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Evaluation of the proton transfer kinetics of potential electrolytes in non-aqueous solutions using electrochemical techniques
Part 1. Kinetic analysis of the general CE mechanism at stationary and rotating electrodes

Abstract The transport and kinetics of potential electrolytes (such as weak organic acids) at stationary and rotating electrodes have been examined in detail. A coherent mathematical analysis enabling the normalised current response to be evaluated has been developed, and various rate limiting scenarios have been identified and examined.

Key words Proton transfer kinetics · CE mechanisms · Potential step chronoamperometry · Rotating disc voltammetry · Reaction/diffusion equations

Introduction

Attention has been focused in recent years on extending the applicability of electrochemical measurement techniques to examine systems of real chemical interest. In this paper we discuss how well-established electrochemical methods [1] such as potential step chronoamperometry (PSCA) and rotating disc voltammetry (RDV) may be used to obtain quantitative information on the proton transfer/reprotonation kinetics of weak or potential[1] electrolytes in non-aqueous solutions. Solid kinetic data for electrochemical reactions in aprotic solvents are not readily available. Acquisition of the latter kinetic data is useful since the rate constants so derived may be used to obtain quantitative estimates of the equilibrium acidities of these materials. Equilibrium acidities (pK_a values) are usually determined via methods such as spectrophotometry [2], conductivity [3, 4] or potentiometry [5]. Dynamic electrochemical techniques such as PSCA or RDV have been less frequently used, although the classical work of Albery [6, 7] and the more recent work reported by Sawyer and co-workers [8] should be noted.

In the present paper we give a unified and comprehensive theoretical analysis of the transport and kinetics of weak acid dissociation near the surface of an electrode and indicate how this analysis may be used to extract useful kinetic information on proton transfer events in a thin reaction layer adjacent to the electrode surface. Although aspects of this analysis have been published previously by other workers, that analysis has been incomplete [9] (in many cases, only some final results have been quoted and not derived), and in some respects certain key theoretical results pertaining to the weak acid dissociation problem quoted in the literature have contained ambiguities [10] and errors.

The early work of Albery [6] and Albery and Bell [11] indicated that dynamic electrochemical methods (such as RDV) could be usefully employed to obtain quantitative kinetic information of the proton transfer kinetics of weak acids in aqueous solutions. However, the potential afforded by such methods has not been extensively

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[1] We adopt the terminology suggested by Bockris and Reddy in their classic monograph *Modern Electrochemistry*; they proposed that electrolytes can be classified as potential (e.g. acetic acid) which, in the pure state, consist of uncharged molecules, and true electrolytes (e.g. sodium chloride) which, in the pure state, consist of ions. This definition is more general than the more traditional classification into weak and strong electrolytes which is made on the basis of their behaviour in one particular solvent such as water

recognised by the research community, and, to the authors' knowledge, dynamic electrochemical methods have not yet been employed to examine proton transfer kinetics of potential electrolytes in non-aqueous solutions.

Analysis of the proton transfer kinetics of electroinactive potential electrolytes via amperometric detection

Many potential electrolytes such as, for example, acetic acid, are electroinactive and therefore do not give rise directly to a current response when monitored amperometrically. Instead, the proton transfer kinetics may be monitored by measuring the reaction flux due to the electroreduction of protons (to form molecular hydrogen) generated via pre-dissociation of the acid at a detector electrode surface. The latter reaction sequence is designated as a CE mechanism:

$$HA \rightleftharpoons H^+ + A^- \quad C$$
$$H^+ + e^- \longrightarrow 1/2 H_2 \quad E$$
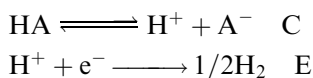
The thermodynamics of the dissociation is governed by the acid dissociation constant K_A, which is in turn related to the proton transfer/reprotonation kinetics via $K_A = k_1/k_{-1}$, where k_1 is the unimolecular rate constant for proton transfer and k_{-1} is the bimolecular recombination rate constant.

It is useful to consider the local geometry near an electrode surface during the occurrence of a CE process. We present a schematic representation of the latter geometry in Fig. 1. We define two characteristic regions: a diffusion layer of thickness δ and a very thin reaction layer of thickness μ. The dissociation equilibrium involving the weak acid species HA will be in balance within the diffusion layer. However, in the reaction layer close to the detector electrode surface there will be more HA dissociating than H^+ and A^- recombining, due to the fact that H^+ is being removed at the electrode surface owing to the occurrence of interfacial electron transfer processes.

We can make some further observations. In the solution outside the reaction layer we can assume that the concentration of acid is considerably greater than the proton concentration, since the acid is weak and the acid dissociation constant K_A is small. We also can experimentally ensure that a salt MA (where M^+ denotes an electrochemically inert cation) is present in large excess in the solution. In our experimental studies we ensured that $[A^-] = 20 [HA]$. This simplifies data analysis considerably. The situation near the interface becomes considerably more complicated if excess salt is not present in the solution.

In recent work reported by Osteryoung and coworkers [12–15] it has been shown that the reduction current of slightly dissociated weak acids depends strongly on the concentration of supporting electrolyte. The steady state current recorded at Pt ultra-microelectrodes in the absence of supporting electrolyte exceeds that with excess supporting electrolyte by a factor of two. Also, Osteryoung and co-workers [12] showed, on the basis of a fairly simple theoretical model, that the shape of the concentration profile of the anion in the interfacial region depends markedly on the concentration of the supporting electrolyte present. The surface concentration of the anion is zero in the complete absence of supporting electrolyte, and approaches its bulk value with increasing concentration of supporting electrolyte. The latter conclusion was also predicted by

Fig. 1 Schematic representation of reaction/diffusion processes describing weak acid dissociation near the surface of a rotating disc electrode. The diffusion layer and reaction layer are both illustrated but are not drawn to scale
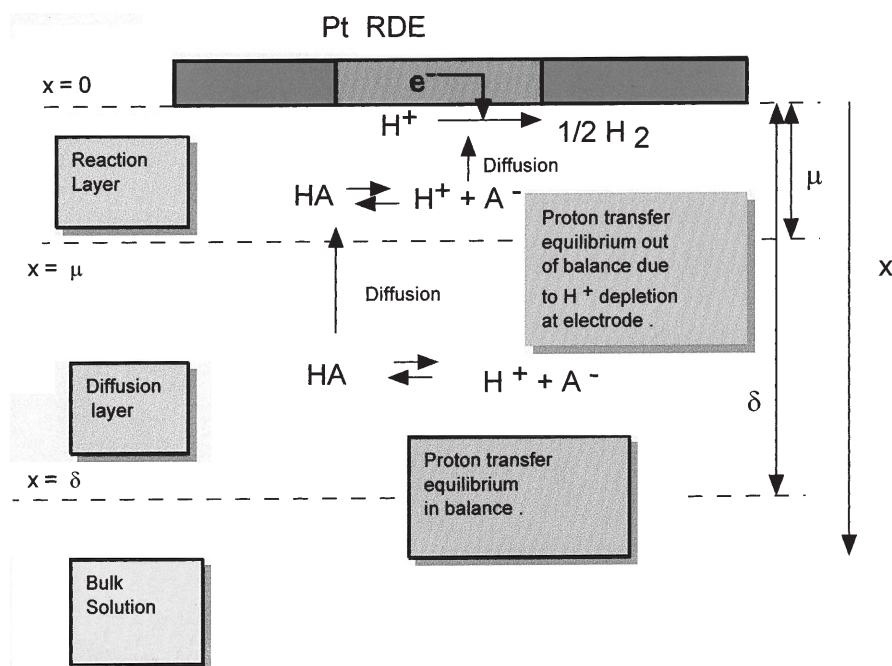
Albery [6] a number of years before, using a somewhat more complex approach. Oldham [16] in a recent paper has also addressed this problem of diffusion/migration coupled with a homogeneous chemical reaction from a somewhat more general and comprehensive viewpoint. Hence in our work we have specifically chosen experimental conditions such that the concentration of the anion does not vary appreciably with distance in the interfacial region, and consequently electromigration effects can be neglected. Consequently the transport and kinetics are well described in terms of relatively simple reaction/diffusion equations (whether steady state or time dependent).

CE mechanisms under transient and steady state conditions: re-evaluation and synthesis

Introduction

In this section we examine the pertinent reaction/diffusion equations describing a general CE process and indicate how the latter equations may be solved rigorously using the technique of non-dimensional variables and Laplace transformation. We have used such general methods in previous work published on the modelling of amperometric chemical sensors utilising electronically conducting polymer materials [17–19]. This type of general analysis has also been recently developed by Bartlett and Eastwick-Field [20] in the context of ECE mechanisms. We shall present an analysis of two important electrochemical techniques which have been adopted in our current experimental programme. The first is the transient technique of PSCA. The second is a steady state method, RDV.

In general terms the CE process may be described in the following manner:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad \text{C step}$$

$$B \overset{+ne^-}{\rightleftharpoons} P \qquad \text{E step}$$
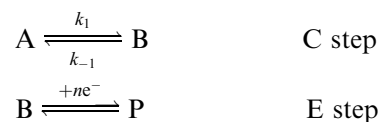
where we assume that the preceding chemical reaction is first order in the forward and reverse direction and that the equilibrium constant K for the reaction is given by $K = k_1/k_{-1} = b/a$. We assume for simplicity that the electron transfer step is fast and can be described in terms of the Nernst equation. Note we assume that species A is electroinactive and species B is electroactive. It is also possible to consider the situation of slow electron transfer (in this case the latter is described in terms of the Butler-Volmer equation), but this results in an unnecessary complication. Since the electron transfer kinetics are fast, we can assume that the observed current is entirely governed by the chemical reaction and diffusion of the reactants.

It has been established that the net behaviour of the CE reaction can be quantified in terms of a parameter λ

and the equilibrium constant K. The quantity λ has been termed the kinetic competition parameter by Saveant [21]. The latter parameter compares homogeneous kinetics and diffusion. In fact one can readily show that $\sqrt{\lambda} = \delta/\mu$, where δ denotes the diffusion layer thickness and μ represents the reaction layer thickness. Hence the larger the value of the competition parameter the *more rapid* are the *kinetics* of the homogeneous chemical reaction compared with diffusion.

