The paper is concerned with the theory of linear sweep voltammetry (LSV) and cyclic voltammetry (CV) at spherical electrodes, for the electrochemical reaction mechanism:

\[ \text{O}_{\text{ad}} + n\text{e}^{-} = \text{R}_{\text{ad}} \quad (\text{Nernstian, formal potential } E^{0}), \]

\[ \text{R}_{\text{ad}} + \text{C}_{\text{sol}} \rightleftharpoons \text{D}_{\text{sol}} \quad (\text{reversible, rate constants } k \text{ and } k^{-}). \]

The corresponding overall reaction, obtained by summing steps (1) and (2), is:

\[ \text{C}_{\text{sol}} + n\text{e}^{-} = \text{D}_{\text{sol}} \quad (\text{formal potential } E^{0}). \]

Species \( \text{O}_{\text{ad}} \) and \( \text{R}_{\text{ad}} \) form a redox catalyst couple attached to the electrode surface, and \( \text{C}_{\text{sol}} \) and \( \text{D}_{\text{sol}} \) are species soluble in the electrolyte. Direct reduction of \( \text{C}_{\text{sol}} \) to \( \text{D}_{\text{sol}} \) in a single step equivalent to the overall reaction (3) is not considered. The catalytic effect occurs if the steps (1) and (2) are kinetically more favourable than the direct charge transfer (3).

A number of electrochemical systems is known to follow mechanism (1) and (2), either with irreversible, or reversible reaction (2). In all cases electrocatalysis of species in solution is carried out by different complexes immobilized at the electrode surface. The examples include: reduction of \( \text{O}_{2} \) at a graphite electrode modified with a Cu–phenanthroline complexes [1]; oxidation of dopamine at a platinum electrode modified by nickel-hexacyanoferrate and Nafion [2]; reduction of \( \text{H}_{2}\text{O}_{2} \) at a mercury electrode modified with heteropolytungstates [3]; oxidation of \( \text{NADH} \) at a complex Toluidine Blue O-modified carbon fiber electrode [4]; oxidation of \( \text{NADH} \) at a gold electrode modified with a ruthenium complex [5]; epinephrine oxidation at an electrode modified with an Osmium complex and Nafion [6]; and ferrocyanide oxidation at an indium-tin oxide electrode modified with a ruthenium complex [7].

The theory of CV for this mechanism was presented long ago for planar electrodes. Analogous rigorous theory for spherical electrodes has not been available thus far, despite the fact that the use of spherical microelectrodes for kinetic studies is often advantageous. By adopting the integral equation formalism, combined with the recently developed adaptive Huber method for integral equations, we obtain such a rigorous theory. The theory is applicable for any value of the electrode radius \( r_{0} \), from planar electrodes \( (r_{0} \rightarrow \infty) \), to ultramicroelectrodes \( (r_{0} \rightarrow 0) \). With the decreasing electrode radii the current functions increase, gradually approaching steady-state sigmoidal waves. Equations for the dependences of the forward peak potentials on dimensionless parameter estimation.
ing planar electrodes and other conditions from Ref. [9], Molina and co-workers [11,12] discussed the theory of a number of transient techniques for mechanism (1) and (2) with irreversible reaction (2), at the assumption of the excess of substances C_{sol} and D_{sol}, when the diffusion transport (and consequently electrode geometry) do not play a role. In the most recent work [13] they have developed an easily manageable approximate explicit formula for the CV responses, assuming diffusion at spherical electrodes. The approximation works well in the limit of spherical electrodes of small size and ultramicroelectrodes, and provides accurate values of the peak potentials, even for planar electrodes. However, it does not provide accurate currents in the intermediate cases of (almost planar) spherical macroelectrodes with large radii. It is also not applicable to the case of non-negligible backward reaction (2).

With the aim of giving a more general theoretical view, in the present work a rigorous theory of the transient LSV and CV will be outlined, especially focusing on the intermediate cases of spherical electrodes, and either irreversible or reversible rapid chemical reaction (2), for which cases no theoretical results seem to be available in the literature. The present work can therefore be viewed as an extension of the theory of Aoki et al. [10], onto the case of spherical electrodes. The choice of spherical electrodes (and generally microelectrodes) for kinetic studies is well known to be advantageous over planar (macro-) electrodes [14]. In turn, the elucidation of the influence of the backward reaction (2) is important, because a too fast backward reaction may mean a reduction or even elimination of the catalytic effect. From the theory presented, simplified explicit expressions for some particular cases of interest for mechanism (1) and (2) will be obtained.

2. Theory

For consistency with Refs. [9,13], we discuss the situation when the first step (1) is realised as a reduction, during the forward CV sweep. The reverse reaction is entirely analogous, and the final equations obtained can be applied to it after appropriate change of the current/potential signs. Following Refs. [9,10,13] we assume reversible reaction (1) with negligible interactions between adsorbates. The surface coverage fractions θ_{0}(t) and θ_{k}(t) for species O_{ad} and R_{ad} are therefore linked by the Nernst equation, and they sum up to unity, which leads to their dependencies on electrode potential E(t) that in the case of the LSV or CV transients is a function of time t:

$$\theta_{0}(t) = \frac{I_{0}(t)}{I_{T}} = \frac{\exp[\eta(t)]}{1 + \exp[\eta(t)]},$$

(4)

$$\theta_{k}(t) = \frac{I_{k}(t)}{I_{T}} = \frac{1}{1 + \exp[\eta(t)]},$$

(5)

with

$$\eta(t) = \frac{nF}{RT} (E(t) - E^{0}),$$

(6)

where \(I_{0}(t)\) and \(I_{k}(t)\) are surface concentrations of O_{ad} and R_{ad}. \(I_{T} = I_{0}(t) + I_{k}(t)\), and F, R and T have their usual meaning. The CV potential perturbation is \(E(t) = E_{\text{start}} - S(y, z)\), where \(S(y, z)\) is the saw-tooth function defined by

$$S(y, z) = \begin{cases} y & \text{for } y \leq z, \\ 2z - y & \text{for } y > z. \end{cases}$$

