interaction between the adsorbed reactants on a.c. waves is characterized implicitly by the parameter a in Eqs. 27a and 27b; that is, the terms r_1, r_2, y_1, y_2, x_1, and x_2 are reduced to

$$r_1=\left[(\alpha+\beta)nF(nF/RT)k_{\mathrm{sap}}(1)\Gamma_{\mathrm{t}}\frac{(\sqrt{K})^{\alpha/(\alpha+\beta)}\rho^{\beta/(\alpha+\beta)}\rho}{(1+\sqrt{K}\rho+\rho^2)}\right]^{-1} \tag{26a}$$

$$r_2=\left[(\alpha+\beta)nF(nF/RT)k_{\mathrm{sap}}(2)\Gamma_{\mathrm{t}}\frac{(\sqrt{K})^{\beta/(\alpha+\beta)}\rho^{\beta/(\alpha+\beta)}}{(1+\sqrt{K}\rho+\rho^2)}\right]^{-1} \tag{26b}$$

$$y_1=\left[(\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}\frac{\sqrt{K}\rho^2}{(1+\sqrt{K}\rho+\rho^2)(\sqrt{K}+\rho)}\right]^{-1} \tag{26c}$$

$$y_2=\left[(\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}\frac{\sqrt{K}\rho}{(1+\sqrt{K}\rho+\rho^2)(\sqrt{K}\rho+1)}\right]^{-1} \tag{26d}$$

$$x_1=-x_2=\left[(\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}\frac{\sqrt{K}\rho}{(1+\sqrt{K}\rho+\rho^2)}\right]^{-1} \tag{26e}$$

where

$$k_{\mathrm{sap}}(1)=k_{\mathrm{s}}(1)B_{\mathrm{O}}(1)^{-\beta/(\alpha+\beta)}B_{\mathrm{S}}(1)^{-\alpha/(\alpha+\beta)}\exp(-a\theta_{\mathrm{t}}) \tag{27a}$$

$$k_{\mathrm{sap}}(2)=k_{\mathrm{s}}(2)B_{\mathrm{S}}(2)^{-\beta/(\alpha+\beta)}B_{\mathrm{R}}(2)^{-\alpha/(\alpha+\beta)}\exp(-a\theta_{\mathrm{t}}) \tag{27b}$$

$$K=\exp[(\alpha+\beta)(nF/RT)(E'_{\mathrm{o1}}-E'_{\mathrm{o2}})] \tag{28}$$

$$\rho=\exp[(\alpha+\beta)(nF/RT)(E_{\mathrm{dc}}-E'_{\mathrm{o}})] \tag{29}$$

with

$$E'_{\mathrm{o1}}=E_{\mathrm{o1}}+[RT/(\alpha+\beta)nF]\ln[B_{\mathrm{S}}(1)/B_{\mathrm{O}}(1)] \tag{30}$$

$$E'_{\mathrm{o2}}=E_{\mathrm{o2}}+[RT/(\alpha+\beta)nF]\ln[B_{\mathrm{R}}(2)/B_{\mathrm{S}}(2)] \tag{31}$$

$$E'_{\mathrm{o}}=(E'_{\mathrm{o1}}+E'_{\mathrm{o2}})/2. \tag{32}$$

In these equations K corresponds to the formation constant of the adsorbed intermediate $\mathrm{S_{ad}}$ defined by

$$K=[\mathrm{S_{ad}}]^2/[\mathrm{O_{ad}}][\mathrm{R_{ad}}] \tag{33}$$

and E'_{o} to the formal standard potential of the adsorbed redox couple $\mathrm{O_{ad}/R_{ad}}$.