This competition parameter is defined differently according to the type of electrochemical technique being used. We show in Table 1 the various definitions of λ corresponding to the most common techniques of RDV, PSCA and linear sweep voltammetry (LSV). In the latter table we set $k = k_1 + k_{-1}$, δ denotes the thickness of the diffusion layer, D is the diffusion coefficient of the reactant, θ represents the measurement time in the potential step chronoamperometric experiment and v denotes the potential sweep rate.

Potential step chronoamperometry

Definition of the boundary value problem

An *approximate* theoretical analysis of the current response to a potential step perturbation has been provided by Koutecky and Brdicka [22] and by Delahay and Oka [23]. Here we provide a detailed and more rigorous derivation. We do this because such an analysis is not readily available in the literature.

The pertinent reaction diffusion equations are:

$$\frac{\partial a}{\partial t} = D\frac{\partial^2 a}{\partial x^2} - k_1 a + k_{-1} b$$
$$\frac{\partial b}{\partial t} = D\frac{\partial^2 b}{\partial x^2} + k_1 a - k_{-1} b \qquad (1)$$

where we have assumed that $a(x,t)$ and $b(x,t)$ represent the concentrations of species A and B, respectively, k_1 and k_{-1} denote the first-order rate constants for the homogeneous chemical reaction, and we have also assumed that the diffusion coefficients of species A and B are equal and are given by the common value D. This latter restriction can be modified to consider non-equal values for the diffusion coefficients. However, the increase in complexity inherent in this procedure is not warranted and we shall not pursue such a development here. Note also that x and t represent the distance and time variables, respectively.

Table 1 Values adopted for the kinetic competition parameter λ

Technique	Kinetic competition parameter λ
RDV	$\lambda = \dfrac{k\delta^2}{D}$
PSCA	$\lambda = k\vartheta$
LSV	$\lambda = \dfrac{RT}{nF}\left\{\dfrac{k}{v}\right\}$

Since the equilibrium constant $K = k_1/k_{-1}$, then we write that $k_1 = k_{-1}K$ and so Eq. 1 can be written as:

$$\frac{\partial a}{\partial t} = D\frac{\partial^2 a}{\partial x^2} - k_{-1}(Ka - b)$$
$$\frac{\partial b}{\partial t} = D\frac{\partial^2 b}{\partial x^2} + k_{-1}(Ka - b)$$
(2)

where $b - Ka$ represents a measure of the departure from equilibrium in the reaction layer next to the electrode surface. Note that the reaction diffusion equations expressed in Eq. 2 are *coupled* since they both include the concentration variables a and b.

To solve the latter expressions we must introduce the initial and boundary conditions which are mathematical statements describing the specific experiment being considered. In the context of potential step chronoamperometry we state:

$$t = 0 \quad x \geq 0 \quad a = a^\infty \quad b = b^\infty \quad K = \frac{b}{a}$$
$$t > 0 \quad x \to \infty \quad b \to b^\infty \quad a \to a^\infty \quad \frac{b}{a} \to K \quad (3)$$
$$t > 0 \quad x = 0 \quad b = 0 \quad D\left(\frac{\partial a}{\partial x}\right)_0 = 0$$

The first statement in Eq. 3 defines the initial condition before the experiment is turned on. The concentrations of A and B are given by their bulk equilibrium values a^∞ and b^∞. The second statement in Eq. 3 represents the situation very far from the electrode surface when the experiment is in operation. Here the concentration terms attain their bulk values as the distance from the electrode surface becomes great. It is only in regions of space close to the electrode surface that there will be significant deviations in reactant species concentrations from those predicted from consideration of the A/B equilibrium brought about by the electrochemical reaction of species B. The final statement in Eq. 3 pertains to the situation at the electrode surface. Here we state that species B reacts at a diffusion controlled rate and so its surface concentration is zero (i.e. it reacts as soon as it reaches the electrode surface) and that species A does not react directly at the electrode surface since it is assumed to be electroinactive. It should be noted, however, that the final condition presented in Eq. 3 will not be valid when the dissociation rate is fast enough such that the concentration of species A drops to zero. This will not happen if the electrolyte is weak, since in this case the dissociation rate constant will be much smaller than the recombination rate constant. In the present paper we only consider the situation of weak electrolytes and so the final boundary condition presented in Eq. 3 is valid.

Finally, to complete the definition of the problem we specify an expression for the current response which is a mathematical statement of the Faraday law of electrolysis:

$$i = nFAD\left(\frac{\partial b}{\partial x}\right)_0$$
(4)

We now must solve the system of equations specified in Eq. 2 subject to the initial and boundary conditions outlined in Eq. 3. Once this is done we use Eq. 4 to evaluate the current response.

Transformation to normalised variables

The most effective way to proceed is to express the boundary value problem in terms of non-dimensional variables. This results in a considerable simplification in the algebraic manipulation and is also mathematically more elegant. To do this we define:

$$u = \frac{a}{c_\Sigma} \quad v = \frac{b}{c_\Sigma} \quad c_\Sigma = a^\infty + b^\infty$$
$$\chi = \frac{x}{\sqrt{D\vartheta}} \quad \tau = \frac{t}{\vartheta} \quad \lambda = k\vartheta \quad k = k_1 + k_{-1}$$
(5)

where ϑ represents the total measurement time and λ is the competition parameter defined in Table 1. Substituting Eq. 5 into Eq. 2 we obtain, after some manipulation, the following equation:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} + \frac{\lambda}{1 + K}(v - Ku)$$
(6)

Using a similar method of analysis we can show that:

$$\frac{\partial v}{\partial \tau} = \frac{\partial^2 v}{\partial \chi^2} - \frac{\lambda}{1 + K}(v - Ku)$$
(7)

Hence Eqs. 6 and 7 represent the defining reaction/diffusion equations cast in non-dimensional form. We note that these expressions are still rather complex since they involve the non-dimensional concentration variables u and v. To make matters simpler we introduce two new non-dimensional variables ζ and η which we define as:

$$\zeta = u + v$$
$$\eta = v - Ku$$
(8)

If the latter quantities are substituted into Eqs. 6 and 7 a more mathematically transparent set of differential equations is obtained. As outlined in Appendix A, we note that the system of reaction/diffusion equations reduces to the following simple expressions:

$$\frac{\partial \zeta}{\partial \tau} = \frac{\partial^2 \zeta}{\partial \chi^2}$$
$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \chi^2} - \lambda\eta$$
(9)

To complete the transformation of the boundary value problem we need to transform the initial and boundary conditions presented in Eq. 3. We first consider the initial condition. We can readily show that the transformed initial condition is given by:

$$\tau = 0 \quad \chi \geq 0 : \zeta = 1 \quad \eta = 0$$
(10)

Taking the boundary condition very far from the electrode surface we readily show that:

$$\tau > 0 \quad \chi \to \infty : \quad \zeta \to 1 \quad \eta \to 0 \tag{11}$$

Finally we consider the boundary condition at the electrode surface. We can show that:

$$\tau > 0 \quad \chi = 0 : \quad \eta(\chi = 0) = -K\zeta(\chi = 0)$$

$$\left(\frac{\partial \eta}{\partial \chi}\right)_0 = \left(\frac{\partial \zeta}{\partial \chi}\right)_0 \tag{12}$$

We finally require an expression for the normalised current response. This is given by:

$$\psi = \left(\frac{\partial v}{\partial \chi}\right)_0 = \left(\frac{\partial \eta}{\partial \chi}\right)_0 \tag{13}$$

where:

$$\psi = \frac{i\sqrt{\vartheta}}{nFAc_\Sigma\sqrt{D}} \tag{14}$$

Solution of the reaction/diffusion equations in terms of the Laplace transformation

We are now in a position to solve the problem using the technique of Laplace transformation [24]. Turning first to the ζ equation we have on application of the definition of the Laplace transform:

$$\frac{d^2\bar{\zeta}(\chi,p)}{d\chi^2} - p\bar{\zeta}(\chi,p) + \zeta(\chi,\tau = 0) = 0 \tag{15}$$

Since we recall that $\zeta(\chi,\tau = 0) = 1$, then Eq. 15 reduces to:

$$\frac{d^2\bar{\zeta}}{d\chi^2} - p\bar{\zeta} + 1 = 0 \tag{16}$$

Note that Eq. 16 is an *ordinary* differential equation independent of the time and containing only the variables χ and the Laplace parameter p. Looking at the η equation we again apply the Laplace transformation to show that:

$$\frac{d^2\bar{\eta}}{d\chi^2} - p\bar{\eta} + \eta(\chi,\tau = 0) - \lambda\bar{\eta} = 0 \tag{17}$$

and we note that $\eta(\chi,\tau = 0) = 0$. Then Eq. 17 takes the form:

$$\frac{d^2\bar{\eta}}{d\chi^2} - (p + \lambda)\bar{\eta} = 0 \tag{18}$$

Again this is a rather simple ordinary differential equation. The solution of the latter equation is given by:

$$\bar{\eta}(\chi,p) = A\exp[-\sqrt{p+\lambda}\chi] + B\exp[\sqrt{p+\lambda}\chi] \tag{19}$$

where A and B are constants to be determined from the boundary conditions set for the problem. Now physi-

cally $\bar{\eta}$ must be bounded as $\chi \to \infty$. Hence we note that $B = 0$. Also we note that when $\chi = 0$, $\quad \bar{\eta} = \bar{\eta}(\chi = 0)$ and so substituting this result into Eq. 19 we note that $A = \bar{\eta}(\chi = 0)$. Consequently the formal solution of Eq. 18 is:

$$\bar{\eta}(\chi,p) = \bar{\eta}(\chi = 0)\exp[-\sqrt{p+\lambda}\chi] \tag{20}$$

We now examine Eq. 16. The solution to this equation is given by:

$$\bar{\zeta}(\chi,p) = \frac{1}{p} + A'\exp[-\sqrt{p}\chi] + B'\exp[\sqrt{p}\chi] \tag{21}$$

where A' and B' are constants to be determined. Again since the solution $\bar{\zeta}$ must be bounded as $\chi \to \infty$ we state that $B' = 0$. When $\chi = 0$, $\quad \bar{\zeta} = \bar{\zeta}(\chi = 0)$ and so from Eq. 21 we note that $\bar{\zeta}(\chi = 0) = 1/p + A'$; hence $A' = \bar{\zeta}(\chi = 0) - 1/p$. Substituting the latter result into Eq. 21 we note that the formal solution to Eq. 16 is:

$$\bar{\zeta}(\chi,p) = \frac{1}{p} + \left\{\bar{\zeta}(\chi = 0) - \frac{1}{p}\right\}\exp[-\sqrt{p}\chi] \tag{22}$$

