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The non-integer cyclovoltammetric electron-exchange numbers of reversible redox reactions of adsorbates: theoretical considerations

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Abstract Two types of non-integer electron-exchange numbers from uniform and reversible surface-redox reactions without side reactions have been distinguished. The first being the apparent number, n_{app} , of the apparent faradaic charge corresponding to cyclovoltammetric peak areas above the interpolated baseline, and the second the thermodynamically defined surface-redox valency, n' , of Nernstian slopes of cyclovoltammetric peak potentials depending on different solution pH. An analytical expression has been derived for n_{app} based on a simplified capacitive equivalent circuit and for n' using the potential-dependent free adsorption energies of the reactants involved. It should be pointed out that the different experimental values of n_{app} and n' refer to the same integer number of electrons per molecule oxidized or reduced.

Keywords Chemically modified electrodes · Cyclic voltammetry · Double layer · Adsorption

Introduction

It is well known that in contrast to thin-layer voltammetry of dissolved species [1, 2] the voltammetry of redoxactive adsorbates [3], polymer layers [3] and self-assembled monolayers [4] is characterized by non-ideal Nernstian responses, mainly caused by lateral interaction [3, 5, 6, 7, 8], interfacial potential distribution (IPD) of the electrical double layer [9] and/or slow electron transfer (ET) [10], which can cause the peaks to become broader or narrower. The computation of such systems is complicated by the possible superimposition of these effects, which require multiparameter fits; however, in some special cases analytical expressions can be derived. In this study, analytical expressions have been derived for the non-integer electron-exchange number, n_{app} , of

the apparently lowered faradaic charge of cyclovoltammetric (CV) peak areas and for the non-integer electron-exchange numbers, n' , in relation to the dependence of the peak potential, E_p , on the pH of the redoxactive adsorbates. In a preceding article n' was thermodynamically defined as the “surface redox valency” [11]. The physicochemical origins of these numbers are quite different: n_{app} can be deduced from the IPD model developed by Smith and White [9], whereas n' is derived from the potential dependence of the free adsorption energies of the molecules involved. In both cases side reactions should be excluded.

Taking lateral interaction into consideration, the concentration-dependent surface-activity coefficients were sometimes replaced by a mean value, g , which includes the electron number, n , and allows the calculation of broadened ($g < 1$) or sharpened ($g > 1$) peaks [12, 13, 14, 15]. Here, it is shown that the faradaic charge of the area of a CV peak is unchanged by lateral interaction. Some former experimental results for n_{app} are discussed in the Results and discussion section.

Theoretical considerations

Lateral interaction

Generally the lateral interaction of adsorbates is taken into account by inserting the surface-activity coefficients γ_{O} and γ_{R} into the Nernst equation [3, 5, 6, 7, 8]

$$\gamma_{\text{O}} = \exp[-(r_{\text{OO}}\Gamma_{\text{O}} + r_{\text{OR}}\Gamma_{\text{R}})], \quad (1)$$

$$\gamma_{\text{R}} = \exp[-(r_{\text{RR}}\Gamma_{\text{R}} + r_{\text{RO}}\Gamma_{\text{O}})], \quad (2)$$

for the oxidized and reduced species O and R, respectively, where r_{OO} , r_{OR} , r_{RR} and r_{RO} are the lateral interaction parameters for OO, OR, RR and RO interactions due mainly to electrostatic forces and $\Gamma_{\text{O,R}}$ the corresponding surface concentrations. The possibility that these parameters are dependent upon potential should be neglected. The surface concentration, Γ_{O} , is given by [3, 5, 6, 7, 8]

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$$\Gamma_O = \Gamma_T \frac{\exp P}{1 + \exp P}, \quad (3)$$

where $P = (nF/RT)(E - E'_o) + (r_O + r_R)\Gamma_O - r_R\Gamma_T$, with $r_O = r_{OO} - r_{OR}$, $r_R = r_{RR} - r_{RO}$ and $\Gamma_T = \Gamma_O + \Gamma_R \cdot E'_o$ is the halfwave (peak) potential in the absence of lateral interaction. In Eq. (3) $(r_O + r_R)\Gamma_O - r_R\Gamma_T$ can also be written as $r_O\Gamma_O - r_R\Gamma_R$. In a coupled proton transfer, where the adsorbate charges, z , remain unchanged during the redox reaction, ideal Nernstian behaviour can also be expected at $\Gamma_T \neq 0$. Hence, in taking into account the mainly electrostatic contributions

$$r_{OO} = r_{OR} = r_{RR} = r_{RO} \quad (4)$$

the interaction parameters cancel out.