(7)

The stoichiometric balance of species in reactions (1) and (2) implies that

$$\frac{dI_{0}(t)}{dt} = - \frac{dI_{k}(t)}{dt} = -\frac{I(t)}{nF} + k_{F} \frac{\theta_{k}(t) C_{C}(r_{0}, t) - k_{F} \theta_{0}(t) C_{D}(r_{0}, t)}{t_{T}},$$

(8)

where \(I(t)\) is the electric current (that we assume to be positive for reduction and negative for oxidation), A is the electrode surface area, \(k_{F}\) and \(k_{R}\) are the forward and backward rate constants of the reaction (2), \(C_{C}(r_{0}, t)\) and \(C_{D}(r_{0}, t)\) are the concentrations of species C_{sol} and D_{sol}, dependent on the distance \(r\) from the electrode centre, and time \(t\), and \(r_{0}\) is the electrode radius. The electric current is therefore a sum of the two terms \(I_{0}(t)\) and \(I_{k}(t)\) given by the formulae:

$$\frac{I_{0}(t)}{nF} = \frac{dI_{0}(t)}{dt},$$

(9)

$$\frac{I_{k}(t)}{nF} = k_{F} \frac{\theta_{k}(t) C_{C}(r_{0}, t) - k_{F} \theta_{0}(t) C_{D}(r_{0}, t)}{t_{T}}.$$

(10)

In the absence of species C_{sol} and D_{sol} the current reduces to the first term, which is easily obtainable by the differentiation of Eq. (5) with respect to \(t\). In view of Eq. (6) the differentiation yields:

$$\frac{I_{0}(t)}{nF} = \pm nF \frac{I(t)}{RT} \frac{\exp[\eta(t)]}{1 + \exp[\eta(t)]},$$

(11)

where “+” and “−” refer to the forward and backward potential sweeps, respectively. The second term represents a contribution from the catalytic reaction (2), and in order to calculate it, one needs to determine the concentrations \(C_{C}(r_{0}, t)\) and \(C_{D}(r_{0}, t)\) at the electrode surface \((r = r_{0})\). The main theoretical difficulty is therefore with the determination of the component \(I_{k}(t)\), so that below we concentrate on this problem. Component \(I_{0}(t)\) is given by the analytic expression (11), which can be easily applied to the experimental surface peaks, allowing one to determine parameters \(I_{T}\) and \(E^{0}\). Further discussion of \(I_{0}(t)\) is therefore unnecessary.

Assuming that diffusion is the sole mode of transport of species C_{sol} and D_{sol}, the concentrations \(C_{C}(r, t)\) and \(C_{D}(r, t)\) obey the partial differential equations:

$$\frac{\partial C_{C}(r, t)}{\partial t} = D_{C} \left[ \frac{\partial^{2} C_{C}(r, t)}{\partial r^{2}} + \frac{2}{r} \frac{\partial C_{C}(r, t)}{\partial r} \right],$$

(12)

$$\frac{\partial C_{D}(r, t)}{\partial t} = D_{D} \left[ \frac{\partial^{2} C_{D}(r, t)}{\partial r^{2}} + \frac{2}{r} \frac{\partial C_{D}(r, t)}{\partial r} \right],$$

(13)

with initial conditions

$$C_{C}(r, 0) = C_{C}^{0},$$

(14)

$$C_{D}(r, 0) = 0,$$

(15)

and boundary conditions

$$C_{C}(\infty, t) = C_{C}^{*},$$

(16)

$$C_{D}(\infty, t) = 0,$$

(17)

$$k_{F} \theta_{k}(t) C_{C}(r_{0}, t) - k_{F} \theta_{0}(t) C_{D}(r_{0}, t) - D_{C} \frac{\partial C_{C}(r, t)}{\partial r} \bigg|_{r = r_{0}} = 0,$$

(18)

$$D_{D} \frac{\partial C_{D}(r, t)}{\partial r} \bigg|_{r = r_{0}} + D_{D} \frac{\partial C_{D}(r, t)}{\partial r} \bigg|_{r = r_{0}} = 0,$$

(19)

where \(C_{C}^{0}\) is the bulk concentration of species C_{sol}, and \(D_{C}\) and \(D_{D}\) are diffusion coefficients of species C_{sol} and D_{sol}. Eqs. (18) and (19) allow one to express the current component \(I_{k}(t)\) as a concentration flux of C_{sol} or D_{sol} at the electrode.

We shall determine the catalytic current component \(I_{k}(t)\) by employing the classical method of integral equations [15]. The method relies on converting Eqs. (12)–(17) into convolution relationships between the concentrations and concentration fluxes at the electrode surface, which for spherical electrodes take the form...
(see, for example, Goodisman [16]):

\[
\begin{align*}
q_C(t_0, t) &= q_C^0 - D_C^{1/2} \int_0^t \left[ \pi^{-1/2}(t-t')^{-1/2} - \frac{D_C^{1/2}}{\rho_{\text{erex}}(t)} \exp \left( \frac{D_C^{1/2}}{\rho_{\text{erex}}(t)}(t-t')^{1/2} \right) \right] \\
& \times \frac{\partial q_C(t, r)}{\partial t} |_{t_0} \, dt,
\end{align*}
\]