We now use Eqs. 20 and 22 to obtain an expression for the current response in Laplace space. We firstly differentiate Eq. 20 to obtain:

$$\left(\frac{d\bar{\eta}}{d\chi}\right)_0 = -\sqrt{p+\lambda}\,\bar{\eta}(\chi = 0) \tag{23}$$

and so the normalised current response in Laplace space is given by:

$$\bar{\psi} = \left(\frac{d\bar{\eta}}{d\chi}\right)_0 = -\sqrt{p+\lambda}\,\bar{\eta}(\chi = 0) \tag{24}$$

and our problem reduces to evaluating the quantity $\bar{\eta}(\chi = 0)$. We recall from Eq. 12 that in Laplace space:

$$\bar{\eta}(\chi = 0) = -K\bar{\zeta}(\chi = 0) \tag{25}$$

We also recall from the last relationship expressed in Eq. 12 that:

$$\left(\frac{d\bar{\eta}}{d\chi}\right)_0 = \left(\frac{d\bar{\zeta}}{d\chi}\right)_0 \tag{26}$$

We therefore use the relationships presented in Eqs. 25 and 26 to evaluate $\bar{\eta}(\chi = 0)$ and hence to evaluate the Laplace transformed current response given by Eq. 24.

Firstly, differentiating Eq. 22 with respect to the normalised distance variable and setting $\chi = 0$ we obtain:

$$\left(\frac{d\bar{\zeta}}{d\chi}\right)_0 = -\sqrt{p}\bar{\zeta}(\chi = 0) + \frac{1}{\sqrt{p}} \tag{27}$$

We now use the expression presented in Eq. 26 and noting Eqs. 23 and 27 to obtain:

$$-\bar{\eta}(\chi = 0)\sqrt{p+\lambda} = -\sqrt{p}\,\bar{\zeta}(\chi = 0) + \frac{1}{\sqrt{p}} \tag{28}$$

From Eq. 25 we immediately modify Eq. 28 to read:

$$K\bar{\zeta}(\chi = 0)\sqrt{p + \lambda} = -\sqrt{p}\,\bar{\zeta}(\chi = 0) + \frac{1}{\sqrt{p}} \tag{29}$$

The latter expression only involves $\bar{\zeta}(\chi = 0)$ and can be readily solved for the latter quantity to obtain:

$$\bar{\zeta}(\chi = 0) = \frac{1}{\sqrt{p}\{\sqrt{p} + K\sqrt{p + \lambda}\}} \tag{30}$$

Noting Eq. 25 we immediately obtain that:

$$\bar{\eta}(\chi = 0) = -\frac{K}{\sqrt{p}\{\sqrt{p} + K\sqrt{p + \lambda}\}} \tag{31}$$

Finally, from Eq. 24 we obtain the detailed expression for the normalised current response to the potential step expressed in Laplace space:

$$\bar{\psi} = \left(\frac{d\bar{\eta}}{d\chi}\right)_0 = -\sqrt{p + \lambda}\,\bar{\eta}(\chi = 0) = \frac{K\sqrt{p + \lambda}}{\sqrt{p}\{\sqrt{p} + K\sqrt{p + \lambda}\}} \tag{32}$$

As outlined in Appendix B, we can show that the normalised chronoamperometric current response is given by:

$$\psi(\tau) = \frac{1}{\sqrt{\pi\tau}} - \frac{1}{1 - K^2}$$
$$\times \left\{ \frac{1}{\sqrt{\pi\tau}} + \sqrt{\gamma}\,\exp[\gamma\tau]\,\text{erf}[\sqrt{\gamma\tau}] - \frac{K\exp[-\lambda\tau]}{\sqrt{\pi\tau}} \right.$$
$$\left. - K\sqrt{\lambda + \gamma}\,\exp[\gamma\tau]\,\text{erf}[\sqrt{(\lambda + \gamma)\,\tau}] \right\} \tag{33}$$

where we have defined the factor γ as:

$$\gamma = \frac{K^2\lambda}{1 - K^2} \tag{34}$$

or in more complete terms the normalised current response profile is given by:

$$\psi(\tau) = \frac{1}{\sqrt{\pi\tau}} \left\{ 1 - \frac{1}{1 - K^2}[1 - K\exp[-\lambda\tau]] - \frac{1}{1 - K^2} \right.$$
$$\times \left\{ K\sqrt{\frac{\lambda}{1 - K^2}}\exp\left[\frac{K^2\lambda\tau}{1 - K^2}\right]\text{erf}\left[K\sqrt{\frac{\lambda\tau}{1 - K^2}}\right] \right.$$
$$- K\sqrt{\lambda\left(1 + \frac{K^2}{1 - K^2}\right)}\exp\left[\frac{K^2\lambda\tau}{1 - K^2}\right]$$
$$\left. \left. \times \text{erf}\left[\sqrt{\lambda\left(1 + \frac{K^2}{1 - K^2}\right)\tau}\right] \right\} \right\} \tag{35}$$

This is our final result, which turns out, of course, to have quite a complex mathematical form. The latter result is valid for $K^2\lambda/(1 - K^2) > 0$ and $\lambda\{1 + [K^2/(1 - K^2)]\} > 0$. The latter inequalities mean that the solution presented in Eq. 35 will be valid only for $K < 1$.

This is gratifying since in our experimental work we deal with the dissociation of weak acids where K will indeed be quite small in magnitude. Clearly, a different analytical development is necessary if the situation of $K > 1$ is to be considered.

Limiting approximate expressions
for the transient current response

We are now in a position to examine various limiting approximations to the general current response expression presented in Eq. 35. We note that the current response ψ is a function of the equilibrium constant K and the competition parameter λ, and we note the general restriction that K must be less than unity, although λ can have any value so long as it is positive. If the kinetics of the homogeneous A/B interconversion process are very slow then we set $\lambda \to 0$ and so $K^2\lambda/(1 - K^2) \to 0$. In such a situation, Eq. 35 reduces to:

$$\psi(\tau) \xrightarrow{\lambda \to 0} \left\{ 1 - \frac{1}{1 - K^2}[1 - K] \right\}\frac{1}{\sqrt{\pi\tau}} = \left\{ \frac{K}{1 + K} \right\}\frac{1}{\sqrt{\pi\tau}} \tag{36}$$

The latter expression is not unlike the chronoamperometric response expected for a simple rapid electron transfer process in the absence of a preceding homogeneous chemical reaction (the well-known Cottrell equation). In the latter case the expected transient current response is:

$$\phi = \frac{1}{\sqrt{\pi\tau}} \tag{37}$$

We outline this response in Fig. 2, here we have used Mathematica v.3.0 (Wolfram Research) to evaluate Eq. 36 for values of the equilibrium constant in the range $10^{-4} < K < 0.1$ and for τ values between 0 and 1.

Hence Eq. 36 describes *a modified diffusion (MD) limiting case*, since the normalised current response can be written as:

$$\psi = \left\{ \frac{K}{1 + K} \right\}\phi \tag{38}$$

and the simple current transient response expected for a diffusion controlled, rapid electron transfer process is modified by a simple pre-factor containing the equilibrium constant K.

We note that at any given value of the normalised time τ the current response increases with increasing value of the equilibrium constant K. It should also be noted that we have chosen the initial value of the time τ as 10^{-4} since the current function increases to infinity as $\tau \to 0$ owing to the presence of the inverse square root term in the current expression given in Eq. 36.

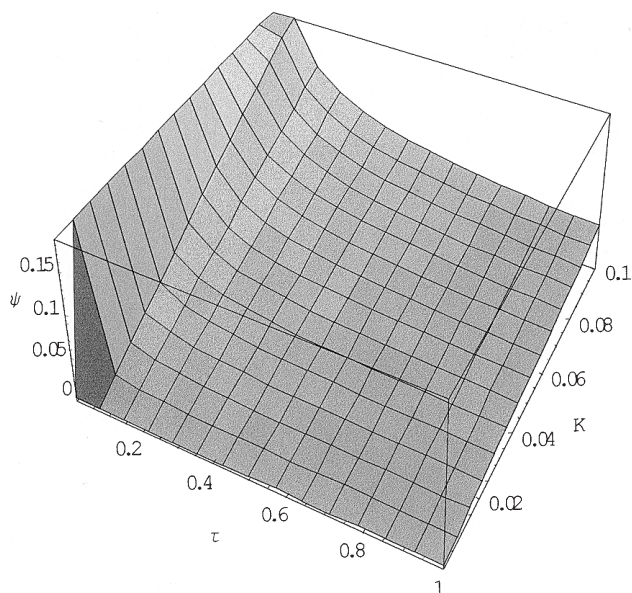We now consider the opposite situation where the competition parameter λ is very large. This limiting case

Fig. 2 Three-dimensional surface plot computed using Mathematica (version 3) illustrating the variation of normalised chronoamperometric current ψ with normalised time τ for various values of the equilibrium constant K. The plot represents Eq. 36, the situation of modified diffusion (MD)

is of considerable significance since we can extract information on the kinetics of the homogeneous chemical reaction if the chemical system exhibits a competition parameter value within the correct range.

