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Theory of A.c. Polarization and A.c. Polarography and Voltammetry of Surface Redox Reaction

Tadaaki KAKUTANI* and Mitsugi SENDA

Department of Agricultural Chemistry, Faculty of Agriculture, Kyoto University, Kyoto 606

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Theoretical equations are presented of the a.c. polarization and of the a.c. polarography and voltammetry for the surface redox reaction ($O_{ad}+ne \rightleftarrows R_{ad}$) in which charge transfer reaction takes place exclusively between the adsorbed reactants O_{ad} and R_{ad}, and both reactants are adsorbed so strongly that the amount of O or R brought to or removed from the electrode surface can be neglected. The interaction between adsorbed molecules is assumed to be expressed by Frumkin's *a*-parameters. Also the effect of the double layer impedance is taken into account. Some simplified cases are discussed in detail.

Electrochemistry with electroactive reactants irreversibly or strongly adsorbed on or chemically bonded to electrode surface is an active field of current research (for reviews, see Refs. 1 and 2). In the majority of cases the electrochemical behavior of such electrodes has been studied by using linear sweep cyclic voltammetry and differential pulse polarography. Also the coulostatic technique[3)] and the second harmonic a.c. voltammetric technique[4)] were used for the study of electron transfer reactions between reactants irreversibly or strongly adsorbed on or chemically bonded to electrode surface. We have applied the a.c. polarographic technique to elucidate the electrode processes of ferredoxins irreversibly adsorbed on the surface of mercury electrode.[5a)] The results indicated that the a.c. polarography is a powerful technique, in particular, for determining the electrochemical kinetic parameters.

Theory of the faradaic impedance or a.c. polarography of the electrode processes with specific adsorption has been given in a general form[6)] which involves terms of mass transfer, adsorption and charge transfer. Although the general expressions are very involved, the expressions will become very simple[7)] when the charge transfer reaction takes place exclusively between adsorbed molecules and the amount of electroactive species (O or R) brought to or removed from the electrode surface by mass transfer can be neglected in comparison with the amount which remains adsorbed. These conditions will be satisfied in the case of strongly or irreversibly adsorbed or chemically bonded species.

In this paper, we present theoretical expressions of the faradaic impedance and of the a.c. polarography and voltammetry of the electrode processes with reactants irreversibly adsorbed on or chemically bonded to electrode surface (hereafter we call this the "surface redox reaction") on the basis of the general expressions[6)]. In the following derivation we shall make several assumptions: (a) the charge transfer reaction takes place exclusively between the adsorbed molecules, (b) both O and R are adsorbed so strongly (irreversibly) that the amount of O or R brought to or removed from the electrode surface can be neglected, and (c) the interaction between adsorbed molecules can be expressed by Frumkin's *a*-parameters. The effect of the double layer impedance is also considered.

Theory of Faradaic and Non-faradaic Currents

We consider an *n*-electron surface redox reaction,

$$O_{ad} + ne \rightleftarrows R_{ad}. \tag{1}$$

Since the surface redox reaction proceeds exclusively between the adsorbed molecules (assumption (a)), the faradaic current density I_F is a function of the electrode potential, E, and the surface concentrations of the adsorbed species O and R, Γ_O and Γ_R; $I_F=g(E, \Gamma_O, \Gamma_R)$. For small variations of the potential, δE, superimposed on the "d.c." potential, E_{dc}, ($E=E_{dc}+\delta E$), the surface concentration will change around the mean ("d.c.") value, $\overline{\Gamma}_i$, with small variations, $\delta\Gamma_i$; $\Gamma_i=\overline{\Gamma}_i+\delta\Gamma_i$ (i=O and R) and the faradaic current will be given by[6)]

$$I_F = I_{dc} + \delta I_F. \tag{2}$$

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

$$\delta_1 I_F = (\partial I/\partial E)\delta_1 E + (\partial I/\partial \Gamma_O)\delta_1\Gamma_O + (\partial I/\partial \Gamma_R)\delta_1\Gamma_R, \tag{3}$$

where $\delta_1 E$ and $\delta_1\Gamma_i$'s represent the first harmonic variations of E and Γ_i's respectively. From the assumption (b) we further have[6)]

$$d(\delta_1\Gamma_i)/dt = j\omega\delta_1\Gamma_i = \pm(\delta_1 I_F/nF). \tag{4}$$

Here the upper and lower sings correspond to O and R, respectively, j is the operator $(-1)^{1/2}$, and ω the angular frequency of sinusoidal variations.

By combination of Eqs. 3 and 4 we obtain the *I-E* characteristic for sinusoidal variations of small amplitude,

$$\delta_1 I_F = \delta_1 I_F^{\text{real}} + j\delta_1 I_F^{\text{imag}} = (r-jy)^{-1}\delta_1 E, \tag{5a}$$

$$\delta_1 I_F^{\text{real}} = \frac{(r/y)^2}{1+(r/y)^2}\cdot\frac{1}{r}\delta_1 E, \tag{5b}$$

and

$$\delta_1 I_F^{\text{imag}} = \frac{1}{1+(r/y)^2}\cdot\frac{1}{y}\delta_1 E, \tag{5c}$$

where $\delta_1 I_F^{\text{real}}$ and $\delta_1 I_F^{\text{imag}}$ are thc real and imaginary components of the faradaic a.c. current, respectively, and r and y are given by

$$r = 1/(\partial I/\partial E), \tag{6a}$$

and

$$y=y_O + y_R = (1/nF\omega)[-(\partial I/\partial \Gamma_O)/(\partial I/\partial E) + (\partial I/\partial \Gamma_R)/(\partial I/\partial E)]. \tag{6b}$$

In harmony with the assumption (b) (see Eq. 4) the general theory[6] would give the same expressions as above when

$$(\partial\phi_O/\partial\Gamma_R) = (\partial\phi_R/\partial\Gamma_O) = 0,\quad |\zeta_i| \ll 1,$$
$$\text{and } (\omega/2D_i)^{1/2}(\partial\Gamma_i/\partial C_i^\circ) \gg 1$$

(see Ref. 6 regarding the notations).