(20)

\[
\begin{align*}
q_0(t_0, t) &= -D_0^{1/2} \int_0^t \left[ \pi^{-1/2}(t-t')^{-1/2} - \frac{D_0^{1/2}}{\rho_{\text{erex}}(t)} \exp \left( \frac{D_0^{1/2}}{\rho_{\text{erex}}(t)}(t-t')^{1/2} \right) \right] \\
& \times \frac{\partial q_0(t, r)}{\partial t} |_{t_0} \, dt,
\end{align*}
\]

(21)

where \( \rho_{\text{erex}}(z) = \exp(z^2)\text{erfc}(z) \). Eq. (18) combined with Eqs. (19)–(21) becomes a weakly singular Volterra integral equation of the second kind, for the unknown gradient \( \partial q_C(t, r)/\partial r |_{t_0} \). In order to obtain a dimensionless form of the integral equation, we introduce the following parameters: potential normalising factor, \( \eta = (nF/R\nu) \); dimensionless starting potential relative to the formal potential, \( u = (nF/R\nu)(E_{\text{start}} - E^0) \); dimensionless potential range, \( \lambda = (nF/R\nu)(E_{\text{start}} - E_{\text{form}}) \); dimensionless electrode curvature indicator, \( \rho = (D_0^2\alpha)^{1/2}/\rho_{\text{erex}} \); diffusion coefficient ratio, \( \gamma = (D_0/D_C)^{1/2} \); dimensionless forward rate constant of reaction (2), \( \Lambda = k_1^0 / (aD_C)^{1/2} \); and dimensionless formal potential separation \( \Delta u = (nF/R\nu)(E^0 - E^0_1) \). With these parameters, the integral equation can be written:

\[
\psi^{\text{cat}}(at) = \frac{A}{1 + \exp[u - S(at, \lambda)]} \left\{ 1 - \int_0^\infty \left[ \pi^{-1/2}(at-z)^{-1/2} - \rho_{\text{erex}} \right] \Psi^{\text{cat}}(z) dz \right\}.
\]

(22)

The unknown to be determined from Eq. (22) is the dimensionless current function defined as follows:

\[
\psi^{\text{cat}}(at) = \frac{\rho\text{fac}(t)}{nFA_C^2(aD_C)^{1/2}}.
\]

(23)

\[\psi^{\text{cat}}(at)\] differs from the current function \( \chi(\rho) \) encountered in other LSV literature [17], by the multiplicative factor \( \pi^{1/2} \).

Parameter \( \Delta u \) is basically the dimensionless difference between \( E^0 \) and \( E^0_1 \), but it can also be perceived as a measure of the equilibrium constant \( k_{jk} \). This is because there is a connection between the equilibrium constant \( k_{jk} \) and formal potentials \( E^0 \) and \( E^0_1 \), which arises owing to the fact that reactions (1)–(3) are linearly dependent.

Based on the experience from Refs. [9,10,13], a considerable diversity of the shapes of the CV \( \rho\text{fac}(at) \) responses is expected for mechanism (1) and (2) at spherical electrodes, including well formed forward peaks formally identical to those for irreversible charge transfer reactions involving soluble species, forward/reverse peak pairs formally identical to those for reversible charge transfer reactions involving soluble species, sigmoidal waves with no peaks, and intermediate shapes. These diverse responses correspond to a number of limiting cases of Eq. (22). Below we describe these limiting cases.

A. Case of very small values of \( \Lambda \)

When \( \Lambda \) tends to zero (at \( \Delta u \) negative and fixed), Eq. (22) reduces (see Appendix A) to the known formula [9,10,13]:

\[
\psi^{\text{cat}}(at) = \frac{A}{1 + \exp[u - S(at, \lambda)]} = \frac{A}{1 + \exp[\eta(t)]}.
\]

(24)

In this case there is no influence of diffusion (and consequently electrode geometry) on the voltammograms, which according to Eq. (24) then have a shape of sigmoidal waves.

B. Case of large values of \( \Lambda \)

If \( \Lambda \) is large, the left-hand side of Eq. (22) can be neglected in comparison with the right-hand side, which yields

\[
1 - \int_0^\infty \left[ \pi^{-1/2}(at-z)^{-1/2} - \rho_{\text{erex}} \right] \Psi^{\text{cat}}(z) dz = 0.
\]

(25)

Eq. (25) describes a cyclic voltammogram for the reversible reaction (3). Hence, in this limiting case the catalytic effect amounts to the realisation of the overall reaction (3) effectively as if it were a direct, single step, Nernstian charge transfer. Note that Eq. (25) does not depend on \( \Lambda \). In situations close to this limiting case it is useful to consider and apply the CV method rather than the single sweep LSV method, since the shape of the reverse response can serve as one of the diagnostic criteria, and the information content of the reverse responses may contribute to the quality of parameter estimations.

C. Case of \( \Delta u \ll 0 \)

This limiting case corresponds to an effectively irreversible reaction (2). By omitting the reverse reaction term, Eq. (22) becomes:

\[
\psi^{\text{cat}}(at) = \frac{A}{1 + \exp[u - S(at, \lambda)]} \left\{ 1 - \int_0^\infty \left[ \pi^{-1/2}(at-z)^{-1/2} - \rho_{\text{erex}} \right] \Psi^{\text{cat}}(z) dz \right\}.
\]

(26)

For \( \rho = 0 \) (planar electrodes) Eq. (26) further reduces to the integral equation in Ref. [9]. Equation (26) is very similar to that describing voltammograms for a simple irreversible charge transfer reaction involving a diffusing reactant. Formally, the only difference is that in Eq. (26) instead of a multiplicative exponential reaction rate term (characteristic for the irreversible charge transfer), we now have a rational function \( \Lambda [1 + \exp[u - S(at, \lambda)] \) involving such exponential. This similarity means that the current component \( \rho\text{fac}(t) \) possesses some features analogous to the LSV responses for irreversible charge transfer reaction involving a diffusing reactant, among other things it lacks the reverse peak in the case of potential sweep reversal. In such circumstances it is rather uninteresting to consider the CV method for the case C, since little information can be obtained from experimental data corresponding to reverse potential sweeps. We therefore focus on the single sweep method only, in this limiting case.