For the peak potential, E_p , at $\Gamma_O = \Gamma_R = \Gamma_T/2$ the exponent of Eq. (3) must be zero. Then, E_p becomes [3, 5, 6, 7, 8]

$$E_p = E'_o + RT(r_R - r_O)\Gamma_T/2nF. \quad (5)$$

For the faradaic charge, Q , it holds that $Q = nF\Gamma_O$, where Γ_O is given by Eq. (3). The current is obtained by differentiation [3, 5, 6, 7, 8],

$$i = dQ/dt = \frac{n^2 F^2 N_T v \exp P}{RT \{ [1 + \exp P]^2 - (r_O + r_R)\Gamma_T \exp P \}} \equiv C_{ps} v, \quad (6)$$

considering that $nFN_T (d\Gamma_O/dt) = nFA\Gamma_T (d\Gamma_O/dt) = \Gamma_T i$, $dE/dt = v$ and A is the electrode area. With $P=1$, the peak current, i_p , becomes

$$i_p = \frac{n^2 F^2 N_T v}{RT [4 - \Gamma_T (r_O + r_R)]}. \quad (7)$$

In Eq. (6) C_{ps} , can be defined as a redox pseudocapacitance [1].

Now the faradaic charge can be expressed by the integral

$$Q = \int_{-\infty}^{\infty} C_{ps} d(E - E'_o) = \frac{nFN_T \exp P}{1 + \exp P} \Big|_{E-E'_o=-\infty}^{\infty} = nFN_T, \quad (8)$$

which is another way of expressing Eq. (3). According to Eq. (8) the integration gives the integer electron numbers of Faraday's law which are not influenced by lateral interaction.

The apparent non-integer charge number

In order to derive an analytical expression for n_{app} the IPD model of an electroactive film developed by Smith and White [9] is transformed into a suitable equivalent circuit of an ad-layer consisting of the two capacitive parallel circuits shown in Fig. 1. Because only reversible redox reactions are taken into consideration, no

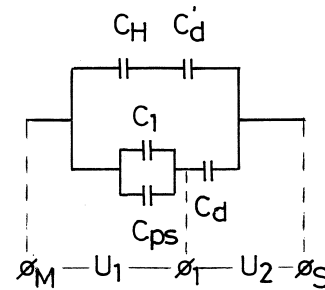


Fig. 1. Simplified equivalent parallel circuit for an electroactive adsorbate: the *top circuit*, with the capacitances C_H of the Helmholtz layer, and C'_d of the diffuse layer in series, refers to the uncovered electrode surface, the *bottom circuit* to the electroactive adsorbate with the potential-dependent redox pseudocapacitance, C_{ps} , together with its inherent capacitance, C_1 , both being in series with C_d of the corresponding diffuse double layer. ϕ_M , ϕ_1 and $\phi_S=0$ are the Galvani potentials of the electrode, the adsorbate and the electrolyte, respectively. ϕ_1 should coincide with ϕ_{PET} , the potential at the plane of electron transfer. The potential differences are $U_1 = \phi_M - \phi_1$ and $U_2 = \phi_1 - \phi_S = \phi_1$

resistances are introduced. The top circuit, with the capacitances, C_H , of the Helmholtz layer and C'_d of the diffuse double layer, in series, refers to the uncovered electrode surface. In further evaluation, its charging current can be neglected because it cancels out by baseline subtraction. In the bottom circuit, referring to the electroactive adsorbate, the redox pseudocapacitance C_{ps} is introduced. In the absence of lateral interaction and double-layer effects it can be written as [1]

$$C_{ps} = \frac{n^2 F^2 N_T \exp [nF(E - E'_o)/RT]}{RT \{ 1 + \exp [nF(E - E'_o)/RT] \}^2}. \quad (9)$$

C_1 in Fig. 1 is the inherent capacitance of the redox-inactive backbone of the adsorbate

$$C_1 = \epsilon_o \epsilon_1 / d_1, \quad (10)$$

where Δ_o is the permittivity of free space, Δ_1 the dielectric constant and d_1 the thickness of the ad-layer.