Because of adsorption of O and R, the double layer impedance, *i.e.*, the non-faradaic impedance may differ from that observed in the absence of O and R. In this case we can assume that the surface charge density on the electrode, q, is a function of E, Γ_O, and Γ_R only, so that for sinusoidal variations of the non-faradaic current-density we have for the first harmonic[6,8]

$$\delta_1 I_{NF} = (dq/dt)_{ac} = j\omega[(\partial q/\partial E)\delta_1 E + (\partial q/\partial\Gamma_O)\delta_1\Gamma_O + (\partial q/\partial\Gamma_R)\delta_1\Gamma_R]. \tag{7}$$

From Eqs. 4 and 7, we obtain for the non-faradaic ac current

$$\delta_1 I_{NF} = (1/nF)[(\partial q/\partial\Gamma_O)-(\partial q/\partial\Gamma_R)]\delta_1 I_F + j\omega(\partial q/\partial E)\delta_1 E. \tag{8}$$

Thus we have for the total (faradaic and non-faradaic) ac current

$$\delta_1 I_t = \delta_1 I_F + \delta_1 I_{NF} = \{1+(1/nF)[(\partial q/\partial\Gamma_O)-(\partial q/\partial\Gamma_R)]\}\delta_1 I_F + j\omega(\partial q/\partial E)\delta_1 E, \tag{9}$$

and the observable real and imaginary components are

$$\delta_1 I_{obsd}^{real} = \{1+(1/nF)[(\partial q/\partial\Gamma_O)-(\partial q/\partial\Gamma_R)]\}\delta_1 I_F^{real}, \tag{10a}$$

and

$$\delta_1 I_{obsd}^{imag} = \{1+(1/nF)[(\partial q/\partial\Gamma_O)-(\partial q/\partial\Gamma_R)]\}\delta_1 I_F^{imag} + \omega(\partial q/\partial E)\delta_1 E, \tag{10b}$$

respectively. The second term on the right-hand side of Eq. 10b, $\omega(\partial q/\partial E)\delta_1 E$, (*i.e.*, so-called "wahre Käpazität" term[8]) can be estimated from double-layer capacity measurements employing very high frequencies. This term is generally a reverse-S-shaped or S-shaped variation of the capacity current and for practical purpose can approximately be eliminated by a conventional method of correction for ac base current as usually used in a.c. polarographic technique:

$$\delta_1 I_{corr}^{imag} = \delta_1 I_{obsd}^{imag} - \omega(\partial q/\partial E)\delta_1 E = \{1+(1/nF)[(\partial q/\partial\Gamma_O)-(\partial q/\partial\Gamma_R)]\}\delta_1 I_F^{imag}. \tag{10c}$$

On the other hand it is very difficult to estimate the term $[(\partial q/\partial\Gamma_O)-(\partial q/\partial\Gamma_R)]$ experimentally. However, since the potential range in which the faradaic current appears does not exceed a few tenths of a volt, it can be assumed that this term is practically a constant within the range studied:

$$\delta_1 I_{obsd}^{real} = (m/n)\delta_1 I_F^{real}, \tag{11a}$$
$$\delta_1 I_{corr}^{imag} = (m/n)\delta_1 I_F^{imag}, \tag{11b}$$
$$(m/n) = \{1+(1/nF)[(\partial q/\partial\Gamma_O)-(\partial q/\partial\Gamma_R)]\} \tag{11c}$$

We call the constant, m, defined by Eq. 11c the apparent number of electrons associated with the surface redox reaction (1).

Equations for Faradaic Impedance and A.c. Polarography and Voltammetry

Laitinen and Randles[9] first gave theoretical expressions of the faradaic impedance for the surface redox reaction. However, they did not take the interaction between the adsorbed molecules into account. We assume that the current-potential-concentration characteristic can be written as[7]

$$(I_F/nF) = \overleftarrow{V} - \overrightarrow{V}, \tag{12a}$$
$$\overleftarrow{V} = k_s'(1-f)\theta_t B_R^{-1}\exp[\beta(nF/RT)(E-E_0)] \times \exp[-a_{RR}(1-f)\theta_t - a_{RO}f\theta_t], \tag{12b}$$
$$\overrightarrow{V} = k_s' f\theta_t B_O^{-1}\exp[-\alpha(nF/RT)(E-E_0)] \times \exp[-a_{OO}f\theta_t - a_{OR}(1-f)\theta_t], \tag{12c}$$