To make the algebraic analysis simpler we return to Eq. 33 and see how the latter expression may be simplified. We examine the situation when λ is large and when $K \ll 1$. Under such circumstances we note that $exp[-\lambda\tau] \to 0, K^2 \ll 1, \quad \gamma \approx K^2\lambda, \lambda + \gamma \approx \lambda(1 + K^2) \approx \lambda$ and $\sqrt{\gamma} \approx K\sqrt{\gamma + \lambda}$. Keeping the latter approximations in mind, then Eq. 33 reduces to:

$$\psi(\tau) \approx \sqrt{\gamma}\exp[\gamma\tau]\,\mathrm{erf}\left[\sqrt{(\gamma + \lambda)\tau}\right] - \sqrt{\gamma}\exp[\gamma\tau]\,\mathrm{erf}[\sqrt{\gamma\tau}]$$

$$= K\sqrt{\lambda}\exp[K^2\lambda\tau]\left\{\mathrm{erf}\left[\sqrt{\lambda\tau}\right] - \mathrm{erf}\left[K\sqrt{\lambda\tau}\right]\right\} \quad (39)$$

Now Eq. 39 may be simplified still further if we note the following identity:

$$\mathrm{erf}[x] \approx 1 - \frac{\exp\left[-x^2\right]}{\sqrt{\pi}x}$$

$$\times \left\{1 - \frac{1}{2x^2} + \frac{1 \cdot 3}{(2x^2)^2} - \frac{1 \cdot 3 \cdot 5}{(2x^2)^3} + \cdots\right\} \quad (40)$$

When the argument x is large then $\exp[-x^2] \to 0$ and so, for large $x, \mathrm{erf}[x] \to 1$. Hence for $\sqrt{\lambda\tau}$ large, $\mathrm{erf}\left[\sqrt{\lambda\tau}\right] \to 1$. Note, however, that the quantity $K\sqrt{\lambda\tau}$ is not necessarily large since K is $\ll 1$. Hence Eq. 39 reduces to the simpler form:

$$\psi(\tau) \approx K\sqrt{\lambda}\exp[K^2\lambda\tau]\left\{1 - \mathrm{erf}\left[K\sqrt{\lambda\tau}\right]\right\}$$

$$= K\sqrt{\lambda}\exp[K^2\lambda\tau]\,\mathrm{erfc}\left[K\sqrt{\lambda\tau}\right] \quad (41)$$

This expression defines the intermediate kinetic (KI) case. If we let $Z = K^2\lambda$, then Eq. 41 takes the form:

$$\psi(\tau) = \sqrt{Z}\exp[Z\tau]\,\mathrm{erfc}\left[\sqrt{Z\tau}\right] \quad (42)$$

We outline the latter expression in 3D format in Fig. 3. We note from the plot that the normalised current decays in a regular manner with increasing normalised time. This is due to the fact that the function $\exp[Z\tau]$ increases very rapidly, whereas the function $\mathrm{erfc}[\sqrt{Z\tau}]$ suffers a dramatic decrease, as both Z and τ increase. This property is useful experimentally since it enables one to measure accurately the current/time response profile over a convenient time window. Equation 42 has been quoted (without detailed proof) in the literature.

We now examine various limiting forms of Eq. 42. If we now perform a power series expansion as follows:

$$\exp\left[Y^2\right]\mathrm{erfc}\left[Y\right] = \left(1 + Y^2 + \frac{Y^4}{2!} + \frac{Y^6}{3!} + \cdots\right)$$

$$\times \left\{1 - \frac{2}{\sqrt{\pi}}\left[Y - \frac{Y^3}{3} + \frac{Y^5}{5.\,2!} - \cdots\right]\right\}$$

$$(43)$$

where $Y = \sqrt{Z\tau}$ and assume that when the normalised time τ is small we can neglect all powers of the parameter Y larger than the first, we obtain the particularly simple result that:

$$\exp\left[Y^2\right]\mathrm{erfc}\left[Y\right] \cong 1 - \frac{2Y}{\sqrt{\pi}} \quad (44)$$

Substituting this result into Eq. 43 for the normalised current response we get:

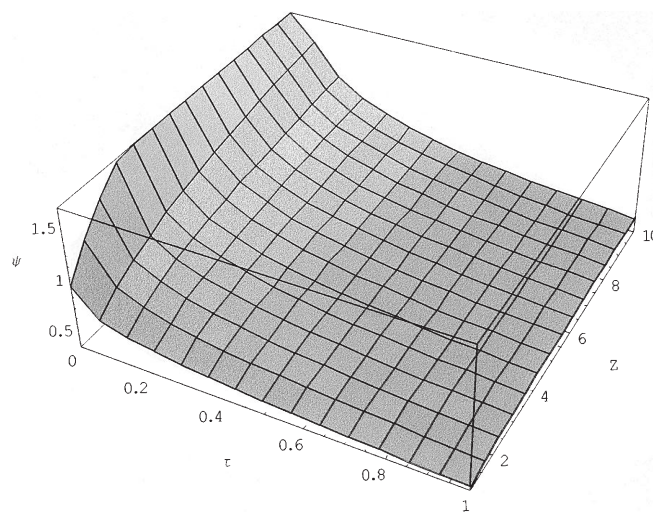**Fig. 3** Three-dimensional surface plot computed using Mathematica (version 3) illustrating the variation of normalised chronoamperometric current ψ with normalised time τ for various values of the kinetic parameter Z. The plot represents Eq. 42, the situation of intermediate kinetics (KI) where both diffusion and homogeneous chemical kinetics are equally important

$$\psi \cong K\sqrt{\lambda}\left\{1 - \frac{2K\sqrt{\lambda\tau}}{\sqrt{\pi}}\right\} \tag{45}$$

Hence when $\tau = 0$ we are left with the following expression for the normalised current at zero time:

$$\psi(\tau = 0) = K\sqrt{\lambda} \tag{46}$$

We recall that in PSCA we have:

$$\psi = \frac{i\sqrt{\vartheta}}{nFAc_\Sigma D^{1/2}} \qquad \lambda = k\vartheta \tag{47}$$

Substituting Eq. 47 into Eq. 46 results in the following:

$$i(t = 0) = nFAc_\Sigma K\sqrt{kD} \tag{48}$$

We note immediately that the expression presented in Eq. 48 can be used to obtain an accurate estimate of the kinetically significant product Kk via analysis of the experimental current/time transient response curve. Note that:

$$i(t = 0) = nFAc_\Sigma K\sqrt{kD} = nFAc_\Sigma \sqrt{K^2 kD}$$

$$= nFAc_\Sigma \sqrt{D}\left\{\sqrt{\frac{k_1^2}{k_{-1}^2}(k_1 + k_{-1})}\right\}$$

$$= nFAc_\Sigma \sqrt{D}\left\{\sqrt{\frac{k_1}{k_{-1}}\left(\frac{k_1}{k_{-1}}[k_1 + k_{-1}]\right)}\right\}$$

$$= nFAc_\Sigma \sqrt{D}\left\{\sqrt{K(k_1[1 + K])}\right\}$$

$$= nFAc_\Sigma \sqrt{D}\sqrt{Kk_1} \tag{49}$$

since we assume that $K \ll 1$.

What happens when Y is large? In such a situation we can show that:

$$\exp[Y^2]\,\text{erfc}[Y] \approx \frac{1}{Y\sqrt{\pi}}\left\{1 - \frac{1}{2Y^2}\right\}$$

$$\approx \frac{1}{Y\sqrt{\pi}} = \frac{1}{K\sqrt{\pi\lambda\tau}} \tag{50}$$

and so the normalised current response is given by:

$$\psi(\tau) \approx K\sqrt{\lambda}\left\{\frac{1}{\sqrt{K^2\pi\lambda\tau}}\right\} = \frac{1}{\sqrt{\pi\tau}} \tag{51}$$

and we expect that the normalised current response should vary inversely in a linear manner with the square root of the normalised time. In fact Eq. 51 represents the normalised current response expected for a fast electron transfer reaction in the absence of any complicating homogeneous kinetic factors. Hence we conclude that at long times the current response reflects that of simple diffusion control involving Nernstian electron transfer at the electrode/solution interface. Note *that no kinetic or thermodynamic information* can be extracted from the current transient recorded at long times.

Table 2 Approximate expressions for the normalised current response obtained under chronoamperometric conditions

Case	Conditions	Normalised current
G	$K \ll 1$, all λ values with λ positive.	$\psi(\tau) = \frac{1}{\sqrt{\pi\tau}}\left\{1 - \frac{1}{1-K^2}[1 - K\exp[-\lambda\tau]]\right\}$
	$\frac{K^2\lambda}{1-K^2} > 0$ and	$\qquad -\frac{1}{1-K^2}\left\{\begin{array}{l} K\sqrt{\frac{\lambda}{1-K^2}}\exp\left[\frac{K^2\lambda\tau}{1-K^2}\right]\text{erf}\left[K\sqrt{\frac{\lambda\tau}{1-K^2}}\right] \\ -K\sqrt{\lambda\left(1+\frac{K^2}{1-K^2}\right)}\exp\left[\frac{K^2\lambda\tau}{1-K^2}\right]\text{erf}\left[\sqrt{\lambda\left(1+\frac{K^2}{1-K^2}\right)\tau}\right] \end{array}\right\}$
	$\lambda\left\{1 + \frac{K^2}{1-K^2}\right\} > 0$	
DM Rate control via diffusion but modified by homogeneous chemical kinetics	$K \ll 1$ and $\lambda \to 0$ all τ values	$\psi(\tau) = \left\{\frac{K}{1+K}\right\}\frac{1}{\sqrt{\pi\tau}}$
KI Joint rate control by diffusion and homogeneous chemical kinetics	λ large, $K \ll 1$ all τ values	$\psi(\tau) \approx K\sqrt{\lambda}\exp[K^2\lambda\tau]\left\{1 - \text{erf}\left[K\sqrt{\lambda\tau}\right]\right\}$ $\qquad = K\sqrt{\lambda}\exp[K^2\lambda\tau]\,\text{erfc}\left[K\sqrt{\lambda\tau}\right]$
KP	λ large, $K \ll 1$	$\psi \cong K\sqrt{\lambda}\left\{1 - \frac{2K\sqrt{\lambda\tau}}{\sqrt{\pi}}\right\}$
Rate control via homogeneous chemical kinetics No influence of diffusion	$K\sqrt{\lambda\tau} \ll 1$ τ.small	
DP	λ large, $K \ll 1$	$\psi(\tau) = \frac{1}{\sqrt{\pi\tau}}$
Rate control via simple diffusion No influence of homogeneous chemical kinetics	$K\sqrt{\lambda\tau} \gg 1$ τ large	

We provide a summary of the approximate forms of the normalised transient current response to a large amplitude potential step in Table 2.