In the case of a proton-coupled redox reaction without changing the charge number, z , C_1 can be assumed to be independent of potential. Within the potential range of the redox reaction the total capacitance of the ad-layer is the sum of C_{ps} and C_1 :

$$C_{ad} = C_{ps} + C_1. \quad (11)$$

Outside the peak with $C_{ps}=0$, C_{ad} becomes C_1 . The ad-layer should be in direct contact with the electrolyte solution; therefore, C_2 of an additional insulating layer [9] is not needed here. C_d in series with C_{ad} is again the diffuse-layer capacitance governed by the Gouy-Chapman model [1]. ϕ_M , ϕ_1 and $\phi_S=0$ are the Galvani potentials of the electrode, the adsorbate and the solution, respectively. The potential differences are denoted as

$$U_1 = \phi_M - \phi_1 \quad (12)$$

and

$$U_2 = \emptyset_1 - \emptyset_s = \emptyset_1. \quad (13)$$

\emptyset_1 (\emptyset_2 , or ψ in the literature) should also be the potential in the plane of the redox centres, also denoted as the plane of ET (PET). The Potential drop, U , between the electrode and the solution is given by

$$U = U_1 + U_2 \quad (14)$$

and the total capacitance, C_T , of the bottom circuit by

$$1/C_T = 1/(C_1 + C_{ps}) + 1/C_d. \quad (15)$$

With these denotations U_1/U becomes

$$\begin{aligned} U_1/U &= C_T/(C_1 + C_{ps}) = \left\{ [1/(C_1 + C_{ps}) + 1/C_d] (C_1 + C_{ps}) \right\}^{-1} \\ &= [1 + (C_1 + C_{ps})/C_d]^{-1} \end{aligned} \quad (16)$$

The apparent faradaic charge, Q_{app} , of the CV peak is calculated by background subtraction followed by integration. The baseline should be constructed by interpolation of the baselines beyond the peak, where C_{ps} is zero. Then, Q_{app} can be expressed as

$$\begin{aligned} Q_{app} &= \int [C_T - (1/C_1 + 1/C_d)] dU \\ &= \int \left\{ [1/(C_1 + C_{ps}) + 1/C_d]^{-1} - (1/C_1 + 1/C_d)^{-1} \right\} dU. \end{aligned} \quad (17)$$

However, Eq. (17) cannot be integrated directly, because C_{ps} is here a function of the reduced potential drop $U_1 - U_{o1}$ but not of the entire potential drop $U - U_o$, where U_o and U_{o1} are the reference potentials of the electrode against the PET at $\Gamma_o = \Gamma_R$ outside or inside the diffuse double layer. If one expresses dU by dU_1 by using Eq. (16), then Eq. (17) becomes

$$\begin{aligned} Q_{app} &= \int \left\{ [1/(C_1 + C_{ps}) + 1/C_d]^{-1} - (1/C_1 + 1/C_d)^{-1} \right\} \\ &\quad \left(1 + \frac{C_1 + C_{ps}}{C_d} \right) dU_1 \\ &= \int \left[\frac{(C_1 + C_{ps})C_d}{C_1 + C_{ps} + C_d} - \frac{1}{1/C_1 + 1/C_d} \right] \frac{C_1 + C_{ps} + C_d}{C_d} dU_1 \\ &= \int \left[C_1 + C_{ps} - \frac{C_1 + C_{ps} + C_d}{1 + C_d/C_1} \right] dU_1 \\ &= \int \left[\left(1 - \frac{1}{1 + C_d/C_1} \right) C_{ps} + C_1 - \frac{C_1 + C_d}{1 + C_d/C_1} \right] dU_1 \\ &= \frac{1}{1 + C_1/C_d} \int_{U_1 - U_{o1} = -\infty}^{\infty} C_{ps} d(U_1 - U_{o1}) \\ &= \frac{Q}{1 + C_1/C_d} = \frac{nFN_T}{1 + C_1/C_d} = n_{app}FN_T, \end{aligned} \quad (18)$$