where B_i is the constant representing the adsorption energy of i on the electrode surface at $E=E_0$, E_0 being the reference electrode potential (see below), a_{ij} the Frumkin's a-parameter of interaction between the adsorbed molecules i and j (a_{ij} is positive for an attraction and negative for a repulsion),[10] θ_t the total coverage defined by $\theta_t=\Gamma_t/\Gamma_m=\theta_O+\theta_R$ with $\theta_O=\Gamma_O/\Gamma_m$, $\theta_R=\Gamma_R/\Gamma_m$, and $\Gamma_t=\Gamma_O+\Gamma_R=\overline{\Gamma}_O+\overline{\Gamma}_R$, Γ_m the maximum value of the total surface concentration, $f=\theta_O/\theta_t$, $k_s'=k_s\Gamma_m$ and k_s (in s^{-1}) the rate constant of the charge transfer reaction at the standard potential of the surface redox reaction, E_0', which is defined by

$$E_0' = E_0 + [RT/(\alpha+\beta)nF][\ln(B_R/B_O) - (1/2)(a_{OO}-a_{RR}+a_{OR}-a_{RO})\theta_t]. \tag{13}$$

The equilibrium dc potential, E_{eq}, at $I_F=0$ is given by

$$E_{eq} = E_0' + [RT/(\alpha+\beta)nF][\ln(f/(1-f)) + (1/2)(1-2f)G\theta_t]_{eq} \tag{14}$$

where G is defined by Eq. 19. α and β are the transfer coefficients for cathodic and anodic charge transfer reaction, respectively. Similar expression of the current-potential-concentration characteristic has been used by Conway *et al.*[11,12] in the kinetic theory of the linear sweep voltammetry of the surface redox reaction, and by Laviron,[13] Brown and Anson,[14] and Murray *et al.*[15] in theoretical expressions of the reversible linear sweep voltammogram of the surface redox reaction. It can generally be shown that the peak potential of the d.c. reversible (*i.e.*, d.c. Nernstian) linear sweep voltammogram, E_p^{dc}, is equal to E_0' defined by Eq. 13. In the following we assume that the a_{ij}-parameters are independent of the electrode potential. In Eqs. 12b and 12c the terms $\exp[\beta(nF/RT)(E-E_0)]$ and $\exp[-\alpha(nF/RT)(E-E_0)]$ represent the dependence of both the activation free energy of charge transfer and the adsorption free energy of reactants on the electrode potential. The quadratic dependence of these energies on the electrode potential has been described. In the following, however, we assume in the first approximation that the coefficients α and β are independent of the electrode potential. The reference electrode potential, E_0, may be considered as corresponding to the standard potential of the redox couple supposedly in the bulk of solution.

From Eqs. 6a, 6b, 12a, 12b, and 12c we obtain

$$r = (1/nF)[\beta(nF/RT)\overleftarrow{V}_{\mathrm{dc}}+\alpha(nF/RT)\overrightarrow{V}_{\mathrm{dc}}]^{-1} \tag{15}$$

and

$$\begin{aligned} y = (r/\omega)\{&\overrightarrow{V}_{\mathrm{dc}}[(1/\overline{\Gamma}_{\mathrm{O}})-(a_{\mathrm{OO}}-a_{\mathrm{OR}})(\theta_{\mathrm{t}}/\Gamma_{\mathrm{t}})] \\ &+\overleftarrow{V}_{\mathrm{dc}}[(1/\overline{\Gamma}_{\mathrm{R}})-(a_{\mathrm{RR}}-a_{\mathrm{RO}})(\theta_{\mathrm{t}}/\Gamma_{\mathrm{t}})]\}. \end{aligned} \tag{16}$$

Here $\overleftarrow{V}_{\mathrm{dc}}=\overleftarrow{V}(E=E_{\mathrm{dc}}, f=\bar{f})$ and $\overrightarrow{V}_{\mathrm{dc}}=\overrightarrow{V}(E=E_{\mathrm{dc}}, f=\bar{f})$ with $\bar{f}=\overline{\Gamma}_{\mathrm{O}}/\Gamma_{\mathrm{t}}$ and these are related to the dc faradaic current by

$$(I_{\mathrm{F}})_{\mathrm{dc}}/nF = \overleftarrow{V}_{\mathrm{dc}} - \overrightarrow{V}_{\mathrm{dc}}. \tag{17a}$$

When the surface redox reaction is d.c. reversible (dc Nernstian), *i.e.*, $(4RTk_{\mathrm{s}}/nFv)\gg 1$ in a.c. voltammetry with the potential sweep rate, v, or $k_{\mathrm{s}}\tau\gg 1$ in a.c. polarography with the drop time, τ, $\bar{f}$ or $\overline{\Gamma}_{\mathrm{O}}$, and $\overline{\Gamma}_{\mathrm{R}}$ can be estimated by

$$(\overleftarrow{V}_{\mathrm{dc}}-\overrightarrow{V}_{\mathrm{dc}})_{\mathrm{dc\ reversible}} = 0 \tag{17b}$$

and given by

$$\begin{aligned} E_{\mathrm{dc}} = E_0' &+ [RT/(\alpha+\beta)nF] \\ &\times [\ln(\bar{f}/(1-\bar{f}))+(1/2)(1-2\bar{f})G\theta_{\mathrm{t}}], \end{aligned} \tag{18}$$

with

$$G = a_{\mathrm{OO}} + a_{\mathrm{RR}} - a_{\mathrm{OR}} - a_{\mathrm{RO}}. \tag{19}$$