By pursuing the analogy with the irreversible charge transfer reaction, it is possible to obtain an explicit, infinite exponential series solution of Eq. (26), similar to those introduced by Reimnuth [18] and derived for a number of simple kinetic mechanisms [17]. For the forward potential sweep the series is:

\[
\psi^{\text{cat}}(at) = \sum_{j=1}^{\infty} b_j \exp[-j(u - at)],
\]

(27)

with expansion coefficients:

\[
b_j = \begin{cases} 
\Lambda & \text{for } j = 1 \\
\Lambda(-1)^{j-1} \prod_{i=1}^{j-1} \left( 1 + \frac{\Lambda}{T_{j+1}^2 + \rho} \right) & \text{for } j > 1 
\end{cases}
\]

(28)
The series is rigorously applicable when $\Delta u$ is sufficiently large (greater than about 4), but as we shall see below, the usefulness of the series is limited, due to practical convergence problems for still larger $\Delta u$ values.

D. Case of $\Delta u \gg 0$

When $\Delta u \gg 0$, the catalytic effect is not expected to occur, hence this case is of little interest to theoretical and applied studies, and it will not be analysed here.

E. Case of $\rho = 0$

The limit $\rho = 0$ corresponds to $r_0 \to \infty$, when the electrode becomes effectively planar. This situation has been studied by Aoki et al. [10].

F. Case of $\rho \gg 1$

When parameter $\rho$ is very large (which corresponds to very small electrode radii) the concentration profiles approach steady-state concentrations characterised by $\partial C_2(r, t)/\partial t = 0$ and $\partial C_0(r, t)/\partial t = 0$ in Eqs. (12) and (13). By replacing the integrals involving kernel functions $\text{erex}(\rho(at - z)^{1/2})$ and $\text{erex}((\rho/\gamma)(at - z)^{1/2})$ in Eq. (22), by their asymptotic forms for $\rho \gg 1$ we obtain (see Appendix A) the steady-state current function for this limiting case:

$$
\psi^{\text{cat}}(at) = \frac{1}{1 + (\Delta u/\rho)} + \frac{1}{1 + (\Delta u/\rho) + \exp(\Delta u)} + \exp(-\Delta u)
$$

The maximum (limiting) steady-state current function value $\psi^{\text{cat}}_{\text{max}}$ resulting from Eq. (29) is:

$$
\psi^{\text{cat}}_{\text{max}} = \frac{\Lambda}{1 + \Lambda/\rho},
$$

so that the half-wave potential $E_{1/2}$ defined by the condition $\psi^{\text{cat}}(at) = \psi^{\text{cat}}_{\text{max}}/2$ is:

$$
E_{1/2} = E^0 + \frac{RT}{nF} \ln \left[ \frac{1 + \Lambda/\rho}{1 + (\Lambda/\rho) + \exp(\Delta u)} \right].
$$

The slope of the normalised steady-state current function versus $\eta(t)$ at $E(t) = E_{1/2}$ is independent of model parameters, and equals $d[\psi^{\text{cat}}(at)/\psi^{\text{cat}}_{\text{max}}]/d\eta(t)|_{E(t) = E_{1/2}} = 1/4$.

3. Computational

Eq. (22) was solved using the recently developed adaptive Huber method [19–22]. Results for the limiting case of $\Delta u \to -\infty$ have been obtained by analogously solving the integral equation (26) corresponding to the irreversible reaction (2), rather than by substituting highly negative finite values for $\Delta u$ in Eq. (22). The adaptive Huber method yields results with the accuracy close to the prescribed error tolerance. Absolute error tolerance $tol = 10^{-6}$ for the errors of the $\psi^{\text{cat}}(at)$ function values was used in all calculations. For the determination of peak positions, the current functions have been tabulated with the $at$ step of 0.001, which provides an estimate of the accuracy of the peak positions.

4. Results and discussion

We first present results for the limiting case C, which is easier to comprehend and to analyse than the general case, and then we pass to considering the effect of the backward reaction (2). Finally, we provide some suggestions for the experimental data analysis.

While interpreting the effect of variations of dimensionless parameters $\Lambda$ and $\rho$, on the voltammograms, one should keep in mind that the variations may occur in a single electrochemical system as a result of changing the sweep rate $v$, but they can also occur when $v$ is kept constant, but different systems are considered (differing by rate constant $k$, diffusion coefficients, or electrode radius).