with

$$n_{app} = \frac{n}{1 + C_1/C_d}. \quad (19)$$

In contrast to the derivation just given, the true, but hypothetical, baseline correction should yield the true faradaic charge, Q : the total charge is expressed again by the first term of Eq. (18), but the true baseline charge must be smaller by the factor $C_1/(C_{ps} + C_1)$. Then, Eq. (18) becomes

$$\begin{aligned} Q &= \int \left[\frac{1}{1/(C_1 + C_{ps}) + 1/C_d} - \frac{C_1}{C_1 + C_{ps}} \cdot \frac{1}{1/(C_1 + C_{ps}) + 1/C_d} \right] \times \\ &\quad \times \left(1 + \frac{C_1 + C_{ps}}{C_d} \right) dU_1 \\ &= \int \frac{1}{1/(C_1 + C_{ps}) + 1/C_d} \left(1 - \frac{C_1}{C_1 + C_{ps}} \right) \left(1 + \frac{C_1 + C_{ps}}{C_d} \right) dU_1 \\ &= \int \frac{(C_1 + C_{ps})C_d}{C_1 + C_{ps} + C_d} \cdot \frac{C_{ps}}{C_1 + C_{ps}} \cdot \frac{C_1 + C_{ps} + C_d}{C_d} dU_1 \\ &= \int_{U_1 - U_{o1} = -\infty}^{\infty} C_{ps} d(U_1 - U_{o1}) = nFN_T \end{aligned} \quad (20)$$

Thus, it has been shown that the underestimation of the faradaic charge of the CV peak of an adsorbate can be attributed to the simplified construction of a baseline by interpolation. It fails to take into account that the true nonmeasurable baseline goes through a minimum at the peak maximum, as was already pointed out in Smith and White's computation [9].

A prerequisite of these calculations was the constancy of C_1 and C_d under the wave. If z , and consequently C_1 changes, $1 + C_1/C_d$ of Eq. (19) can be approximated by a mean value accounting for different C_1/C_d values before and after the wave. The same holds for larger \emptyset_1 values, where, in agreement with the Gouy–Chapman model, C_d becomes potential-dependent. According to Eq. (7) lateral interaction would also have no influence on the integrals in Eqs. (18) and (20) providing that the corresponding parameters are potential-independent. The correction factor $f = 1/(1 + C_1/C_d)$ of Eqs. (18) and (19) is somewhat surprising, because it is no longer a function of C_{ps} . The interpretation would be that in conformity with Eq. (16) the relative potential drop, U_1/U , at $C_{ps} = 0$ is given by

$$U_1/U = 1/(1/C_1 + 1/C_d)C_1 = 1/(1 + C_1/C_d) = f. \quad (21)$$

Considering that the integration of the wave yields the same factor, it must be independent of potential. The same holds for Q_{app}/Q and i_{app}/i . The next line of inquiry is how the true baseline current, i_{oo} , could be calculated.

According to Fig. 2 it holds that

$$i_{true} = i_{app} + i'_{app} = i_{true}/(1 + C_1/C_d) + i'_{app} \quad (22)$$

or

$$i'_{app} = i_{true}/(1 + C_d/C_1) = C_{ps, (U - U_o)}v/(1 + C_d/C_1) \quad (23)$$

and

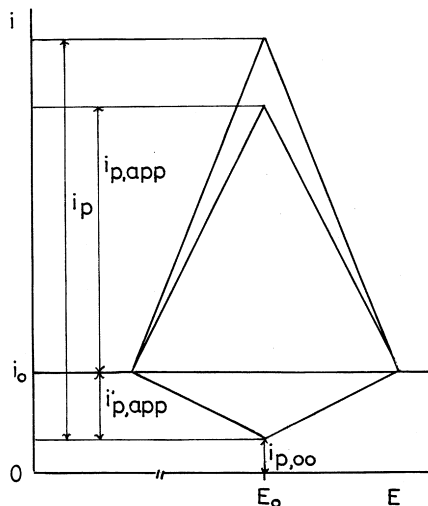


Fig. 2. Schematic representation of the different cyclic voltammetric currents i_p , i_{app} , i'_{app} , i_o and i_{oo} of an electroactive ad-layer, where i_o is the interpolated and i_{oo} the hypothetical baseline having a minimum at the peak maximum. i_p is the true and i_{app} the measured apparent peak current