In this case r and y are given by

$$r = \frac{1}{(\alpha+\beta)}\cdot\frac{RT}{nF}\cdot\frac{1}{I_0}, \tag{20}$$

and

$$y = \frac{1}{(\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}}\cdot\frac{1-G\theta_{\mathrm{t}}(1-\bar{f})\bar{f}}{(1-\bar{f})\bar{f}}, \tag{21}$$

where I_0 is the exchange current density at $E=E_{\mathrm{dc}}$ and given by

$$\begin{aligned} I_0 = nFk_{\mathrm{s}}\Gamma_{\mathrm{t}}&\bar{f}^{\beta/(\alpha+\beta)}(1-\bar{f})^{\alpha/(\alpha+\beta)}B_{\mathrm{O}}^{-\beta/(\alpha+\beta)}B_{\mathrm{R}}^{-\alpha/(\alpha+\beta)} \\ &\times \exp\{-(\beta/(\alpha+\beta))[a_{\mathrm{OO}}\bar{f}+a_{\mathrm{OR}}(1-\bar{f})]\theta_{\mathrm{t}}\} \\ &\times \exp\{-(\alpha/(\alpha+\beta))[a_{\mathrm{RR}}(1-\bar{f})+a_{\mathrm{RO}}\bar{f}]\theta_{\mathrm{t}}\}. \end{aligned} \tag{22}$$

The phase angle, ϕ, is given by

$$\begin{aligned} \cot\phi &= (r/y) = (\delta_1 I_{\mathrm{F}}^{\mathrm{real}}/\delta_1 I_{\mathrm{F}}^{\mathrm{imag}}) = (\delta_1 I_{\mathrm{obsd}}^{\mathrm{real}}/\delta_1 I_{\mathrm{corr}}^{\mathrm{imag}}) \\ &= \frac{\omega}{\phi_0}\cdot\frac{(1-\bar{f})\bar{f}}{1-G\theta_{\mathrm{t}}(1-\bar{f})\bar{f}}, \end{aligned} \tag{23}$$

with $\phi_0=I_0/nF\Gamma_{\mathrm{t}}$.

These equations 18, 20, 21, and 23 are applicable without alteration to a.c. polarization of the surface redox reaction at the equilibrium (dc) potential.

Simplified Cases

In the following we shall consider several simplified cases, in which the surface redox reaction is assumed to be dc reversible.

A.c. Reversible Case. When the rate constant is so large that the condition $(r/y)\ll 1$ is satisfied, Eqs. 5a, 5b, and 5c are reduced to

$$\begin{aligned} (\delta_1 I_{\mathrm{F}})_{\mathrm{rev}} &= (\delta_1 I_{\mathrm{F}}^{\mathrm{imag}})_{\mathrm{rev}} = \frac{1}{y}\delta_1 E \\ &= (\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}\cdot\frac{\bar{f}(1-\bar{f})}{1-G\theta_{\mathrm{t}}(1-\bar{f})\bar{f}}\delta_1 E, \end{aligned} \tag{24}$$

and $\cot\phi=0$. That is, $\delta_1 I_{\mathrm{F}}^{\mathrm{real}}$ becomes vanishingly small and ϕ approaches 90°. The a.c. wave has a maximum at $\bar{f}=1/2$ and is symmetrical with respect to the peak potential. The peak current, $(\delta_1 I_{\mathrm{F}}^{\mathrm{p}})_{\mathrm{rev}}$, peak potential, $E_{\mathrm{p}}^{\mathrm{rev}}$, and half-peak width, $\Delta E_{\mathrm{p/2}}^{\mathrm{rev}}$, are given by

$$(\delta_1 I_{\mathrm{F}}^{\mathrm{p}})_{\mathrm{rev}} = (\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}(4-G\theta_{\mathrm{t}})^{-1}\delta_1 E, \tag{25}$$

$$E_{\mathrm{p}}^{\mathrm{rev}} = E_0', \tag{26}$$

and

$$\Delta E_{\mathrm{p/2}}^{\mathrm{rev}} = \frac{2RT}{(\alpha+\beta)nF}\left|\ln\frac{1+\gamma}{1-\gamma}-(1/2)G\theta_{\mathrm{t}}\gamma\right| \tag{27}$$

with

$$\gamma = \sqrt{(4-G\theta_{\mathrm{t}})/(8-G\theta_{\mathrm{t}})}. \tag{28}$$

As seen from these equations, both $(\delta_1 I_{\mathrm{F}}^{\mathrm{p}})_{\mathrm{rev}}$ and $\Delta E_{\mathrm{p/2}}^{\mathrm{rev}}$ depend remarkably on the adsorption parameter $G\theta_{\mathrm{t}}$ and also on the coefficient $(\alpha+\beta)$. It is noted that these equations are the same as those of the reversible linear sweep voltammogram[13] if the term $\omega\delta_1 E$ is replaced by the sweep rate v. Namely, in this case the shape of the a.c. wave is the same as that of the reversible linear sweep voltammogram and $E_{\mathrm{p}}^{\mathrm{rev}}$ coincides with $E_{\mathrm{p}}^{\mathrm{dc}}$.