4.1. Results for the limiting case C

Conventional LSV experiments require that the starting potential $E_{\text{start}}$ be chosen sufficiently distant from $E^0$ so that the voltammograms become independent on $E_{\text{start}}$. In the case of solving Eq. (26), this has been ascertained by taking $u = 15$. For $u \geq 15$ no visible effect of $u$ was recorded. The remaining two dimensionless model parameters of Eq. (26) were varied in the domain $0.05 \leq \Lambda \leq 10^4$ and $0 \leq \rho \leq 1$. The calculations reveal that both parameters have a significant influence on the current function. Fig. 1 presents selected simulated current functions, showing that with the increase of the $\rho$ parameter values (which corresponds to the decrease of the electrode radius) the current function values increase, gradually (but rather slowly) approaching the steady-state in which the current function has a sigmoidal shape (limiting case $F$ previously mentioned). The effect of $\Lambda$ on the current function is, in turn, analogous to that observed for planar electrodes [9,10]. For very small $\Lambda$ a relatively small sigmoidal wave is observed at highly negative potentials, which corresponds to the limiting case $A$ previously mentioned. With increasing $\Lambda$, the current function maximum increases, a distinct peak shape is observed, and the peak moves towards more positive potentials. Figs. 2 and 3 illustrate this behaviour more quantitatively, in terms of the computed dependencies of the current function peak height $\psi^{\text{cat}}_p$ and potential $E_p$ on $\Lambda$ and $\rho$. A close inspection of these results reveals that in the limit of large $\Lambda$ and small $\rho$ (which is the case of main interest for the present study), the current function peak height $\psi^{\text{cat}}_p$ approaches the value $0.9458 = 0.2797\pi^{1/2}$, characteristic of a single irreversible charge transfer reaction involving a diffusing reactant, at planar electrodes, and subject to Butler–Volmer kinetics with a charge transfer coefficient equal unity [17]. The value also agrees with Fig. 1 in Ref. [9].
Fig. 2. Theoretical effect of model parameter $\lambda$, on the current function forward peak height $\Psi_{p}^{\text{cat}}$ (a) and dimensionless peak potential $n_{p} = (nF/RT)(E_{p} - E^*)$ (b) in the limiting case C, at various values of the parameter $\phi$ (for the lines from bottom to top, $\phi = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and $1.0$). Points joint by dashed lines denote results of solving Eq. (26). Solid lines denote predictions of the approximate formulae (32) and (33).

The behaviour is well comprehensible in view of the aforementioned similarity of this limiting case to the LSV theory for such irreversible charge transfer reaction. For large $\lambda$ the unity in the denominator of Eqs. (5) and (26) can be neglected, compared to the exponential term, because the peak is located at highly positive $u = at = \eta(t)$ values. Eq. (26) then becomes equivalent to that for the irreversible charge transfer involving a diffusing reactant, with $\lambda$ playing the role of the conditional rate constant of the heterogeneous charge transfer reaction. Owing to the fact that at small $\rho$ the effect of electrode sphericity can be considered as a correction (in the framework of the perturbation analysis) with $\rho$ being the perturbation parameter [16], the effect of $\rho$ on $\Psi_{p}^{\text{cat}}$ is approximately described by a linear function of $\rho$, or by a low order polynomial in $\rho$, at small $\rho$.

Based on the simulation data obtained, an approximate formula

$$\Psi_{p}^{\text{cat}} \approx 0.4958 + 0.7251 \rho + 0.1110 \rho^2$$

(32)

has been deduced to describe well the $\Psi_{p}^{\text{cat}}$ variations in this limiting case of large $\lambda$ (for $\lambda$ greater than about 200, as is seen in Figs. 2a and 3a), and for $\rho$ within the range considered here. For still larger $\rho$ the dependence of $\Psi_{p}^{\text{cat}}$ on $\rho$ deviates from the almost linear Eq. (32), since for $\rho \to \infty$ Eq. (24) predicts a nonlinear effect of $\rho$ on the current. The analysis of the simulated peak potentials (see Figs. 2b and 3b) reveals in turn that the following approximate formula describes the variations of the forward peak potential with $\lambda$ and $\rho$, when $\lambda$ is greater than about 10, and $\rho$ lies within the range.
considered here \((0 \leq \rho \leq 1)\):
\[
\eta_p = \left( \frac{nF}{RT} \right) (E_p - E^0) \approx -0.7797 + \ln(\Lambda) - 2.4853 \rho + 0.3123 \rho^2.
\]

\(\eta_p\) is the peak potential, \(\Lambda\) is the parameter of the model, \(E_p\) is the peak potential, and \(E^0\) is the standard potential. The peak potential will be a linear function of \(\ln(\Lambda)\) in the limit of large \(\Lambda\) one can combine \(\Lambda\) with \(u\), resulting in an integral equation that depends on \(\ln(\Lambda) - u\) rather than on \(u\) and \(\Lambda\) separately. The peak potential will be a linear function of \(\ln(\Lambda)\) in the limit of large \(\Lambda\). The predictions of Eq. (33), observed in the limit of small \(\Lambda\) (\(\Lambda\) smaller than about 10, see Figs. 2b and 3b), may be partially caused by the difficulty to determine precisely the peak potentials in the situation when the LSV has a nearly sigmoidal wave shape.

Current functions obtained by solving Eq. (26) have been compared with the current functions predicted by the series expansion (27) and (28), and a good agreement between these two methods of computing \(\eta_{\text{cat}}(at)\) has been obtained, confirming the correctness of the calculations. Unfortunately, the series can be computationally summed up practically only for the initial, rising parts of the voltammograms. The potential range in which series (27) and (28) can be safely summed up at \(\rho = 0\) is roughly defined by the condition:
\[
\eta(t) \geq \begin{cases} 
0.02 & \text{for } \Lambda \leq 1.772 \\
0.07 & \text{for } 1.772 < \Lambda < 17.72 \\
\ln(\Lambda) - 1.894 & \text{for } \Lambda \geq 17.72
\end{cases}
\]

which has been determined by numerical experimentation. With increasing \(\rho\) the summability range increases slightly, but it is difficult to provide a specific summability condition dependent both on \(\Lambda\) and \(\rho\). In overall, the series (27) is not very useful for the computations of \(\eta_{\text{cat}}(at)\).