$$i_{oo} = i_o - i'_{app} = \frac{v}{1/C_1 + 1/C_d} - \frac{C_{ps,(U-U_o)}v}{1 + C_d/C_1} \quad (24)$$

$$\frac{C_d v - C_{ps,(U-U_o)}v}{1 + C_d/C_1} = \frac{(C_d - C_{ps,(U-U_o)})v}{1 + C_d/C_1},$$

where i_o is the interpolated baseline current and $C_{ps,(U-U)}$ can be replaced by $C_{ps,(E-E_o)}$, leading only to a parallel shift along the x -axis.

However, the voltammetric relations for calculating n_{app} and n from the background-corrected peak area, A , can be written as

$$n = \frac{A E_x E_y}{N_T F v_{PET}} > \frac{A E_x E_y}{N_T F v} = n_{app}, \quad (25)$$

where E_x is the sensitivity (Vcm^{-1}) and E_y the sensitivity (Acm^{-1}) along the x - and y -axes of the voltammogram, respectively, and v the applied potential scan rate (Vs^{-1}). v_{PET} can be defined as the effective mean potential scan rate at the PET:

$$v_{PET} = \frac{v}{1 + C_1/C_d} \quad (26)$$

The thermodynamic non-integer charge number

In the context of electrocatalytic oxidation of the co-enzyme reduced nicotinamide adenine dinucleotide at enzyme-based biosensors many molecular redox dyes have been tested, such as Nile blue, Meldola blue, brilliant cresyl blue and coelestine blue, which exhibit good adsorption properties at graphite electrodes. An overview is given in Ref. [16]. Owing to the pH dependence of the dehydrogenase reactions as well as of the peak potentials of the adsorbates, mean values of

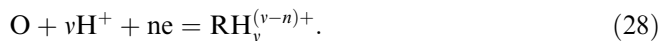
anodic and cathodic sweeps were measured. In some cases they exhibited non-Nernstian responses with decreased slopes,

$$-\Delta E_p/pH < 2.303vRT/nF < 59.16v/n \text{ mV pH}^{-1}, \quad (27)$$

at 25°C, with v being the number of protons involved in the redox reaction. For coelestine blue, for example, the slopes were 45 and 80 $mV \text{ pH}^{-1}$ for the $2e/2H^+$ and $2e/3H^+$ conversions instead of 59 and 89 $mV \text{ pH}^{-1}$. In the case of thin films, non-Nernstian behaviour was interpreted by nonstoichiometric protonation combined with insertion or expulsion of counteranions or counteranions to maintain electroneutrality [18, 19]. Such processes as well as partial charge transfer [11] should be excluded from the following derivation owing to potential-dependent adsorption energies.

A remarkable influence on the free adsorption energies at the graphite electrode can be seen by a comparison of the $E'_{o,ad}$ with the E_o values in solution. Thus, for Neutral Red a shift of -65 mV is observed for the $2H^+/2e$ redox reaction at pH 7.0 [20], which indicates that the oxidized molecules are more strongly adsorbed than the reduced molecules. Considering the previous studies on the potential dependence of adsorptiveness [21, 22, 23, 24, 25, 26], this suggests that the non-Nernstian behaviour has the same cause.