Case of $a=a_{\mathrm{OO}}=a_{\mathrm{RR}}=a_{\mathrm{OR}}=a_{\mathrm{RO}}$. In this case r and y are reduced to

$$r = [(\alpha+\beta)nF(nF/RT)k_{\mathrm{sap}}\Gamma_{\mathrm{t}}\rho^{\beta/(\alpha+\beta)}(1+\rho)^{-1}]^{-1}, \tag{29}$$

and

$$y = [(\alpha+\beta)nF(nF/RT)\omega\Gamma_{\mathrm{t}}\rho(1+\rho)^{-2}]^{-1}, \tag{30}$$

where

$$k_{\mathrm{sap}} = k_{\mathrm{s}}B_{\mathrm{O}}^{-\beta/(\alpha+\beta)}B_{\mathrm{R}}^{-\alpha/(\alpha+\beta)}\exp(-a\theta_{\mathrm{t}}), \tag{31}$$

$$\rho = \exp[(\alpha+\beta)(nF/RT)(E_{\mathrm{dc}}-E_0')], \tag{32}$$

with $E_0'=E_0+[RT/(\alpha+\beta)nF]\ln(B_{\mathrm{R}}/B_{\mathrm{O}})$, because $a_{\mathrm{OO}}-a_{\mathrm{RR}}+a_{\mathrm{OR}}-a_{\mathrm{RO}}=0$ in this simplified case (see Eq. 13). Introducing Eqs. 29 and 30 into Eqs. 5b and 5c leads to equations of the two components of the a.c. wave, from which the two peak potentials, $E_{\mathrm{p}}^{\mathrm{real}}$ and $E_{\mathrm{p}}^{\mathrm{imag}}$, are given as functions of the kinetic parameters, α, β and k_{sap}, which implicitly depends on the adsorption parameter a, as shown, for example, for the case of $\alpha+\beta=1$ in Fig. 1.

For the phase angle we obtain

$$\cot\phi = (\delta_1 I_{\mathrm{F}}^{\mathrm{real}}/\delta_1 I_{\mathrm{F}}^{\mathrm{imag}}) = (\omega/k_{\mathrm{sap}})\rho^{\alpha/(\alpha+\beta)}(1+\rho)^{-1}. \tag{33}$$

Accordingly a plot of cot ϕ against E_{dc} at any frequency has a maximum at the potential

$$[E_{\mathrm{dc}}]_{\cot\varphi=\max} = E_0' + [RT/(\alpha+\beta)nF]\ln(\alpha/\beta) \tag{34}$$

with a magnitude

$$[\cot\phi]_{\max} = (\omega/k_{\mathrm{sap}})[(\alpha/\beta)^{-\alpha/(\alpha+\beta)} + (\alpha/\beta)^{\beta/(\alpha+\beta)}]^{-1}. \tag{35}$$

The relations 33 to 35 are important because we do not need the knowledge on $[(\partial q/\partial\Gamma_{\mathrm{O}})-(\partial q/\partial\Gamma_{\mathrm{R}})]$.

When $\alpha+\beta=1$, we can determine the kinetic param-

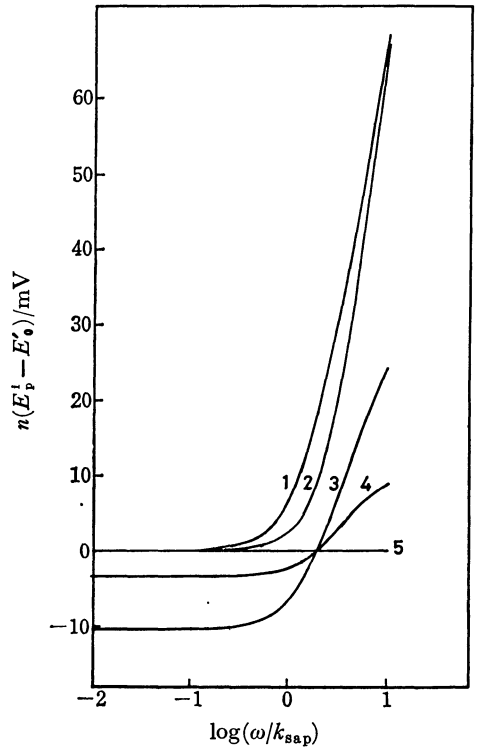

Fig. 1. Variations of E_p^{real} and E_p^{imag} as a function of $\log\,(\omega/k_{sap})$ for the case (2) with $\alpha+\beta=1$. E_p^{imag}: (1) $\alpha=0.2$, (2) $\alpha=0.4$, (5) $\alpha=0.5$ E_p^{real}: (3) $\alpha=0.2$, (4) $\alpha=0.4$, (5) $\alpha=0.5$.

eters, k_{sap} and α, from the relations 33 to 35. Then the adsorption parameter, a, can be determined from the slope of a plot of $\ln k_{sap}$ *versus* θ_t. Furthermore if $\alpha=\beta=0.5$, we have the following simplified relations for the half-peak widths of the two a.c. components, $\Delta E_{p/2}^{real}$ and $\Delta E_{p/2}^{imag}$, and the half-peak width of the $\cot\psi$ *versus* E_{dc} curve, $\Delta E_{p/2}(\cot\psi)$:

$$\Delta E_{p/2}^{i}(\mathrm{i}=\text{real or imag}) = (2RT/nF)\,|\ln\,[(1+\eta^i)/(1-\eta^i)]\,|, \tag{36}$$

$$\Delta E_{p/2}(\cot\psi) = 5.27(RT/nF), \tag{37}$$

In Eq. 36 $\eta^{real}=\sqrt{1-4\xi_{real}}$ with ξ_{real} representing the solution of the equation, $4[4+(\omega/k_{sap})^2]\xi_{real}^{3/2}=(\omega/k_{sap})^2\xi_{real}+1$, and $\eta^{imag}=\sqrt{[4+(\omega/k_{sap})^2]/[8+(\omega/k_{sap})^2]}$.