Rotating disc voltammetry

Statement of the boundary value problem in terms of non-dimensional variables

A characteristic of RDV is that the governing reaction/diffusion equations do not depend on the time variable. For a CE reaction we use the equations presented in Eq. 1, but set the derivatives with respect to time at zero. Hence we obtain:

$$D\frac{\partial^2 a}{\partial x^2} - k_{-1}(Ka - b) = 0$$
$$D\frac{\partial^2 b}{\partial x^2} + k_{-1}(Ka - b) = 0 \tag{52}$$

We now define the following non-dimensional variables:

$$u = \frac{a}{c_\Sigma} \quad v = \frac{b}{c_\Sigma} \quad c_\Sigma = a^\infty + b^\infty$$

$$\chi = \frac{x}{\delta} \quad \lambda = \frac{k\delta^2}{D} \quad \sqrt{\lambda} = \delta\sqrt{\frac{k}{D}} = \frac{\delta}{\mu} \tag{53}$$

$$k = k_1 + k_{-1} \quad \mu = \sqrt{\frac{D}{k}}$$

where δ denotes the Nernst diffusion layer thickness and represents the reaction layer thickness. Hence for RDV the square root of the competition parameter is simply the ratio of diffusion to reaction layer thickness.

As before, the current response is given by:

$$i = nFA\left(\frac{\partial b}{\partial x}\right)_0 \tag{54}$$

and we can define the normalised current response as:

$$\psi = \frac{i\delta}{nFADc_\Sigma} \tag{55}$$

Again we can show that:

$$\frac{\partial^2 u}{\partial \chi^2} + \frac{\lambda}{1+K}(v - Ku) = 0 \tag{56}$$

and

$$\frac{\partial^2 v}{\partial \chi^2} - \frac{\lambda}{1+K}(v - Ku) = 0 \tag{57}$$

Following on from our PSCA analysis we introduce the new auxiliary variables:

$$\zeta = u + v$$
$$\eta = v - Ku \tag{58}$$

and we find that Eqs. 56 and 57 reduce to:

$$\frac{\partial^2 \zeta}{\partial \chi^2} = 0$$
$$\frac{\partial^2 \eta}{\partial \chi^2} - \lambda\eta = 0 \tag{59}$$

Clearly the latter expressions are much simpler than the corresponding time dependent expressions used when we analysed the PSCA response.

We now introduce the boundary conditions governing the problem. Proceeding along similar lines to those presented for the analysis of the PSCA response, we can show that:

$$\chi = 1 \quad \eta = 0 \quad \zeta = 1$$

$$\left(\frac{d\zeta}{d\chi}\right)_0 = \left(\frac{d\eta}{d\chi}\right)_0$$

$$\eta(\chi = 0) = -K\zeta(\chi = 0) \tag{60}$$

We now indicate how the latter boundary value problem may be solved.

Solution of the boundary value problem

The reaction/diffusion equations presented in Eq. 59 may be readily integrated. Solving the second equation presented in Eq. 59 we obtain:

$$\eta(\chi) = A'\cosh\left[\sqrt{\lambda}\chi\right] + B'\sinh\left[\sqrt{\lambda}\chi\right] \tag{61}$$

and:

$$\frac{d\eta}{d\chi} = \sqrt{\lambda}A'\sinh\left[\sqrt{\lambda}\chi\right] + \sqrt{\lambda}B'\cosh\left[\sqrt{\lambda}\chi\right] \tag{62}$$

Since $\eta = 0$ when $\chi = 1$ we obtain:

$$A' = -B'\tanh\left[\sqrt{\lambda}\right] \tag{63}$$

Also when $\chi = 0, \eta = \eta(\chi = 0)$ and so:

$$\eta(\chi = 0) = A' = -B'\tanh\left[\sqrt{\lambda}\right]$$

$$B' = -\eta(\chi = 0)\coth\left[\sqrt{\lambda}\right] \tag{64}$$

Substituting the latter result into Eq. 61 we obtain:

$$\eta(\chi) = \eta(\chi = 0)\left\{\cosh\left[\sqrt{\lambda}\chi\right] - \sinh\left[\sqrt{\lambda}\chi\right]\coth\left[\sqrt{\lambda}\right]\right\} \tag{65}$$

Also from Eq. 62 we obtain that:

$$\left(\frac{d\eta}{d\chi}\right)_0 = -\sqrt{\lambda}\eta(\chi = 0)\coth\left[\sqrt{\lambda}\right] \tag{66}$$

and the normalised current response is given by:

$$\psi = \left(\frac{d\eta}{d\chi}\right)_0 = -\sqrt{\lambda}\eta(\chi = 0)\coth\left[\sqrt{\lambda}\right] \tag{67}$$

Hence the problem reduces to evaluating the unknown quantity $\eta(\chi = 0)$. To do this we examine the solution of the ζ expression outlined in Eq. 59. Integrating the latter expression twice produces:

$$\zeta(\chi) = A\chi + B \tag{68}$$

Since we note that $\zeta = 1$ when $\chi = 1$, we have $A + B = 1$ and so $A = 1 - B$. Also when $\chi = 0, \zeta = \zeta(\chi = 0)$ and so $B = \zeta(\chi = 0)$. Hence we can conclude that $A = 1 - \zeta(\chi = 0)$. Thus:

$$\zeta(\chi) = \chi + \zeta(\chi = 0)\{1 - \chi\}$$
$$\left(\frac{d\zeta}{d\chi}\right)_0 = 1 - \zeta(\chi = 0) \tag{69}$$

From the latter expression we note that:

$$\zeta(\chi = 0) = 1 - \left(\frac{d\zeta}{d\chi}\right)_0 = 1 - \left(\frac{d\eta}{d\chi}\right)_0 \tag{70}$$

Also we recall:

$$\eta(\chi = 0) = -K\zeta(\chi = 0) = -K\left\{1 - \left(\frac{d\eta}{d\chi}\right)_0\right\}$$
$$= -K\{1 - \psi\} \tag{71}$$

We now substitute the result obtained in Eq. 71 into Eq. 67 and obtain:

$$\psi = -\sqrt{\lambda}\{K\psi - K\}\coth\left[\sqrt{\lambda}\right] \tag{72}$$

The latter expression may be readily simplified to:

$$\psi = \frac{K\sqrt{\lambda}\coth\left[\sqrt{\lambda}\right]}{1 + K\sqrt{\lambda}\coth\left[\sqrt{\lambda}\right]} = \frac{K\sqrt{\lambda}}{K\sqrt{\lambda} + \tanh\left[\sqrt{\lambda}\right]} \tag{73}$$

The last expression is the result for the normalised current response expected for a rotating disc electrode. It depends on the value of K, the equilibrium constant, and on the competition parameter λ. We outline in Fig. 4 a 3D plot of Eq. 73. We note that for a given value of the equilibrium constant K, the normalised current increases smoothly as the competition parameter λ increases.

Analysis of approximate expressions
for the normalised current response

We recall from Table 1 that the competition parameter is given by $\lambda = k\delta^2/D = k\delta/k_D$, where k denotes the rate constant characterising the homogeneous chemical kinetics and k_D denotes the diffusional rate constant. We now examine some limiting cases of Eq. 73 and derive approximate values for the normalised current response ψ.

We firstly examine Eq. 73 under conditions where the competition parameter is large, but not too large (< 10). Under such circumstances we note that $\tanh[\sqrt{\lambda}] = 1$, and so the normalised current response is given by:

$$\psi = \frac{K\sqrt{\lambda}}{K\sqrt{\lambda} + 1} \tag{74}$$

which is, as we shall now see, a mathematical signature of mixed reaction/diffusion control (a KI kinetic case).

If we transform Eq. 74 into dimensioned variables we obtain that:

$$i = \frac{nFAc_\Sigma D}{\frac{\mu}{K} + \delta} \tag{75}$$

Inversion of the latter expression produces:

$$\frac{nFA}{i} = \frac{\mu}{c_\Sigma DK} + \frac{\delta}{c_\Sigma D} \tag{76}$$

We now specifically consider the dissociation of a weak acid HA. In this case we can write that $K = k_1/(k_{-1}[A^-]_\infty)$ and recall that $k = k_1 + k_{-1} = k_{-1}$ since we can assume that $k_{-1} \gg k_1$. We also note that the diffusion layer thickness is given by $\mu = \sqrt{(D/k)} = \sqrt{[D/(k_1 + k_{-1})]} \approx \sqrt{(D/k_{-1})}$. We also recall that the diffusion layer thickness is given by $\delta = CD^{1/3}\omega^{-1/2}$, where C represents the convective constant $[C = 0.643(\eta/\rho)^{1/6}]$ and ω denotes the rotation speed of the electrode. We can also assume that $c_\Sigma = [HA]_\infty$ since the equilibrium concentration of protons formed via dissociation of the acid is very small. Substituting all of
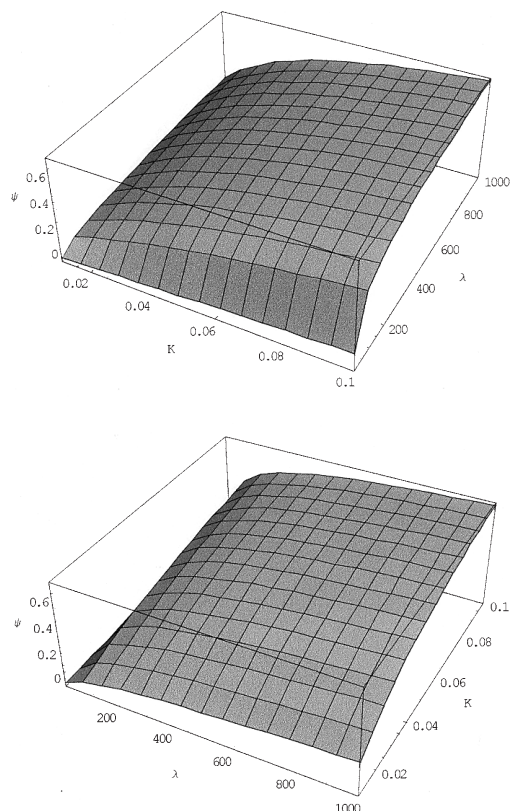

Fig. 4 Three-dimensional surface plot computed using Mathematica (version 3) illustrating the variation of normalised current ψ at a rotating disc electrode with the competition parameter λ for various values of the equilibrium constant K. The plot represents Eq. 73

these relationships into Eq. 76 results in the Koutecky-Levich equation which takes the following form:

$$\frac{nFA}{i} = \sqrt{\frac{[A^-]_\infty}{Dk_1 K_A [HA]_\infty^2} + \frac{C}{D^{2/3}[HA]_\infty}} \; \omega^{-1/2} \qquad (77)$$

The latter expression can be used to evaluate the acid dissociation constant K_A and the proton transfer rate constant k_1 provided that the recombination rate constant is known or can be evaluated. Indeed, in the subsequent paper of this series we will show how simple conductivity measurements can be used to estimate k_{-1} in the absence of any other kinetic data.