4.2. Effect of the backward reaction (2)

In the case of the general Eq. (22), most of the calculations have been performed assuming \(u = 20\). The value of \(u\) has been increased (compared to \(u = 15\) used for solving Eq. (26)), in order to release the adaptive Huber method [19–22] from the efforts to accurately resolve the initial current spike at \(at = 0\), which theoretically occurs as a result of the potential jump to \(E_{\text{start}}\), but which is uninteresting
Fig. 5. Theoretical effect of the model parameter \( \Delta u \) on steady-state cyclic voltammograms calculated from Eq. (29), for \( \Lambda = 10 \) (a); \( 10^3 \) (b); and \( 10^4 \) (c). Parameter \( \rho = 100 \) in every case. The values of \( \Delta u \) are: \(-\infty\), \(-6\), \(-5\), \(-4\), \(-3\), and \(-2\), for the curves from left to right, respectively.

from the point of view of the CV theory and applications, and is normally not discussed. This current spike is more difficult to resolve when the backward reaction (2) is present, because it resembles more the singular current characteristic of potential step transients for reversible charge transfer reactions involving soluble species, and therefore requires very dense time grid close to \( at = 0 \).

Equal diffusion coefficients (\( \rho = 1 \)) have been assumed in calculations, since this is a frequent experimental situation. Parameters \( \Lambda \) and \( \rho \) were again varied in the domains \( 0.05 \leq \Lambda \leq 10^4 \) and \( 0 \leq \rho \leq 1 \). Parameter \( \Delta u \) was varied within the range \( -10 \leq \Delta u \leq 0 \), depending on the actual \( \Lambda \) value.

Qualitatively, the effect of the backward reaction (2) on cyclic voltammograms can be characterised by studying the influence of \( \Delta u \) on the voltammograms obtained for various \( \Lambda \) and \( \rho \) values. Typical results of such investigations pertinent to transient CV responses are depicted in Fig. 4. The qualitative effect of \( \Delta u \) is somewhat different for different \( \Lambda \), but it is not particularly affected by the choice of \( \rho \), as long as \( \rho \) is small enough for the voltammograms to possess a peak shape. For small \( \Lambda \) (see Fig. 4a) the effect of \( \Delta u \) is almost unnoticeable, in agreement with the properties of the limiting case A mentioned above. For moderate and large \( \Lambda \) the increase of \( \Delta u \) (starting from \( \Delta u \rightarrow -\infty \), and negative values), causes a gradual transition between the peak shape typical for irreversible charge transfer reaction involving soluble species \( C_{sol} \) (cf. the case of large \( \Lambda \) in Refs. [9,13]), to the peak shape resembling that for the quasi-reversible charge transfer reaction (3) involving soluble species \( C_{sol} \) and \( D_{sol} \) (with the above mentioned limiting case B obtained when \( \Lambda \rightarrow \infty \)). Among other things this means that for \( \Delta u \rightarrow -\infty \) the reverse CV peak is absent, while for sufficiently large \( \Delta u \) (a value dependent on the choice of \( \Lambda \) both the forward and reverse peaks are seen. Such a pair of peaks moves towards negative potential values when \( \Delta u \) increases, because the peaks follow the formal potential of the overall reaction (3) (cf. Fig. 4b and c).

Similar transition between irreversible/reversible responses is also observed under steady-state conditions for large \( \rho \), for voltammograms described by Eqs. (29)–(31). Representative examples of such voltammograms are depicted in Fig. 5. When \( \Lambda/\rho \ll 1 \), the \( \Delta u \)-dependent terms in the denominator of Eqs. (29) and (31) are small compared to other terms, so that there is almost no effect of \( \Delta u \) on the voltammograms, and \( E_{1/2} = E^0 \), as is expected for an irreversible wave (see Fig. 5a). With increasing \( \Lambda/\rho \) the effect of \( \Delta u \) becomes gradually more noticeable (see Fig. 5b and c), and it amounts to a shift of the wave along the potential axis. When
A quantitative representation of the effect of $\Delta u$ on the transient voltammograms is obtained by considering the dependencies of the forward peak height and potential on the parameters $\Lambda$, $\rho$, and $\Delta u$. Representative plots of such dependencies are depicted in Figs. 6 and 7. As can be seen in Fig. 6a, in the region of moderate $\Lambda$ values the current function peak height $\Psi_{\text{cat}}^\rho$ initially increases with increasing $\Lambda$, and the dependence of $\Psi_{\text{cat}}^\rho$ on $\Lambda$ and $\rho$ is almost identical as it was in the case of $k_0 = 0$. However, for larger $\Lambda$ the peak height slightly decreases, finally reaching the value characteristic of the reversible reaction (3). The more negative $\Delta u$, the later along the $\Lambda$ scale this transition occurs. The $\Psi_{\text{cat}}^\rho$ value corresponding to $\Lambda \to \infty$ depends only on $\rho$. A detailed analysis of the simulation results obtained reveals that the following expression describes well this dependence for $0 \leq \rho \leq 1$:

$$\Psi_{\text{cat}}^\rho \approx 0.4463 + 0.7772 \rho + 0.0927 \rho^2,$$

(35)

where the value $\Psi_{\text{cat}}^\rho = 0.4463 \approx 0.2518 \pi^{1/2}$ is characteristic of the reversible reaction involving soluble species, at planar elec-
trodes [17]. Figs. 6a and 7a reveal that the difference between the $\psi_{\text{cat}}^0$ given by Eq. (35), and the $\psi_{\text{cat}}^0$ given by Eq. (32), specific of the irreversible charge transfer involving soluble species (which is achieved at large $\Lambda$ when $k_c=0$), is generally small, and it decreases with increasing $\rho$, both in absolute and relative values. This suggests that the peak height should not be a particularly useful quantity for the determinations of $\Delta u$ from transient experimental data at spherical electrodes. More promising is the effect of $\Delta u$ on the peak potential. As can be seen in Fig. 6b, the dependencies of $\eta_p = (nF/RT)(E_p - E^0)$ on log$_{10}\Lambda$, which were nearly linear in the case of $k_c=0$ (cf. Fig. 2b), now exhibit a transition between two nearly linear parts. The first (oblique) linear part, corresponding with increasing $\Lambda$ the dependence levels off, and the peak potential reaches a practically constant value, characteristic of reversible reaction (3). This constant value is only a function of $\rho$ and $\Delta u$.