When $\alpha+\beta=1$ and $a=0$, theoretical equations of the a.c. wave are reduced to

$$\delta_1 I_F^{real} = nF(nF/RT)\omega\Gamma_t\frac{\rho}{(1+\rho)^2}\cdot\frac{\omega/(\overrightarrow{k}+\overleftarrow{k})}{[(\omega/(\overrightarrow{k}+\overleftarrow{k}))^2+1]}\delta_1 E, \tag{38}$$

$$\delta_1 I_F^{imag} = nF(nF/RT)\omega\Gamma_t\frac{\rho}{(1+\rho)^2}\cdot\frac{1}{[(\omega/(\overrightarrow{k}+\overleftarrow{k}))^2+1]}\delta_1 E, \tag{39}$$

where $\overrightarrow{k}=k_s B_O^{-\beta/(\alpha+\beta)} B_R^{-\alpha/(\alpha+\beta)}\rho^{-\alpha}$ and $\overleftarrow{k}=k_s B_O^{-\beta/(\alpha+\beta)}\cdot B_R^{-\alpha/(\alpha+\beta)}\rho^{\beta}$ If $B_O=B_R=1$, Eqs. 38 and 39 are reduced to the equations which were previously derived for analysing the electrode processes of ferredoxins irreversibly adsorbed on the mercury electrode.[5a,5b] Quite recently theoretical equations, essentially the same as Eqs. 38 and 39, have been reported by Laviron.[16]

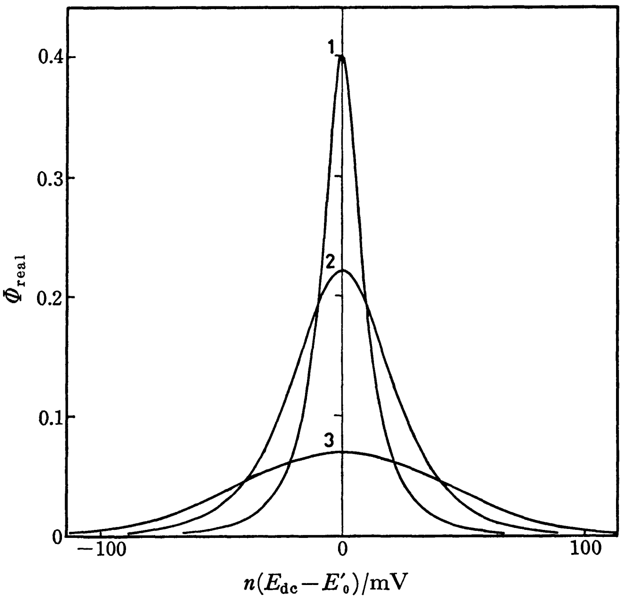

Fig. 2. Normalized real component of a.c. wave calculated by Eqs. 5b, 40, 41 and 44 with $\alpha=\beta=0.5$ and $(\omega/k_{sap})=1$. $G\theta_t$: (1) 3, (2) 1, (3) −1.

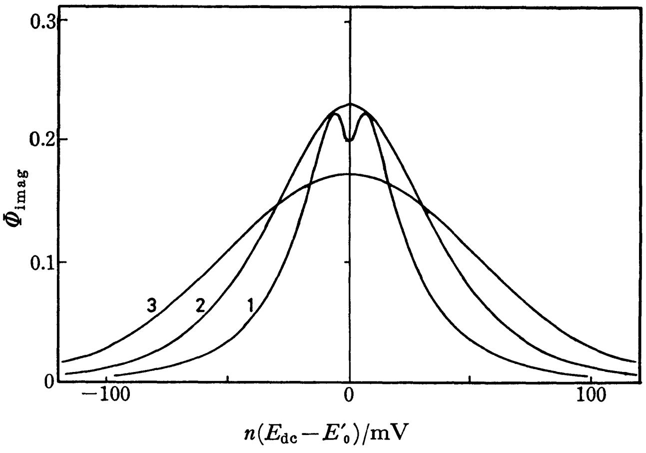

Fig. 3. Normalized imaginary component of a.c. wave calculated by Eqs. 5c, 40, 41 and 44 with $\alpha=\beta=0.5$ and $(\omega/k_{sap})=1$. $G\theta_t$: (1) 3, (2) 1, (3) −1.