From Eqs. 6b, 6c, and 26a to 26e, $\delta_1I_{\mathrm{F}}^{\mathrm{real}}$ and $\delta_1I_{\mathrm{F}}^{\mathrm{imag}}$ are given by

$$\delta_1I_{\mathrm{F}}^{\mathrm{real}}=(\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}\frac{\sqrt{K}\rho\rho^{\alpha/(\alpha+\beta)}}{(1+\sqrt{K}\rho+\rho^2)} \times\frac{\begin{gathered}\{\sqrt{K}[\lambda_1\lambda_2\rho^{2\alpha/(\alpha+\beta)}-(1+\sqrt{K}\rho+\rho^2)][\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}+\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}\rho]+\\(\sqrt{K}+4\rho+\sqrt{K}\rho^2)[\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}(1+\sqrt{K}\rho)+\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}(\sqrt{K}+\rho)]\}\delta_1E\end{gathered}}{\begin{gathered}\{K[\lambda_1\lambda_2\rho^{2\alpha/(\alpha+\beta)}-(1+\sqrt{K}\rho+\rho^2)]^2+[\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}(1+\sqrt{K}\rho)+\\\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}(\sqrt{K}+\rho)]^2\rho^{2\alpha/(\alpha+\beta)}\}\end{gathered}} \tag{34a}$$

$$\delta_1I_{\mathrm{F}}^{\mathrm{imag}}=(\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}\frac{\sqrt{K}\rho}{(1+\sqrt{K}\rho+\rho^2)} \times\frac{\begin{gathered}\{\rho^{2\alpha/(\alpha+\beta)}[\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}+\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}\rho][\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}(1+\sqrt{K}\rho)+\\\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}(\sqrt{K}+\rho)]-\sqrt{K}[\lambda_1\lambda_2\rho^{2\alpha/(\alpha+\beta)}-(1+\sqrt{K}\rho+\rho^2)][\sqrt{K}+4\rho+\sqrt{K}\rho^2]\}\delta_1E\end{gathered}}{\begin{gathered}\{K[\lambda_1\lambda_2\rho^{2\alpha/(\alpha+\beta)}-(1+\sqrt{K}\rho+\rho^2)]^2+[\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}(1+\sqrt{K}\rho)+\\\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}(\sqrt{K}+\rho)]^2\rho^{2\alpha/(\alpha+\beta)}\}\end{gathered}} \tag{34b}$$

with

$$\lambda_1=\omega/k_{\mathrm{sap}}(1) \tag{35a}$$

$$\lambda_2=\omega/k_{\mathrm{sap}}(2). \tag{35b}$$

For the phase angle we obtain

$$\cot\psi=\delta_1I_{\mathrm{F}}^{\mathrm{real}}/\delta_1I_{\mathrm{F}}^{\mathrm{imag}}=\frac{\begin{gathered}\{\sqrt{K}[\lambda_1\lambda_2\rho^{2\alpha/(\alpha+\beta)}-(1+\sqrt{K}\rho+\rho^2)][\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}+\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}\rho]+\\(\sqrt{K}+4\rho+\sqrt{K}\rho^2)[\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}(1+\sqrt{K}\rho)+\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}(\sqrt{K}+\rho)]\}\rho^{\alpha/(\alpha+\beta)}\end{gathered}}{\begin{gathered}\{\rho^{2\alpha/(\alpha+\beta)}[\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}+\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}\rho][\lambda_1(\sqrt{K})^{\beta/(\alpha+\beta)}(1+\sqrt{K}\rho)+\\\lambda_2(\sqrt{K})^{\alpha/(\alpha+\beta)}(\sqrt{K}+\rho)]-\sqrt{K}[\lambda_1\lambda_2\rho^{2\alpha/(\alpha+\beta)}-(1+\sqrt{K}\rho+\rho^2)][\sqrt{K}+4\rho+\sqrt{K}\rho^2]\}\end{gathered}}. \tag{36}$$

Case (I)-(i): A.c. Wave (I). When $k_{\mathrm{sap}}(1)=k_{\mathrm{sap}}(2)=k_{\mathrm{sap}}$ and $\alpha=\beta$, it can easily be shown from Eqs. 34a, 34b, and 36 that both components of the a.c. wave as well as the $\cot\psi$ *versus* E_{dc} curve are symmetrical with respect to the E'_{o}-axis and that the value of $\cot\psi$ at $E_{\mathrm{dc}}=E'_{\mathrm{o}}$, $[\cot\psi]_{E_{\mathrm{dc}}=E'_{\mathrm{o}}}$, is given by