A detailed analysis of the simulated voltammograms reveals that the following approximate expression describes well the dependence of $\eta_p$ on $\rho$ and $\Delta u$ in this limit of large $\Lambda$, when $0 < \rho \leq 1$ and $-6 \leq \Delta u \leq 0$:

$$\eta_p = \frac{nF}{RT}(E_p - E^0) \approx -(1.109 + 1.9635 \rho - 0.3971 \rho^3) - \Delta u. \quad (36)$$

The value of $\eta_p \approx -1.109$ is characteristic of the reversible charge transfer reaction (3) involving soluble species and taking place at planar electrodes (assuming $\gamma = 1$) [17]. The validity of Eq. (36) is confirmed by Fig. 7b. Taking into account the definition of $\Delta u$, Eq. (36) can be rewritten as

$$\frac{nF}{RT}(E_p - E^0) \approx -(1.109 + 1.9635 \rho - 0.3971 \rho^3), \quad (37)$$

which means that under these conditions $(nF/RT)(E_p - E^0)$ is a function of $\rho$ only.

4.3. Implications for the analysis of experimental data

The above discussion reveals that the analysis of the experimental data for mechanism (1) and (2) cannot be trivial. There is generally no simple peak versus $v$ dependence that could be conveniently used for the analysis of the raw LSV data.

In the case of multi-parameter models, it is often most adequate to use some kind of curve fitting (ideally multi-response fitting employing a number of entire voltammograms obtained at different potential sweep rates) to determine statistically meaningful estimates of the model parameters. However, by taking into account the above theoretical results, the following suggestions can be made, with regard to the potentially useful simple procedures of determining rough estimates (or just starting approximations for the subsequent fitting) of both $\Lambda$ and $\Delta u$ from experimental data corresponding to relatively small $\rho$ values ($0 < \rho \leq 1$). In these suggestions we assume that $E^0$, $\rho$, and $\gamma$ are known (or determined using other experimental data).

Let us consider first the transient LSV or CV responses corresponding to not very high $\rho$, for which well formed forward peaks are visible.

(a) In the important case of $k_c=0$ no reverse peaks are observed. One can estimate $\Lambda$, but not $\Delta u$. In order to determine unknown $\Lambda$ values, one can use Eq. (33), assuming that a corresponding series of $\rho$ values is known and $\eta_p$ is determined experimentally (different $\eta_p$ values would typically correspond to different potential scan rates). For this purpose, it is convenient to rewrite Eq. (33) in the form

$$\eta_p \approx -0.7797 + \ln \left( \frac{\Lambda}{\rho} \right) + y - 2.4853 \exp(y) + 0.3123 \exp(2y), \quad (38)$$

where $y = \ln(\rho)$. Eq. (38) can be viewed as a mathematical representation of the working curves depicted in Fig. 8a in Ref. [13] (where a decimal logarithm was used instead of the natural one), which were determined by computational experimentation using the model approximation described in Ref. [13]. The present representation is the most accurate in the limit of large $\Lambda$. Since Eq. (38) is an analytical expression, it is easier to use than the working curves, as arbitrary $\Lambda$ and $\rho$ values can be substituted into the equation. Eq. (38) predicts that $\eta_p$ considered as a function of $y$ has a maximum at $y \approx -0.7892$ (corresponding to $\rho \approx 0.4542$). The position of the maximum is independent of the value of $\Lambda$. This feature can be used as a diagnostic criterion, allowing one to check if the experimental data are consistent with the present theory. Furthermore, by plotting experimental $\eta_p$ values as a function of $y$, the potential scan rate-independent parameter $\Lambda/\rho$ can be determined graphically, or by fitting Eq. (38). From the $\Lambda/\rho$ value obtained, the rate constant $k_c$ can be calculated, if the total surface concentration $\Gamma_1$ is known (for example from the analysis of the first current component $\Gamma_{\text{cat}}^{\text{res}}(t)$).

(b) In the case of $k_c \neq 0$ peaks may have their reverse counterparts, especially if $\Lambda$ is large. It is not likely that large $\Delta u$ can then be determined. Only $\Delta u$ can be estimated, by plotting peak potentials as a function of $\rho$ (which depends on the potential scan rate), extrapolating to $\rho = 0$, and employing Eq. (37) to obtain $E^0$, which then yields $\Delta u$ (a correction for $\gamma \neq 1$ may be needed, if $\gamma$ deviates considerably from unity, since Eq. (37) was obtained assuming $\gamma = 1$).

If some of the voltammograms have reverse peaks, and some do not, then those not possessing reverse peaks, and corresponding to moderate $\Lambda$ values ($\Lambda$ depends on the potential scan rate), can be used for estimating $\Lambda$, as in point (a), and those having the reverse peaks, and corresponding to large $\Lambda$ can be used for evaluating $\Delta u$, as in point (b).