For simplicity the derivation originates from a redox reaction in solution:



The Nernst equation can be written as

$$E = E_o + \frac{RT}{nF} \ln \frac{c_o c_{H^+}^v}{c_R} = E_o + \frac{RT}{nF} \ln \frac{\Gamma_o b_{red} c_{H^+}^v}{\Gamma_R b_{ox}}. \quad (29)$$

The interfacial potential distribution is implicitly given by the adsorption coefficients relating to the Frumkin- or Henry-type isotherm at low coverages [27, 28]:

$$b_1^{-1} = \exp[\Delta G_{i,ad} + z_i F \phi_1 / RT], \quad (30)$$

where ΔG_{ad} is the free chemical adsorption energy and $z_i F \phi_1$ the additional electrical contribution of the potential $\phi_1 = \phi_{PET}$. By analogy with the interaction coefficient, γ_i , b_1^{-1} can be formally defined as the activity coefficient, $\gamma_{i,ad}$, of the adsorbate/surface interaction. No partition coefficient is needed for c_{H^+} , because it refers to the bulk concentration. Inserting Eq. (30) into Eq. (29) gives for the peak potential, E_p , at $\Gamma_o = \Gamma_R$

$$E_p = E_o + \frac{RT}{nF} [\Delta G_{o,ad} - \Delta G_{R,ad} - (v-n)F\phi_1] / RT$$

$$+ \frac{vRT}{nF} \ln c_{H^+} = E_o + (\Delta G_{o,ad} - \Delta G_{R,ad}) / nF - \left(\frac{v}{n} - 1\right) \phi_1$$

$$- \frac{2.303vRT}{nF} \text{pH}. \quad (31)$$

¹Equation (2) of Ref. 17 should be completed with 2.303 and the left side of Eq. (15) with +2e

Differentiation of Eq. (31) with respect to E_p leads to

$$\Delta E_p + \frac{\partial}{\partial E_p} \left[(\Delta G_{R,ad} - \Delta G_{O,ad})/nF + \left(\frac{\nu}{n} - 1\right)\theta_1 \right] \Delta E_p = - \frac{2.303\nu RT}{nF} \Delta pH \quad (32)$$

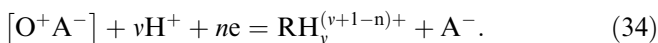
and finally to

$$\Delta E_p/\Delta pH = \frac{2.303\nu RT/nF}{1 + \frac{\partial}{\partial E} \left[(\Delta G_{R,ad} - \Delta G_{O,ad})/nF + \left(\frac{\nu}{n} - 1\right)\theta_1 \right]}. \quad (33)$$

According to an analogous derivation, Eqs. (31) and (33) also apply for the nonlinear Langmuir and Frumkin isotherm at higher concentrations at $\Gamma_O = \Gamma_R = \Gamma_{T/2}$. Following Eqs. (1), (2) and (5) potential-independent lateral interaction parameters would cancel out by differentiation, because $dr_{O,R}/dE = 0$ and at the peak maximum $d\Gamma_{O,R}/dE = 0$.

Equation (33) shows that reduced or increased Nernstian slopes can also arise in the absence of partial charge transfer, where they are only dependent on the differential quotient, which may be positive or negative in sign. It should be noted that at $\nu = n$, θ_1 cancels out, whereby $\Delta E_p/\Delta pH$ becomes independent on θ_1 .

Taking into consideration possible ion-pair formation of the oxidized phenoxazine molecules with anions A^- – possibly indicated by meldola blue precipitation with chromate (reddish-brown), picrate (reddish-brown, soluble in chloroform with a blue colour), ferrocyanide and ferricyanide complexes (violet) and chloranilic acid (violet) – Eq. (28) becomes



In a complete ion pairing, the $\Delta E_p/\Delta pH$ relation would again be that of Eq. (33), but now $G_{O,ad}$ is replaced by $\Delta G_{[O^+A^-],ad}$, which is the free adsorption energy of the ion pair, and $\frac{\nu}{n} - 1$ is replaced by $\frac{\nu+1}{n} - 1$.

Results and discussion

In order to test the validity of Eq. (19) earlier measurements with flavine adenine dinucleotide (FAD), adsorbed on spectrographic graphite rods of 6-mm diameter (Ringsdorff-Werke), were chosen [29]². The sample application of 20 μ l 0.1 mM (2 nmol) of photo-metrically checked FAD solution was done with a Hamilton microlitre syringe, after which the surface was allowed to dry in air. The areas of the cutout peaks were determined gravimetrically. The n_{app} values of seven measurements using 0.1 M phosphate buffer of pH 7 together with 1 M NaCl as a supporting electrolyte were within the range 1.81–1.90. The relative peak areas,