Case of $a_{ii}=a_{OO}=a_{RR}$, $a_{ij}=a_{OR}=a_{RO}$ *and* $\alpha=\beta$. In this case the terms r and y are reduced to

$$r = [2\alpha nF(nF/RT)k_{sap}\Gamma_t\bar{f}^{1/2}(1-\bar{f})^{1/2}]^{-1}, \tag{40}$$

$$y = \left[2\alpha nF(nF/RT)\omega\Gamma_t\frac{(1-\bar{f})\bar{f}}{1-G\theta_t(1-\bar{f})\bar{f}}\right]^{-1}. \tag{41}$$

where

$$k_{sap} = k_s(B_O B_R)^{-1/2}\exp\,[-(1/2)(a_{ii}+a_{ij})\theta_t] \tag{42}$$

and

$$G = 2(a_{ii}-a_{ij}). \tag{43}$$

The relation between E_{dc} and $\bar{f}$ is given by

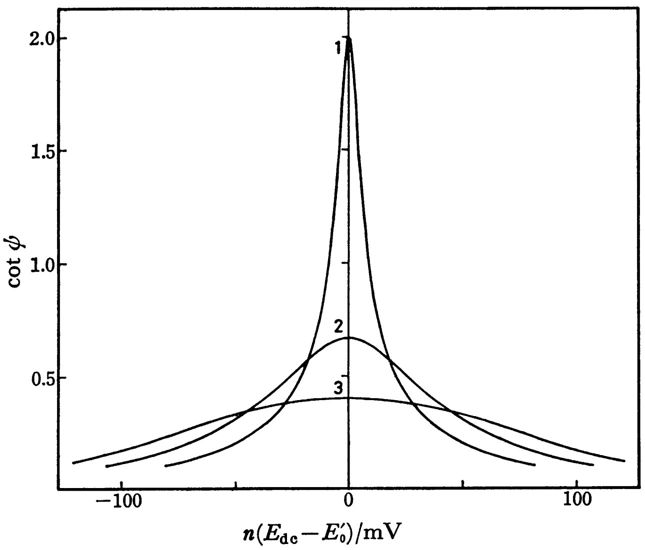

Fig. 4. D.c. dependece of phase angle calculated by Eqs. 45 and 44 with $\alpha=\beta=0.5$ and $(\omega/k_{\rm sap})=1$. $G\theta_{\rm t}$: (1) 3, (2) 1, (3) −1.

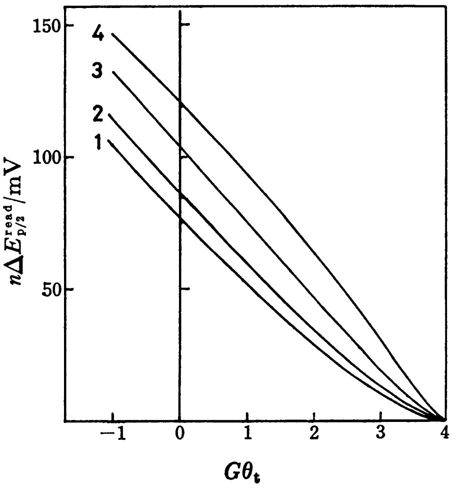

Fig. 5. Variations of $n\Delta E^{\rm real}_{\rm p/2}$ as a function of $G\theta_{\rm t}$ calculated by Eqs. 36 and 47 with $\alpha=\beta=0.5$. λ: (1) 0.5, (2) 1, (3) 2, (4) 4.

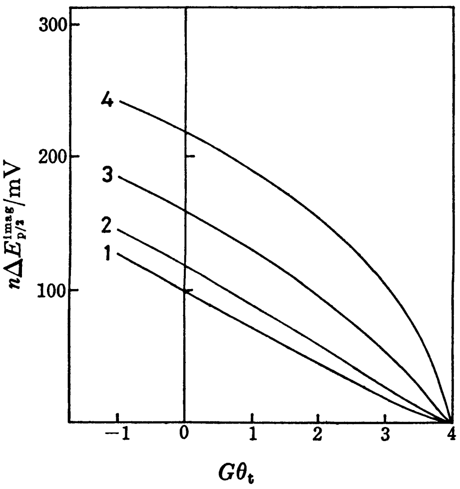

Fig. 6. Variations of $n\Delta E^{\rm imag}_{\rm p/2}$ as a function of $G\theta_{\rm t}$ calculated by Eqs. 36 and 47 with $\alpha=\beta=0.5$. λ: (1) 0.5, (2) 1, (3) 2, (4) 4.

$$E_{\rm dc}=E'_0+(RT/2\alpha nF)[\ln(\bar{f}/(1-\bar{f}))+(1/2)(1-2\bar{f})G\theta_{\rm t}] \tag{44}$$

with $E'_0=E_0+(RT/2\alpha nF)\ln(B_{\rm R}/B_{\rm O})$, because $a_{\rm OO}-a_{\rm RR}+a_{\rm OR}-a_{\rm RO}=0$ in this simplified case. Thus the a.c. wave is expressed by Eqs. 5a, 5b, and 5c with Eqs. 40, 41, and 42 and is shown to be symmetrical with respect to the potential $E'_0=E^{\rm dc}_{\rm p}$. Also Eq. 42 predicts that ln $k_{\rm sap}$ depends lineally on $\theta_{\rm t}$. The normalized a.c. waves, $\Phi_{\rm real}\equiv\delta_1 I^{\rm real}_{\rm F}/nF(nF/RT)\omega\Gamma_{\rm t}\delta_1 E$ and $\Phi_{\rm imag}\equiv\delta_1 I^{\rm imag}_{\rm F}/nF(nF/RT)\omega\Gamma_{\rm t}\delta_1 E$, for different values of $G\theta_{\rm t}$ at $\alpha=\beta=0.5$ and $(\omega/k_{\rm sap})=1$ are illustrated in Figs. 2 and 3.