When the product $K\sqrt{\lambda} \gg 1$, then Eq. 94 reduces to:

$$\psi = \frac{K\sqrt{\lambda}}{K\sqrt{\lambda}+1} \approx \frac{K\sqrt{\lambda}}{K\sqrt{\lambda}} = 1 \qquad (78)$$

and the current response is under pure diffusion control. The chemical reaction is so rapid that it does not influence the form of the current response. A Nernstian response similar to that observed for a fast ET reaction in the absence of any complicating chemical reaction will be observed. In such a situation the A/B equilibrium lies so far to the right that most of the material is already in the form of the electroactive species B. Here species A is really unimportant to the electrode process and pure diffusion conditions (DP case) pertain. Approximate limits defining this zone are $K > 10$ and $\lambda K > 10$.

Examination of the other limiting situation is also informative. When the competition parameter is quite small, then the rate of the homogeneous chemical reaction is considerably slower than that of matter transport via diffusion. Hence the competition parameter $\lambda \ll 1$. Again the preceding chemical reaction will have little effect and a diffusion controlled Nernstian response will be found. In this case the Nernstian response will be modified by a term involving the equilibrium constant of the preceding chemical reaction.

Hence in the limit of small λ we obtain that $\tanh[\sqrt{\lambda}] = \sqrt{\lambda}$, and so Eq. 73 reduces to:

$$\psi \approx \frac{K\sqrt{\lambda}}{K\sqrt{\lambda}+\sqrt{\lambda}} = \frac{K\sqrt{\lambda}}{\sqrt{\lambda}\{1+K\}} = \frac{K}{1+K} \approx K \qquad (79)$$

which again is a fairly simple result. We see that the normalised current response is similar to that for a simple diffusion controlled process but it is modified by the equilibrium constant term K. This corresponds to the modified diffusion (DM) case. Approximate limits defining the DM zone are $K < 10 < \lambda K$.

When the competition parameter is large and when the equilibrium constant K is small so that the chemical reaction is sluggish, then the product $K\sqrt{\lambda} \ll 1$. This defines the pure kinetic (KP) zone of the case diagram. Typically for the KP case we have $\lambda K < 0.1$ and $\lambda > 1$. Hence the general expression for the normalised current response presented in Eq. 73 reduces to:

$$\psi \approx K\sqrt{\lambda} \qquad (80)$$

Useful kinetic information can be extracted from this expression. Re-transforming Eq. 80 into a dimensional form:

$$i = nFAc_\Sigma K\sqrt{kD} \qquad (81)$$

We see that the current response does not depend on rotation speed and one can obtain an expression for the product $Kk^{1/2}$ from the latter current response. It is interesting to note that the latter expression is the same as that obtained for the chronoamperometric response at zero time which was presented previously in Eq. 48.

The various limiting cases can be summarised in a kinetic case diagram. We do this in Fig. 5. We also provide, in Table 3, a summary of the approximate equations defining the normalised current response observed for a CE reaction when examined using rotating disc voltammetry.

An alternative analysis of the RDV problem

The RDV response for the intermediate kinetic case (i.e. joint rate control via homogeneous chemical reaction and diffusional transport) may also be derived (specifically for the situation of weak acid dissociation) via a somewhat more simple theoretical analysis which does not directly involve solving the reaction/diffusion equations. Rather, one examines the net reaction flux at steady state directly. To do this we re-examine Fig. 1 and formulate a kinetic model as follows.

Since the concentration of weak acid [HA] is very much greater than the proton concentration [H$^+$], we can assume that the HA species supplies protons for the subsequent electrode reaction. Hence we only consider the diffusional transport of the weak acid species in the
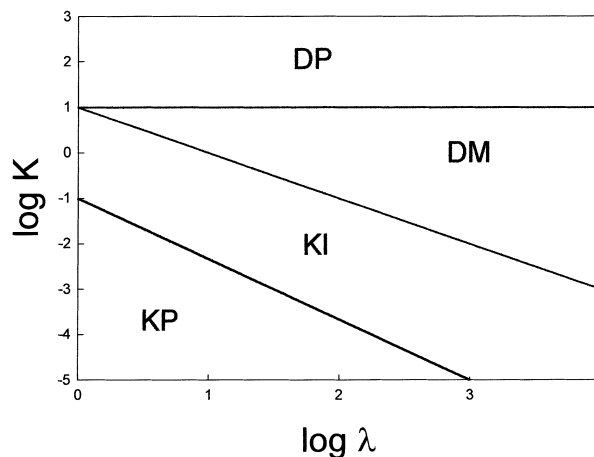

Fig. 5 Kinetic case diagram illustrating four major regions of limiting kinetic behaviour. The notation used originates with Saveant. *DP* pure diffusion control, *DM* diffusion control but modified by homogeneous chemical reaction, *KI* joint rate control via homogeneous chemical kinetics and diffusion, *KP* rate control via homogeneous chemical kinetics

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Table 3 Approximate expressions for the normalised current response obtained under rotating disc voltammetry conditions

Case	Conditions	Normalised current
G	All K values, $\lambda > 0$	$\psi = \dfrac{K\sqrt{\lambda}\coth\left[\sqrt{\lambda}\right]}{1 + K\sqrt{\lambda}\coth\left[\sqrt{\lambda}\right]}$ $= \dfrac{K\sqrt{\lambda}}{K\sqrt{\lambda} + \tanh\left[\sqrt{\lambda}\right]}$
KI Joint rate control via diffusion and homogeneous chemical reaction	λ large but not too large $\tanh\left[\sqrt{\lambda}\right] = 1$	$\psi = \dfrac{K\sqrt{\lambda}}{K\sqrt{\lambda} + 1}$
DP Diffusion control, very rapid homogeneous kinetics	λ large $K\sqrt{\lambda} \gg 1$	$\psi = 1$
DM Diffusion control but rate influenced by homogeneous chemical reaction	λ small $\tanh\left[\sqrt{\lambda}\right] = \sqrt{\lambda}$	$\Psi = \dfrac{K}{1 + K}$
KP Rate control via homogeneous chemical kinetics	λ large $K\sqrt{\lambda} \ll 1$	$\psi \approx K\sqrt{\lambda}$

diffusion layer (the latter being of thickness δ). Hence the reaction flux or rate j for weak acid diffusion is given by:

$$j_1 = \frac{D_{HA}}{\delta}\left\{[HA]_\infty - [HA]_*\right\} \tag{82}$$

where $[HA]_\infty$ represents the bulk concentration of weak acid (valid for distances $x > \delta$) and $[HA]_*$ represents the weak acid concentration just outside the thin reaction layer at $x = \mu$. Also, D_{HA} is the diffusion coefficient of the weak acid species.

We can derive another expression for the reaction flux by considering the transport of protons across the length of the thin reaction layer (which has thickness μ). In this case we assume that:

$$j_2 = \frac{D_{H^+}}{\mu}\left\{[H^+]_* - [H^+]_0\right\} \tag{83}$$

where D_H^+ denotes the diffusion coefficient of the solvated proton and $[H^+]_0$ and $[H^+]_*$ denote the proton concentrations at the electrode surface (at $x = 0$) and just outside the reaction layer (at $x = \mu$), respectively.

Finally, we consider the surface flux describing the rate of the heterogeneous electron transfer reaction in which H^+ is reduced to molecular hydrogen (the primary detection event giving rise to the observed current):

$$j_3 = k_E[H^+]_0 \tag{84}$$

where k_E is the heterogeneous electrochemical rate constant quantifying the rate of interfacial electron transfer. The latter quantity exhibits a marked potential dependence which is described by the well-known Butler-Volmer equation:

$$k_E = k_E^0 \exp\left[-\frac{\alpha FE}{RT}\right] \tag{85}$$

where k_E^0 represents a potential independent rate constant, α is the transfer coefficient, E denotes the electrode

potential and R, F and T represent the gas constant, Faraday constant and temperature, respectively.

Under steady state conditions the net reaction flux j is given by:

$$j = j_1 = j_2 = j_3 \tag{86}$$

Since the bulk acid concentration is known and $[HA]_*$, $[H^+]_*$ and $[H^+]_0$ are unknown quantities, we must manipulate the flux expressions presented in Eqs. 82–84 to eliminate the latter concentration parameters. The algebra involved is rather tedious and is left to Appendix C. There we show that:

$$\frac{1}{j} = \frac{nFA}{i} = \frac{1}{k_D[HA]_\infty} + \frac{1}{k_C[HA]_\infty} + \frac{[A^-]_\infty}{K_A k_E[HA]_\infty} \tag{87}$$

Note that in our analysis we have effected a clean separation between the various rate limiting factors of diffusion, homogeneous chemical reaction and heterogeneous electron transfer kinetics, represented by the first, second and third terms on the rhs of Eq. 87. Note also that the following characteristic rate constants have been introduced:

$$k_D = \frac{D_{HA}}{\delta}$$
$$k_C = \sqrt{\frac{D_{H^+}k_1 K_A}{[A^-]_\infty}} \tag{88}$$

where k_D denotes the diffusional rate constant for weak acid transport through the diffusion layer and k_C is a homogeneous rate constant relating the transport of the solvated proton to the electrode surface to the homogeneous proton transfer/reprotonation kinetics within the reaction layer.