$$[\cot\psi]_{E_{\mathrm{dc}}=E'_{\mathrm{o}}}=\lambda/(K)^{1/4} \tag{37}$$

with $\lambda=\omega/k_{\mathrm{sap}}$. Thus in this simplified case a plot of $[\cot\psi]_{E_{\mathrm{dc}}=E_{\mathrm{o}}}$ against angular frequency yields a straight line passing through the origin with a slope of $k_{\mathrm{sap}}{}^{-1}(K)^{-1/4}$. Since the thermodynamic parameter K can, if n and $(\alpha+\beta)$ are known, be determined from the reversible linear sweep (d.c.) voltammograms as will be described in *Case (I)-(iii)*, we can determine the apparent rate constant, k_{sap}, from this plot.

Case (I)-(ii): Reversible A.c. Wave(I). When

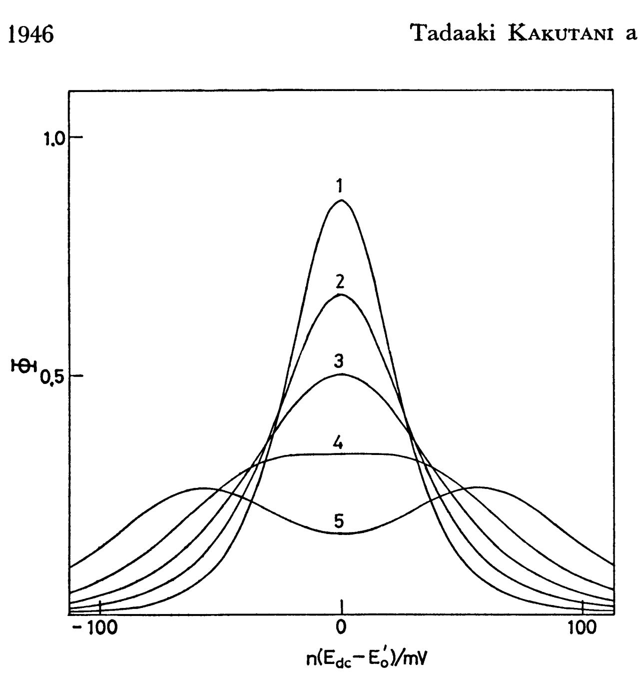

Fig. 1. Normalized reversible a.c. wave(I) calculated by Eq. 38 with $\alpha+\beta=1$.
K: (1); 0.1, (2); 1, (3); 4, (4); 16, (5); 100.

both the rate constants $k_{\text{sap}}(1)$ and $k_{\text{sap}}(2)$ are so large (*i.e.*, $\omega/k_{\text{sap}}(1)\ll 1$ and $\omega/k_{\text{sap}}(2)\ll 1$) that the conditions $(r_1/y_1)\ll 1$ and $(r_2/y_2)\ll 1$ are satisfied, Eq. 6 is reduced to

$$\begin{aligned}(\delta_1 I_{\text{F}})_{\text{rev}} &= (\delta_1 I_{\text{F}}^{\text{imag}})_{\text{rev}} = \frac{y_1+y_2+x_1-x_2}{y_1y_2+x_1x_2}\delta_1 E \\ &= (\alpha+\beta)nF(nF/RT)\omega\Gamma_{\text{t}} \\ &\quad\times\frac{\rho[\rho(\sqrt{K}\rho+2)+(\sqrt{K}+2\rho)]}{(1+\sqrt{K}\rho+\rho^2)^2}\delta_1 E \end{aligned} \tag{38}$$

and

$$\cot\psi \rightarrow 0.$$

Namely, $\delta_1 I_{\text{F}}^{\text{real}}$ becomes vanishingly small and ψ approaches 90°. In Eq. 38 ρ and K are given by Eqs. 29 and 28, respectively. This equation predicts that the reversible a.c. wave (voltammograms with stationary electrode as well as polarograms with d.m.e.) is symmetrical with respect to the potential $E_{\text{dc}}=E'_{\text{o}}$. The normalized a.c. waves, $\Phi\equiv(\delta_1 I_{\text{F}})_{\text{rev}}/nF(nF/RT)\omega\Gamma_{\text{t}}\delta_1 E$, are shown in Fig. 1 for different values of K at $(\alpha+\beta)=1$.