Furthermore we obtain

$$\cot\psi=\frac{\omega}{k_{\rm sap}}\cdot\frac{(\bar{f})^{1/2}(1-\bar{f})^{1/2}}{1-G\theta_{\rm t}(1-\bar{f})\bar{f}} \tag{45}$$

This equation predicts that the $\cot\psi$ *versus* $E_{\rm dc}$ curve has a maximum for $4>G\theta_{\rm t}\geqslant-4$ or minimum for $G\theta_{\rm t}<-4$ at E'_0 with a magnitude

$$[\cot\psi]_{E_{\rm dc}=E'_0}=(\omega/k_{\rm sap})[2/(4-G\theta_{\rm t})]\equiv\lambda. \tag{46}$$

Figure 4 shows the $\cot\psi$ *versus* $E_{\rm dc}$ curves for different values of $G\theta_{\rm t}$ at $\alpha=\beta=0.5$ and $(\omega/k_{\rm sap})=1$.

In this case we can determine the kinetic and adsorption parameters by the following two methods if α is known.

Method (a): When $\alpha=\beta={\rm A}$, $\Delta E^{\rm i}_{\rm p/2}$ is given by (for $G\theta_{\rm t}\neq 0$)

$$\Delta E^{\rm i}_{\rm p/2}=(RT/{\rm A}nF)\left|\ln\frac{1+\sqrt{1-4\xi_{\rm i}}}{1-\sqrt{1-4\xi_{\rm i}}}-(1/2)G\theta_{\rm t}\sqrt{1-4\xi_{\rm i}}\right|. \tag{47}$$

In this equation i=real or imag and $\xi_{\rm real}$ and $\xi_{\rm imag}$ respectively are the solutions of the following two equations; $(4-G\theta_{\rm t})^2(1+\lambda^2)\xi^{3/2}_{\rm real}=(1-G\theta_{\rm t}\xi_{\rm real})^2+(\lambda/2)^2(4-G\theta_{\rm t})^2\xi_{\rm real}$ and $(1-G\theta_{\rm t}\xi_{\rm imag})^2+(\lambda/2)^2(4-G\theta_{\rm t})^2\xi_{\rm imag}=2(4-G\theta_{\rm t})(1+\lambda^2)(1-G\theta_{\rm t}\xi_{\rm imag})\xi_{\rm imag}$, where λ is defined by Eq. 46. Dependences of $\Delta E^{\rm i}_{\rm p/2}$'s on $G\theta_{\rm t}$ for different values of λ at $\alpha=\beta=0.5$ are shown in Figs. 5 and 6. Since λ can be estimated from $(\delta_1 I^{\rm real}_{\rm F}/\delta_1 I^{\rm imag}_{\rm F})_{E_{\rm dc}=E'_0}$ and $\Delta E^{\rm i}_{\rm p/2}$'s are functions of $G\theta_{\rm t}$ and λ only, we can determine $k_{\rm sap}$ and $G\theta_{\rm t}$ from λ and either $\Delta E^{\rm real}_{\rm p/2}$ or $\Delta E^{\rm imag}_{\rm p/2}$. As shown in Fig. 3, $\delta_1 I^{\rm imag}_{\rm F}$ has a maximum or minimum at $E_{\rm dc}=E'_0$. When $\delta_1 I^{\rm imag}_{\rm F}$ has a minimum at $E_{\rm dc}=E'_0$, $\Delta E^{\rm imag}_{\rm p/2}$ of Eq. 47 means a difference between the dc potentials at which the current value is one-half that observed at $E_{\rm dc}=E'_0$.

Method (b): The half-peak width of the $\cot\psi$ *versus* $E_{\rm dc}$ curve, $\Delta E_{\rm p/2}$ $(\cot\psi)$, depends on $G\theta_{\rm t}$ ($G\theta_{\rm t}\neq 0$ in this case) only and is given by

$$\Delta E_{\rm p/2}(\cot\psi)=(RT/{\rm A}nF)\times|\ln[(1+\sqrt{1-4\delta})/(1-\sqrt{1-4\delta})]-(1/2)G\theta_{\rm t}\sqrt{1-4\delta}| \tag{48}$$

with

$$\delta=[1/2(G\theta_{\rm t})^2]\{[2G\theta_{\rm t}+(4-G\theta_{\rm t})^2]-\sqrt{[2G\theta_{\rm t}+(4-G\theta_{\rm t})^2]^2-4(G\theta_{\rm t})^2}\}.$$

Thus we can determine $G\theta_{\rm t}$ from this relation and finally k_{sap} from λ when $G\theta_t$ is given. As described above, the cot ψ *versus* E_{dc} curve has a minimum at E_0' when $G\theta_t<-4$. In this case $\Delta E_{p/2}(\cot\psi)$ of Eq. 48 means a difference between the dc potentials at which the value of cot ψ is one-half that observed at $E_{dc}=E_0'$.

Finally since the sum of the parameters, $(a_{11}+a_{1J})$, can be determined from the slope of a plot of ln k_{sap} against θ_t, the two parameters, a_{11} and a_{1J}, can be determined when G is given.

Application of these simplified equations to the electrode processes of ferredoxins irreversibly adsorbed on the surface of the dropping mercury electrode[17] will be reported in a succeeding paper.

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