For the condition of large applied potentials the heterogeneous electrochemical rate constant becomes very large indeed. Hence if experimental conditions are

fixed so that the applied potential is large enough such that every H^+ species arriving at the electrode surface is immediately reduced to H_2 (i.e. the surface concentration of H^+ is zero), then we can neglect the third term on the rhs of Eq. 87 and obtain:

$$\frac{1}{j_L} = \frac{nFA}{i_L} = \frac{1}{k_D[HA]_\infty} + \frac{1}{k_C[HA]_\infty} \tag{89}$$

Now the thickness δ of the diffusion layer may be calculated exactly for a rotating disc electrode system. It is a well-characterised function of electrode rotation speed. The faster the rotation speed, the thinner the diffusion layer thickness and the greater the diffusional flux towards the electrode surface. Levich [25] has shown that:

$$\delta = 0.643 \left(\frac{\eta}{\rho}\right)^{1/6} D_{HA}^{1/3} \omega^{-1/2} \tag{90}$$

where η is the viscosity of the solvent, ρ is the density of the solvent and ω represents the electrode rotation speed (in Hz). Using the definition of k_D and k_C presented in Eq. 88 we can show that Eq. 89 may be written in the following form:

$$\frac{nFA}{i_L} = S_{KL}\omega^{-1/2} + I_{KL} \tag{91}$$

This is the Koutecky-Levich equation for a CE process, and implies that a plot of inverse limiting current versus inverse square root of rotation speed should be linear with a slope S_{KL} and intercept I_{KL} given by:

$$S_{KL} = 0.643 \left(\frac{\eta}{\rho}\right)^{1/6} D_{HA}^{-2/3} [HA]_\infty^{-1}$$
$$I_{KL} = \frac{1}{k_C[HA]_\infty} = \sqrt{\frac{[A^-]_\infty}{D_{H^+} k_1 K_A [HA]_\infty^2}} \tag{92}$$

It should be noted that Eq. 91 is exactly the same form as that previously derived in Eq. 77 from more general considerations, and that the limiting KP expression for the RDV current response presented in Eq. 81 can, after trivial manipulation, be transformed into the expression for the Koutecky-Levich intercept I_{KL} presented above in Eq. 92. Hence the two approaches are complementary.

Concluding comments

In the present paper we have presented a detailed analysis of kinetic methodologies based on steady state (RDV) and transient (PSCA) electrochemical techniques which can be used to probe the proton transfer and recombination kinetics of potential electrolytes. A coherent theoretical kinetic analysis has been presented and key theoretical predictions arising from the latter analysis have been outlined.

Appendix A

In this appendix we firstly indicate how the reaction diffusion equations presented in Eq. 9 of the text are obtained starting with Eqs. 6–8.

The most effective way to proceed is to express the boundary value problem in terms of non-dimensional variables. To do this we define:

$$u = \frac{a}{c_\Sigma} \quad v = \frac{b}{c_\Sigma} \quad c_\Sigma = a^\infty + b^\infty$$
$$\chi = \frac{x}{\sqrt{D\vartheta}} \quad \tau = \frac{t}{\vartheta} \quad \lambda = k\vartheta \quad k = k_1 + k_{-1} \tag{A1}$$

where ϑ represents the total measurement time and λ is the competition parameter defined in Table 1 of the text. Substituting Eq. A1 into Eq. 2 of the text we obtain for the expression involving species A:

$$\frac{c_\Sigma}{\vartheta}\frac{\partial u}{\partial \tau} = \frac{Dc_\Sigma}{D\vartheta}\frac{\partial^2 u}{\partial \chi^2} + k_{-1}c_\Sigma v - k_1 c_\Sigma u$$
$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} + k_{-1}\vartheta v - k_1 \vartheta u \tag{A2}$$

But we recall that $k_1 = Kk_{-1}$ and so:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} + k_{-1}\vartheta v - k_1 \vartheta u$$
$$= \frac{\partial^2 u}{\partial \chi^2} + k_{-1}\vartheta(v - Ku) \tag{A3}$$

We now introduce the competition parameter:

$$\lambda = k\vartheta = (k_1 + k_{-1})\vartheta \qquad K = \frac{k_1}{k_{-1}}$$
$$\frac{\lambda}{1+K} = \frac{(k_1 + k_{-1})\vartheta}{1 + \frac{k_1}{k_{-1}}} = \frac{(k_1 + k_{-1})\vartheta \, k_{-1}}{k_1 + k_{-1}} = k_{-1}\vartheta \tag{A4}$$

Substituting the result presented in Eq. A4 into Eq. A3 we obtain:

$$\frac{\partial u}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} + \frac{\lambda}{1+K}\,(v - Ku) \tag{A5}$$

Using a similar method of analysis we can show that:

$$\frac{\partial v}{\partial \tau} = \frac{\partial^2 v}{\partial \chi^2} - \frac{\lambda}{1+K}\,(v - Ku) \tag{A6}$$

Hence Eqs. A5 and A6 represent the defining reaction/diffusion equations cast in non-dimensional form. We note that these expressions are still rather complex since they involve both u and v. To make matters simpler we introduce two new non-dimensional variables ζ and η which we define as:

$$\zeta = u + v$$
$$\eta = v - Ku \tag{A7}$$

If the latter quantities are substituted into Eqs. A5 and A6 a more mathematically transparent set of differential equations is obtained. Using the first relation in Eq. A7 we obtain:

$$\frac{\partial \zeta}{\partial \tau} = \frac{\partial u}{\partial \tau} + \frac{\partial v}{\partial \tau} = \frac{\partial^2 u}{\partial \chi^2} + \frac{\lambda}{1+K}(v - Ku) + \frac{\partial^2 v}{\partial \chi^2} - \frac{\lambda}{1+K}(v - Ku)$$
$$= \frac{\partial^2 u}{\partial \chi^2} + \frac{\partial^2 v}{\partial \chi^2} = \frac{\partial^2}{\partial \chi^2}\{u + v\} = \frac{\partial^2 \zeta}{\partial \chi^2} \tag{A8}$$

The second expression in Eq. A7 produces:

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial v}{\partial \tau} - K \frac{\partial u}{\partial \tau} = \frac{\partial^2 v}{\partial \chi^2} - \frac{\lambda}{1+K}(v - Ku) - K\frac{\partial^2 u}{\partial \chi^2} - \frac{\lambda K}{1+K}(v - Ku)$$

$$= \frac{\partial^2}{\partial \chi^2}\{v - Ku\} - \frac{\lambda(1+K)}{1+K}(v - Ku) \tag{A9}$$

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \chi^2} - \lambda \eta$$

Hence we note that our system of reaction/diffusion equations reduces to the following simple expressions:

$$\frac{\partial \zeta}{\partial \tau} = \frac{\partial^2 \zeta}{\partial \chi^2}$$

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \chi^2} - \lambda \eta \tag{A10}$$

which is Eq. 9 presented in the paper.

Equations 10–12 in the paper may be derived as follows. We first consider the initial condition.

$$\tau = 0 \quad \chi \geq 0 \quad a \to a^\infty \quad b \to b^\infty :$$

$$u = \frac{a}{c_\Sigma} = \frac{a}{a^\infty + b^\infty} = \frac{a^\infty}{a^\infty + b^\infty}$$

$$= \frac{1}{1 + \frac{b^\infty}{a^\infty}} = \frac{1}{1+K}$$

$$v = \frac{b}{c_\Sigma} = \frac{b}{a^\infty + b^\infty} = \frac{b^\infty}{a^\infty + b^\infty} \tag{A11}$$

$$= \frac{b^\infty / a^\infty}{1 + \frac{b^\infty}{a^\infty}} = \frac{K}{1+K}$$

$$\zeta = u + v = \frac{1}{1+K} + \frac{K}{1+K} = \frac{1+K}{1+K} = 1$$

$$\eta = v - Ku = \frac{K}{1+K} - \frac{K}{1+K} = 0$$

Consequentially we note that:

$$\tau = 0 \quad \chi \geq 0 \ : \ \zeta = 1 \quad \eta = 0 \tag{A12}$$

This is Eq. 10 of the paper.

Taking the boundary condition very far from the electrode surface we recall that:

$$\tau > 0 \quad \chi \to \infty \quad a \to a^\infty \quad b \to b^\infty$$

$$u \to \frac{1}{1+K} \quad v \to \frac{K}{1+K} \tag{A13}$$

$$\zeta = u + v \to 1$$

$$\eta = v - Ku \to 0$$

Finally, we consider the boundary condition at the electrode surface. Here we recall that:

$$\tau > 0 \quad \chi = 0 \ : \ b = 0 \quad D\left(\frac{\partial a}{\partial x}\right)_0 = 0$$

$$v = 0 \quad \left(\frac{\partial u}{\partial \chi}\right)_0 = 0$$

$$\left(\frac{\partial \zeta}{\partial \chi}\right)_0 = \left(\frac{\partial u}{\partial \chi}\right)_0 + \left(\frac{\partial v}{\partial \chi}\right)_0 = \left(\frac{\partial v}{\partial \chi}\right)_0$$

$$\eta = v - Ku = -Ku$$

$$\zeta = u + v = u$$

$$\eta(\chi = 0) = -K\zeta(\chi = 0) \tag{A14}$$

$$\left(\frac{\partial \eta}{\partial \chi}\right)_0 = \left(\frac{\partial v}{\partial \chi}\right)_0 - K\left(\frac{\partial u}{\partial \chi}\right)_0 = \left(\frac{\partial v}{\partial \chi}\right)_0$$

$$\left(\frac{\partial \eta}{\partial \chi}\right)_0 = \left(\frac{\partial \zeta}{\partial \chi}\right)_0$$

We finally require an expression for the normalised current response (Eq. 14 of the paper). Recall that:

$$i = nFAD\left(\frac{\partial b}{\partial x}\right)_0 = \frac{nFAD}{\sqrt{D\vartheta}}(a^\infty + b^\infty)\left(\frac{\partial v}{\partial \chi}\right)_0$$

$$= \frac{nFAc_\Sigma \sqrt{D}}{\sqrt{\vartheta}}\left(\frac{\partial v}{\partial \chi}\right)_0 \tag{A15}$$

If we introduce the normalised current response ψ as:

$$\psi = \frac{i\sqrt{\vartheta}}{nFAc_\Sigma \sqrt{D}} \tag{A16}$$

Then from Eqs. A15 and A16 we note that the normalised current response is given by:

$$\psi = \left(\frac{\partial v}{\partial \chi}\right)_0 = \left(\frac{\partial \eta}{\partial \chi}\right)_0 \tag{A17}$$

which we required to derive.