When $K\ll 16$, there is only one peak, of which the peak potential $E_{\text{p}}^{\text{rev}}$ is equal to E'_{o}. The peak current, $(\delta_1 I_{\text{F}}^{\text{p}})_{\text{rev}}$, and the half-peak width, $\Delta E_{\text{p/2}}^{\text{rev}}$, are given by

$$(\delta_1 I_{\text{F}}^{\text{p}})_{\text{rev}} = (\alpha+\beta)nF(nF/RT)\omega\Gamma_{\text{t}}\frac{2}{(2+\sqrt{K})}\delta_1 E \tag{39}$$

$$\Delta E_{\text{p/2}}^{\text{rev}} = [2RT/(\alpha+\beta)nF]\,|\ln\xi| \tag{40}$$

where ξ is the solution of the equation: $\xi^4-K\xi^3+(K-4\sqrt{K}-6)\xi^2-K\xi+1=0$.

On the other hand, there are two peaks for $K>16$. Their peak potentials $E_{\text{p1}}^{\text{rev}}$ and $E_{\text{p2}}^{\text{rev}}$ are given by

$$\begin{aligned}E_{\text{p1}}^{\text{rev}} &= E'_{\text{o}} + [RT/(\alpha+\beta)nF] \\ &\quad\times\ln[(K-8)+\sqrt{(K-4)(K-16)}]/2\sqrt{K}\end{aligned} \tag{41a}$$

$$\begin{aligned}E_{\text{p2}}^{\text{rev}} &= E'_{\text{o}} + [RT/(\alpha+\beta)nF] \\ &\quad\times\ln[(K-8)-\sqrt{(K-4)(K-16)}]/2\sqrt{K}.\end{aligned} \tag{41b}$$

Thus the thermodynamic parameter K can be determined from the half-peak width, $\Delta E_{\text{p/2}}^{\text{rev}}$, for $K\leqslant 16$, or from the peak separation, $|E_{\text{p1}}^{\text{rev}}-E_{\text{p2}}^{\text{rev}}|$, for $K>16$, if $(\alpha+\beta)$ and n are known.

Case (I)-(iii): Reversible D.c. Wave. Furthermore it can be shown that the theoretical expression of the reversible linear sweep (d.c.) voltammogram is the same as that of the reversible a.c. wave if the term $\omega\delta_1 E$ is replaced by the potential sweep rate v. That is, the shape of the reversible linear sweep (d.c.) voltammogram is the same as that of the reversible a.c. wave, and the peak potential of the reversible linear sweep (d.c.) voltammogram, E_{p}^{dc}, coincides with the peak potential of the reversible a.c. wave, $E_{\text{p}}^{\text{rev}}$; $E_{\text{p}}^{\text{dc}}=E_{\text{p}}^{\text{rev}}=E'_{\text{o}}$, and the same discussion as described in *Case (I)-(ii)* is applicable to the reversible linear sweep (d.c.) voltammograms.

Application of these simplified equations given in *Case (I)-(i)* through *(I)-(iii)* to the electrode processes of flavins irreversibly adsorbed on mercury electrode surface will be reported in a succeeding paper.

Case (II): $a_{OO}+a_{SO}=a_{OS}+a_{SS}=a_{OR}+a_{SR}=a_{SO}+a_{RO}=a_{SS}+a_{RS}=a_{SR}+a_{RR}$, $a_{ij}=a_{ji}$ *(i,j=O, S, or R) and* $\alpha=\beta$. In this simplified case, the effects of the interaction between the adsorbed reactants on a.c. waves can be characterized explicitly by an interaction parameter $G=2(a_1-a_2)$ (Eq. 44) and implicitly by (a_1+a_2) (Eq. 43). That is, the terms r_1, r_2, y_1, y_2, x_1, and x_2 are reduced to

$$r_1 = [2\alpha nF(nF/RT)k_{\text{sap}}(1)\Gamma_{\text{t}}(\bar{f}_1\bar{f}_2)^{1/2}]^{-1} \tag{42a}$$