A/A_o , are displayed in Table 1 as a measure of the relative apparent faradaic charges of these FAD electrodes using 0.1 M phosphate buffer alone (ionic strength $J = 0.2224$ M) and the same with additional 1 M NaCl ($J = 1.2224$ M). The scan rates were varied from 800 to 200 $mV s^{-1}$. A/A_o slightly decreased from 0.931 to 0.899, leading to the linearly extrapolated limiting value of $0.8907 \pm 0.4\%$ at $\nu = 0$ $mV s^{-1}$, which permits the approximate calculation of absolute n_{app} values. In the limiting case of small θ_1 values, the factor $f = (1 + C_1/C_d)^{-1}$ can be written as

$$f = (1 + C_1/C_d)^{-1} = \left(1 + \frac{\epsilon_1/\epsilon_d}{d_1\kappa}\right)^{-1}, \quad (35)$$

where ϵ_1 and ϵ_d are the dielectric constants of the adsorbate and of the diffuse double layer having the effective thickness d_1 and κ^{-1} , respectively. Thus, A/A_o becomes

$$A/A_o = f_1/f_2 = \frac{1 + \frac{\epsilon_1/\epsilon_d}{d_1\kappa_2}}{1 + \frac{\epsilon_1/\epsilon_d}{d_1\kappa_1}} = 0.8907. \quad (36)$$

The Debye lengths $1/\kappa_i$ were calculated using $\epsilon = 40$ for the electrical double layer, this being a mean value between 6 of the first water layer and 78 of the solution [28]. They are $1/\kappa_1 = 4.60181 \text{ \AA}$ ($J = 0.2224$ M) and $1/\kappa_2 = 1.96287 \text{ \AA}$ ($J = 1.2224$ M).

Solving Eq. (36) for ϵ_1/d_1 of the adsorbate gives the interesting and plausible value of 2.04685 \AA^{-1} . Finally, the correction factors of Eq. (35) are $f_1 = 0.80940$ and $f_2 = 0.90873$, corresponding to $n_{app} = 1.62$ and 1.82, respectively. Thus, it seems that this good agreement between the experimental results and the approximate calculation may confirm the double-layer model described. In contradiction to these n_{app} values, the slope of the E_p/pH responses was 60 mV/pH , yielding $n' = n = 2.0$ [30]. Comparatively, the CV reduction of methylene blue adsorbed on a HMDE resulted in $n_{app} = 1.66$ [31] in close agreement to $n_{app} = 1.60$ obtained from constant current chronopotentiometric reduction in 0.1 M phosphate buffer [32].

Conclusions

The derivations presented here for the non-integer faradaic, n_{app} , and Nernstian, n' , values of ad-layers using

Table 1. Cyclovoltammetric peak areas of flavine adenine dinucleotide which was adsorbed on a graphite electrode using 0.1 M phosphate buffer of pH 7 relative to A_o , obtained with 0.1 M phosphate buffer / 1 M NaCl at different scan rates, ν

ν ($mV < s^{-1}$)	A/A_o
800	0.931
600	0.913
400	0.910
200	0.899

²Equation (50) of Ref. 29 should include $P_{1,2}^{1/2}$ instead of $P_{1,2}$; for Eq. (52a,b) the denominators should be completed with RT and for Eq. (59) with a factor of 2

an IPD model and various potential dependences of the free adsorption energies of oxidized and reduced molecules indicate that a net partial charge transfer need not be assumed, which, however, cannot be excluded in the case of chemisorbed species. Through analogy with the Frumkin effect on kinetics measurements, the influence of the double layer on n_{app} can easily be detected by varying the supporting electrolyte concentration. However, further analysis of n' would require tedious adsorption equilibrium measurements at different electrode potentials. Finally, it should be noted that also in cases with $\nu \neq n$ no significant contribution of the ϕ_1 term from Eqs. (31) and (33) on the measured peak potentials [20] and slopes could be established.

Potential-independent lateral interaction parameters would not change the differential quotient of Eq. (33); otherwise $d\Delta G_{\text{O,R}}/dE \gg d(r\Gamma)_{\text{O,R}}/dE$, which may be applicable at low coverages.

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