In the opposite case of steady-state conditions for very large $\rho$, Eqs. (29)–(31) can be utilised for parameter determinations. In this case we additionally assume that the initial concentration $c^0$ and the electrode area are known. This allows one to use Eq. (23) to obtain current function values from experimental catalytic currents. Parameter $\Lambda$ can then be determined from the experimental limiting current function values $\psi_{\text{cat}}^{\text{max}}$, by employing Eq. (30). Eq. (31) can be used subsequently to deduce the value of $\Delta u$ from the measured half-wave potentials, if only $\Lambda$ is not too small, so that $\Delta u$ has a non-negligible effect on the half-wave potential. By inverting Eq. (31), the relevant formula for $\Delta u$ is:

$$\Delta u = \ln \left( \frac{1}{\pi^2} \left\{ \left( \frac{\rho}{\Lambda} + 1 \right) \exp \left[ \frac{nF}{RT}(E_{1/2} - E^0) \right] + \frac{\rho}{\Lambda} \right\} \right). \quad (39)$$

5. Conclusions

The theoretical analysis presented here is applicable to LSV and CV responses of mechanism (1) and (2) at spherical electrodes. An important difference, compared to planar electrodes, is the possibility of the occurrence of steady-state responses corresponding to large $\rho$, and the increase of the currents due to geometrical transport enhancement. The dependence of the voltammograms on $\rho$ offers a possibility for model verification, by investigating the effect of $\rho$ on peak potentials, characterised by a local maximum. The effect of the backward reaction (2) on cyclic voltammograms recorded at spherical electrodes is generally similar as for planar electrodes [10]. When the backward rate constant is not zero, a transition becomes possible, upon changing the potential sweep rate, between the transient voltammograms characteris-
tic of an irreversible charge transfer reaction involving soluble species (which should be observed at moderate potential scan rates, and hence at moderate \( \Lambda \) values), and the voltammograms characteristic of reversible charge transfer reaction involving soluble species (which should be observed at small potential scan rates, and hence at large \( \Lambda \) values). Experimental voltammograms corresponding to these two limiting situations can be analysed separately, to obtain estimates of both the forward and backward rate constants of reaction (2). Approximate equations facilitating such estimations at spherical electrodes have been provided. The steady-state voltammograms also exhibit a similar transition between the irreversible/reversible behaviour, enabling rate constant determinations by using analytical expressions obtained here.

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Appendix A. Determination of diffusionless and steady-state solutions from integral equations

It is instructive to demonstrate that the integral equations allow one to obtain explicit analytical expressions for the voltammograms corresponding to the limiting cases A and F, without any need to resort to separate discussions of diffusionless, or steady-state, kinetic equations. This is one of the advantages of the integral equation approach to kinetic modelling, over direct numerical simulation techniques such as finite-difference or finite element methods.

In particular, in case A, if we assume that \( \Lambda \) is very small, then one can conclude from Eq. (22) that the values of \( \Psi_{\text{cat}}(at) \) must be small too, and simultaneously the integrals at the right-hand side of Eq. (22) can be neglected in comparison with unity, which corresponds to the situation when \( c_{C}(r_{0}, t) \approx c_{C} \) and \( c_{P}(r_{0}, t) \approx 0 \). As a result, we obtain Eq. (24).

Passing to the case F, let us assume that \( \rho \) is very large, so that the kernel function \( \text{erex}(\rho(at - z)\chi^{1/2}) \) in Eq. (22) is practically identical to the first term of its asymptotic expansion [23]:

\[
\text{erex}(\rho(at - z)^{1/2}) \approx \rho^{1/2}(at - z)^{-1/2},
\]

except for a very narrow interval of \( z \), close to \( z = at \). Function \( \Psi_{\text{cat}}(z) \) does not vary significantly in this narrow interval of \( z \), so that \( \Psi_{\text{cat}}(z) \) values can be assumed to be identical to \( \Psi_{\text{cat}}(at) \) in this interval, which results in the following approximation:

\[
\int_{0}^{at} \text{erex}(\rho(at - z)^{1/2}) \Psi_{\text{cat}}(z)dz \approx \pi^{1/2}/\rho^{-1}
\]

\[
\int_{0}^{at} (at - z)^{-1/2} \Psi_{\text{cat}}(z)dz - \Psi_{\text{cat}}(at)
\]

\[
\int_{0}^{at} [\pi^{1/2}/\rho^{-1}(at - z)^{-1/2} - \text{erex}(\rho(at - z)^{1/2})]dz.
\]

The second integral in the right-hand side of Eq. (A2) can be calculated analytically:

\[
\int_{0}^{at} [\pi^{1/2}/\rho^{1}(at - z)^{-1/2} - \text{erex}(\rho(at - z)^{1/2})]dz
\]

\[
= \rho^{2} - \text{erex}(\rho(at)^{1/2}),
\]

where the term \( \text{erex}(\rho(at)^{1/2}) \) can be neglected for sufficiently large \( at \), which happens for the major part of the voltammogram, if only \( u \) is sufficiently large. Consequently, owing to the cancellation of the integral terms involving kernels \( (at - z)^{-1/2} \), we obtain:

\[
\int_{0}^{at} [\pi^{1/2}/\rho^{1}(at - z)^{-1/2} - \rho \text{erex}(\rho(at - z)^{1/2})] \Psi_{\text{cat}}(z)dz
\]

\[
\approx \Psi_{\text{cat}}(at)/\rho,
\]

The second kernel function \( \text{erex}((\rho/\gamma)\chi(z)^{1/2}) \) in Eq. (22) is transformed in the same way. As a result, Eq. (22) becomes:

\[
\Psi_{\text{cat}}(at) = \frac{\Lambda}{1 + \exp[u - S(at, \lambda)]} \left\{ \frac{1 - \Psi_{\text{cat}}(at)}{\rho} - \gamma^{2} \exp \left[ (u + \Delta u - S(at, \lambda)) \Psi_{\text{cat}}(at)/\rho \right] \right\}.
\]

A rearrangement of Eq. (A5) yields Eq. (29).

References