$$r_2 = [2\alpha nF(nF/RT)k_{\text{sap}}(2)\Gamma_{\text{t}}\bar{f}_2{}^{1/2}(1-\bar{f}_1-\bar{f}_2)^{1/2}]^{-1} \tag{42b}$$

$$y_1 = [2\alpha nF(nF/RT)\omega\Gamma_{\text{t}}]^{-1}[(1/\bar{f}_1)+(1/\bar{f}_2)-G\theta_{\text{t}}] \tag{42c}$$

$$y_2 = [2\alpha nF(nF/RT)\omega\Gamma_{\text{t}}]^{-1}[(1/\bar{f}_2)+(1/(1-\bar{f}_1-\bar{f}_2))-G\theta_{\text{t}}] \tag{42d}$$

$$x_1 = -x_2 = [2\alpha nF(nF/RT)\omega\Gamma_{\text{t}}]^{-1}[(1/\bar{f}_2)-(1/2)G\theta_{\text{t}}] \tag{42e}$$

where

$$k_{\text{sap}}(1) = k_{\text{s}}(1)(B_{\text{O}}(1)B_{\text{S}}(1))^{-1/2}\exp[-(1/2)(a_1+a_2)\theta_{\text{t}}] \tag{43a}$$

$$k_{\text{sap}}(2) = k_{\text{s}}(2)(B_{\text{S}}(2)B_{\text{R}}(2))^{-1/2}\exp[-(1/2)(a_1+a_2)\theta_{\text{t}}] \tag{43b}$$

and G is given by

$$G = 2(a_1-a_2) \tag{44}$$

with

$$a_1 = a_{\text{OO}} = a_{\text{SS}} = a_{\text{RR}} = a_{\text{OR}} = a_{\text{RO}} \tag{45a}$$

$$a_2 = a_{\text{OS}} = a_{\text{SO}} = a_{\text{SR}} = a_{\text{RS}}. \tag{45b}$$

The mean fractions of the surface coverages $\overline{f_1}$ and $\overline{f_2}$ are related to the d.c. potential E_{dc} by

$$\begin{aligned}E_{\text{dc}} &= E'_{\text{o}} + [RT/2\alpha nF][\ln\sqrt{K}+\ln(\bar{f}_1/\bar{f}_2) \\ &\quad-(1/2)(1-2\bar{f}_2)G\theta_{\text{t}}]\end{aligned} \tag{46a}$$

$$\begin{aligned}E_{\text{dc}} &= E'_{\text{o}} + [RT/2\alpha nF][-\ln\sqrt{K}+\ln(\bar{f}_2/(1-\bar{f}_1-f_2)) \\ &\quad+(1/2)(1-2\bar{f}_2)G_{\text{t}}]\end{aligned} \tag{46b}$$

where E'_{o} and K are respectively defined as

$$E'_{\text{o}} = (E'_{\text{o1}}+E'_{\text{o2}})/2 \tag{47}$$

$$K = \exp[(2\alpha nF/RT)(E'_{o1} - E'_{o2})] \qquad (48)$$

with $E'_{o1} = E_{o1} + [RT/2\alpha nF]\ln[B_S(1)/B_O(1)]$ and $E'_{o2} = E_{o2} + [RT/2\alpha nF]\ln[B_R(2)/B_S(2)]$.

The a.c. wave is expressed by Eq. 6 with Eqs. 42a to 48, and the phase angle by Eq. 24 with Eqs. 42a to 48, which are, when $G=0$, reduced to the same equations as given in *Case (I)*.

Case (II)-(i): A.c. Wave(II). When it is further assumed that $k_{sap}(1) = k_{sap}(2) = k_{sap}$, it can easily be shown from these equations that both components of the a.c. wave as well as the cot ϕ *versus* E_{dc} curve are symmetrical with respect to the E'_o-axis. Furthermore the value of cot ϕ at $E_{dc} = E'_o$, $[\cot\phi]_{E_{dc}=E'_o}$, is given by

$$[\cot\phi]_{E_{dc}=E'_o} = (\omega/k_{sap})[2A/(2B - C - G\theta_t)] \qquad (49)$$

with

$$A = [2/\eta(1-\eta)]^{1/2} \qquad (50a)$$

$$B = (1+\eta)/\eta(1-\eta) \qquad (50b)$$

$$C = 2/\eta \qquad (50c)$$

$$\eta = \{1 + (2/\sqrt{K})\exp[(1/2)(1-2\eta)G\theta_t]\}^{-1}. \qquad (50d)$$

That is, $[\cot\phi]_{E_{dc}=E'_o}$ is proportional to angular frequency but in this case the slope of a plot of $[\cot\phi]_{E_{dc}=E'_o}$ *versus* ω depends on the interaction parameter $G\theta_t$ as well as K and k_{sap}. Since K and $G\theta_t$ can, if n and α are given, be determined from the reversible linear sweep (d.c.) voltammograms as will be described in *Case (II)-(iii)*, these three parameters, *i.e.*, k_{sap}, $G\theta_t$, and K, can be determined by combination of the a.c. and d.c. measurements.

Application of these simplified equations to the electrode processes of a ferredoxin irreversibly adsorbed on the surface of the dropping mercury electrode has been reported in another article.[5]

Case (II)-(ii): Reversible A.c. Wave(II). When the rate constant k_{sap} is so large compared to ω that $(r_1/y_1) \ll 1$ and $(r_2/y_2) \ll 1$, then, the a.c. wave(II) is reduced to the reversible a.c. wave(II), $\delta_1 I_F^{rev}$, which is expressed by

$$\delta_1 I_F^{rev} = (\delta_1 I_F^{imag})_{rev} = \frac{y_1 + y_2 + x_1 - x_2}{y_1 y_2 + x_1 x_2}\delta_1 E \qquad (51)$$

and the phase angle approaches 90°. In this equation the terms y_1, y_2, and $x_1 = -x_2$ are given by Eqs. 42c, 42d, and 42e, respectively. The mean fractions of the surface coverages $\overline{f_1}$ and $\overline{f_2}$ are related to the d.c. potential E_{dc} by Eqs. 46a and 46b.

These equations predict that the a.c. wave is also symmetrical with respect to the E'_o-axis. However, in contrast to *Case (I)-(ii)*, the wave shape will change with changing the total surface coverage θ_t. That is, with increasing $G\theta_t$, the normalized peak current, $\Phi_p \equiv (\delta_1 I_F^{rev})_p / nF(nF/RT)\omega\Gamma_t$, becomes larger and the half-peak width, $\Delta E_{p/2}^{rev}$, smaller, as shown, for example, for the case of $K=1$ in Fig. 2. Thus the two parameters K and G can be determined from the reversible a.c. waves measured at various values of θ_t if n and α are given.

Case (II)-(iii): Reversible D.c. Wave. It can easily be shown that the theoretical equations of the reversible linear sweep (d.c.) voltammogram are the same as those of the reversible a.c. wave if the term $\omega\delta_1 E$ is replaced by the potential sweep rate v. Thus the same discussion as described in *Case (II)-(ii)* is applicable to the reversible linear sweep (d.c.) voltammograms.

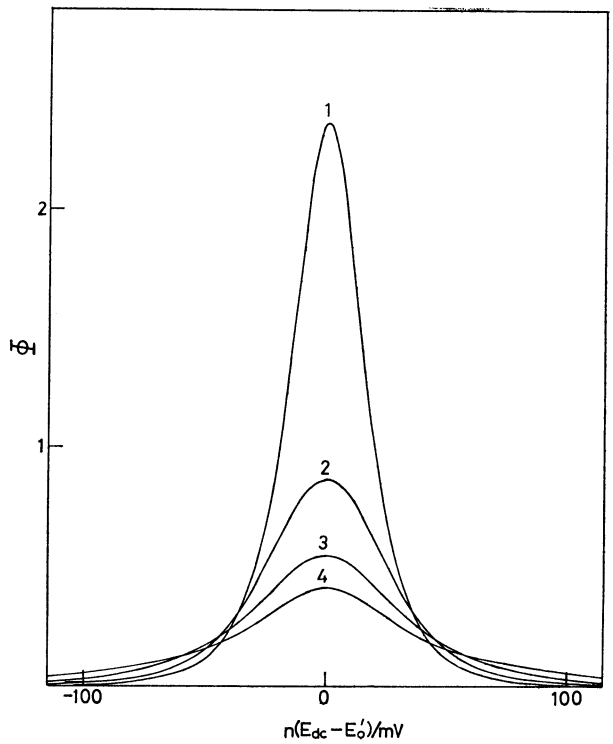

Fig. 2. Normalized reversible a.c. wave(II) calculated by Eqs. 51, 42c, 42d, 42e, 46a, and 46b with $\alpha = \beta = 0.5$ and $K=1$.
$G\theta_t$: (1); 3, (2); 1, (3); −1, (4); −3.

References

1) W. R. Heineman and P. T. Kissinger, *Anal. Chem.*, **50**, 166R (1978).

2) D. K. Roe, *Anal. Chen.*, **50**, 9R (1978).

3) T. Kakutani and M. Senda, *Bull. Chem. Soc. Jpn.*, **52**, 3236 (1979).

4) T. Ikeda, K. Toriyama, and M. Senda, *Bull. Chem. Soc. Jpn.*, **52**, 1937 (1979).

5) T. Kakutani, K. Toriyama, T. Ikeda, and M. Senda, *Bull. Chem. Soc. Jpn.*, **53**, 947 (1980).

6) R. Brdička, *Z. Elektrochem.*, **47**, 319 (1941).

7) O. H. Müller, *Ann. N.Y. Acad. Sci.*, **40**, 91 (1940).

8) K. J. Vetter, *Z. Naturforsch., Teil A*, **7**, 328 (1952); **8**, 823 (1953).

9) T. Berzins and P. Delahay, *J. Am. Chem. Soc.*, **75**, 5716 (1953).

10) A. A. Vlček, *Collect. Czech. Chem. Commun.*, **22**, 1736 (1957).

11) M. Suzuki and P. J. Elving, *Collect. Czech. Chem. Commun.*, **25**, 3202 (1960).

12) J. M. Hale, *J. Electroanal. Chem. Interfacial Chem.*, **8**, 181 (1964).

13) I. Ružić, *J. Electroanal. Chem. Interfacial Chem.*, **52**, 331 (1974).

14) M. Senda, M. Senda, and I. Tachi, *Rev. Polarogr. (Kyoto)*, **10**, 142 (1962).

15) H. L. Hung and D. E. Smith, *J. Electroanal. Chem.*

Interfacial Chem., **11**, 236, 425 (1966).

16) I. Ružić and D. E. Smith, *J. Electroanal. Chem. Interfacial Chem.*, **58**, 145 (1975).

17) J. M. Hale, *J. Electroanal. Chem. Interfacial Chem.*, **8**, 408 (1964).

18) S. K. Rangarajan, *J. Electroanal. Chem. Interfacial Chem.*, **55**, 337, 363 (1974).

19) K. J. Bachmann and U. Bertocci, *Electrochim. Acta*, **15**, 1877 (1970).

20) K. J. Bachmann, *J. Electrochem. Soc.*, **118**, 226 (1971).

21) R. Kruse, *Electrochim. Acta*, **21**, 85 (1976).

22) H. Schweickert, A. A. El Miligy, A. Melendez, and W. J. Lorenz, *J. Electroanal. Chem. Interfacial Chem.*, **68**, 19 (1976).

23) M. D. Ryan, *J. Electrochem. Soc.*, **125**, 547 (1978).

24) R. K. Jain, H. C. Gaur, and B. J. Welch, *J. Electroanal. Chem. Interfacial Chem.*, **79**, 211 (1977).

25) V. Plichon and E. Laviron, *J. Electroanal. Chem. Interfacial Chem.*, **71**, 143 (1976).

26) B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, "Adsorption of Organic Compounds on Electrodes," Plenum, New York (1971).

27) M. Senda and P. Delahay, *J. Phys. Chem.*, **65**, 1580 (1961).