Appendix B

In this appendix we derive Eq. 33 for the normalised chronoamperometric response. We begin with the expression for the normalised chronoamperometric response in Laplace space, which is given by:

$$\bar{\psi} = \left(\frac{d\bar{\eta}}{d\chi}\right)_0 = -\sqrt{p+\lambda}\,\bar{\eta}(\chi = 0) = \frac{K\sqrt{p+\lambda}}{\sqrt{p}\{\sqrt{p} + K\sqrt{p+\lambda}\}} \tag{B1}$$

We now must use the inverse Laplace transformation to obtain an expression for the normalised current response in real space. This usually is not a trivial task. Inversion of the expression presented in Eq. B1 may be accomplished with a little bit of ingenuity if we note the following:

$$\frac{K\sqrt{p+\lambda}}{\sqrt{p}\{\sqrt{p} + K\sqrt{p+\lambda}\}} = \frac{\sqrt{p} + K\sqrt{p+\lambda} - \sqrt{p}}{\sqrt{p}\{\sqrt{p} + K\sqrt{p+\lambda}\}}$$

$$= \frac{1}{\sqrt{p}} - \frac{1}{\sqrt{p} + K\sqrt{p+\lambda}} \tag{B2}$$

Hence the time dependent current response in real space is:

$$\psi(\tau) = L^{-1}\{\bar{\psi}(p)\}$$

$$= L^{-1}\left\{\frac{1}{\sqrt{p}}\right\} - L^{-1}\left\{\frac{1}{\sqrt{p} + K\sqrt{p+\lambda}}\right\}$$

$$= \frac{1}{\sqrt{\pi\tau}} - L^{-1}\left\{\frac{1}{\sqrt{p} + K\sqrt{p+\lambda}}\right\} \tag{B3}$$

We now need to evaluate the second term on the rhs of Eq. B3. To do this we resort to some algebra:

$$\frac{1}{\sqrt{p} + K\sqrt{p+\lambda}}$$

$$= \frac{\sqrt{p} - K\sqrt{p+\lambda}}{(\sqrt{p} + K\sqrt{p+\lambda})(\sqrt{p} - K\sqrt{p+\lambda})}$$

$$= \frac{\sqrt{p} - K\sqrt{p+\lambda}}{p - K^2(p+\lambda)}$$

$$= \frac{\sqrt{p}}{p - K^2(p+\lambda)} - \frac{K\sqrt{p+\lambda}}{p - K^2(p+\lambda)}$$

$$= \frac{\sqrt{p}}{p(1 - K^2) - K^2\lambda} - \frac{K\sqrt{p+\lambda}}{p(1 - K^2) - K^2\lambda}$$

$$= \frac{1}{1-K^2}\left\{\frac{\sqrt{p}}{\frac{p(1-K^2)-K^2\lambda}{1-K^2}} - \frac{K\sqrt{p+\lambda}}{\frac{p(1-K^2)-K^2\lambda}{1-K^2}}\right\}$$

$$= \frac{1}{1-K^2}\left\{\frac{\sqrt{p}}{p-\frac{K^2\lambda}{1-K^2}} - \frac{K\sqrt{p+\lambda}}{p-\frac{K^2\lambda}{1-K^2}}\right\} \tag{B4}$$

We now let $\gamma = K^2\lambda/(1-K^2)$. Hence Eq. B4 becomes:

$$\frac{1}{\sqrt{p}+K\sqrt{p+\lambda}} = \frac{1}{1-K^2}\left\{\frac{\sqrt{p}}{p-\gamma} - \frac{K\sqrt{p+\lambda}}{p-\gamma}\right\} \tag{B5}$$

Hence a rather difficult inverse transform has been simplified into the difference of two simpler inverse transforms.

We now find from the tables of inverse Laplace transforms that[2]

$$L^{-1}\left\{\frac{\sqrt{p+\beta}}{p+\alpha}\right\} = \frac{\exp[-\beta\tau]}{\sqrt{\pi\tau}} + \sqrt{\beta-\alpha}\exp[-\alpha\tau]\,\mathrm{erf}[\sqrt{\beta-\alpha}\sqrt{\tau}] \tag{B6}$$

The latter identity may be used to invert Eq. B5. Firstly, setting $\beta = 0$ and $\alpha = -\gamma$ in Eq. B6 we obtain:

$$L^{-1}\left\{\frac{\sqrt{p}}{p-\gamma}\right\} = \frac{1}{\sqrt{\pi\tau}} + \sqrt{\gamma}\exp[\gamma\tau]\mathrm{erf}[\sqrt{\gamma\tau}] \tag{B7}$$

Secondly, setting $\beta = \lambda$ and $\alpha = -\gamma$ in Eq. 49 we find that:

$$L^{-1}\left\{\frac{\sqrt{p+\lambda}}{p-\gamma}\right\} = \frac{\exp[-\lambda\tau]}{\sqrt{\pi\tau}} + \sqrt{\lambda+\gamma}\exp[\gamma\tau]\,\mathrm{erf}\left[\sqrt{(\lambda+\gamma)\,\tau}\right] \tag{B8}$$

We now gather together the results presented in Eqs. B7 and B8 and substitute these into Eq. B3 to obtain an analytical expression for the normalised time dependent current response to a potential step perturbation:

$$\psi(\tau) = \frac{1}{\sqrt{\pi\tau}} - \frac{1}{1-K^2}\left\{\frac{1}{\sqrt{\pi\tau}}\right.$$
$$+ \sqrt{\gamma}\exp[\gamma\tau]\,\mathrm{erf}[\sqrt{\gamma\tau}] - \frac{K\exp[-\lambda\tau]}{\sqrt{\pi\tau}}$$
$$\left. -K\sqrt{\lambda+\gamma}\exp[\gamma\tau]\,\mathrm{erf}\left[\sqrt{(\lambda+\gamma)\,\tau}\right]\right\} \tag{B9}$$

This is Eq. 33 presented in the text as required.

Appendix C

In this appendix we show in detail how the flux expressions presented in Eqs. 82–84 of the paper can be manipulated to produce Eq. 87. Firstly, starting with Eq. 82, we note:

$$j_1 = \frac{D_{HA}}{\delta}\left\{[HA]_\infty - [HA]_*\right\} \tag{C1}$$

Since steady state conditions are assumed, then each sequential step is kinetically balanced and $j_1 = j$. Also setting $k_D = D_{HA}/\delta$, where k_D is the diffusional rate constant, then Eq. C1 reduces to:

$$[HA]_* = [HA]_\infty - \frac{j}{k_D} \tag{C2}$$

---

[2] Note that the error function is defined as:

$$\mathrm{erf}[x] = \frac{2}{\sqrt{\pi}}\int_0^x \exp\left[-y^2\right]\mathrm{d}y$$

$$= \frac{2}{\sqrt{\pi}}\left\{x - \frac{x^3}{3} + \frac{x^5}{10} - \cdots\right\} = \frac{x}{\sqrt{\pi}}\sum_{j=0}^{\infty}\frac{(-x^2)^j}{j!\left(j+\frac{1}{2}\right)}$$

where the infinite series expansion is useful in evaluating the function via computer!

For regions outside the reaction layer the proton transfer reaction is in balance and we can write that $K_A = [H^+]_*[A^-]_\infty/[HA]_*$. We can therefore obtain the following useful result:

$$[H^+]_* = \frac{K_A[HA]_*}{[A^-]_\infty} \tag{C3}$$

where we have assumed that the anion concentration does not vary with distance from the electrode and so the anion concentration just outside the reaction layer is equal to the bulk anion concentration.

We note that:

$$j = \frac{D_{H^+}}{\mu}\left\{[H^+]_* - [H^+]_0\right\} \tag{C4}$$

and substituting Eq. C3 into Eq. C4 yields:

$$j = \frac{D_{H^+}}{\mu}\left\{\frac{K_A}{[A^-]_\infty}[HA]_* - [H^+]_0\right\} \tag{C5}$$

We also note that:

$$j = k_E[H^+]_0 \tag{C6}$$

We now substitute Eq. C3 into Eq. C5 to obtain:

$$j = \frac{D_{H^+}K_A}{\mu[A^-]_\infty}\left\{[HA]_\infty - \frac{j}{k_D}\right\} - \frac{D_{H^+}}{\mu}[H^+]_0 \tag{C7}$$

The latter expression may be rearranged to obtain an expression for the surface concentration of protons at the electrode/solution interface:

$$[H^+]_0 = \frac{K_A[HA]_\infty}{[A^-]_\infty} - \frac{j\mu}{D_{H^+}}\left\{1 + \frac{D_{H^+}K_A}{k_D\mu[A^-]_\infty}\right\} \tag{C8}$$

We now substitute Eq. C8 into Eq. C6 to obtain:

$$j = \frac{k_E K_A[HA]_\infty}{[A^-]_\infty} - \frac{j\,\mu\,k_E}{D_{H^+}}\left\{1 + \frac{D_{H^+}K_A}{k_D\mu[A^-]_\infty}\right\} \tag{C9}$$

We now rearrange this expression to obtain the following equation for the reaction flux j at steady state:

$$j = \frac{k_E K_A[HA]_\infty/[A^-]_\infty}{1 + \frac{k_E\mu}{D_{H^+}} + \frac{k_E K_A}{k_D[A^-]_\infty}} = \frac{k_E[HA]_\infty}{\frac{[A^-]_\infty}{K_A} + \frac{k_E\mu[A^-]_\infty}{D_{H^+}K_A} + \frac{k_E}{k_D}} \tag{C10}$$

The latter expression may be used to compute the theoretical current potential response if so desired. A more transparent method of attack is to invert Eq. C10 to obtain:

$$\frac{1}{j} = \left\{\frac{[A^-]_\infty}{K_A} + \frac{k_E\mu[A^-]_\infty}{D_{H^+}K_A} + \frac{k_E}{k_D}\right\}\frac{1}{k_E[HA]_\infty} \tag{C11}$$

We now consider the factor $k_E\mu[A^-]_\infty/D_{H^+}K_A$. We need to introduce the definition of reaction layer thickness as follows:

$$\mu = \sqrt{\frac{D_{H^+}}{k_{-1}[A^-]_\infty}} \tag{C12}$$

Hence we note that $k_E\mu[A^-]_\infty/D_{H^+}K_A = \sqrt{D_{H^+}/k_{-1}[A^-]_\infty}$ $\{k_E[A^-]_\infty/D_{H^+}K_A\} = \sqrt{[A^-]_\infty/k_1K_AD_{H^+}}\,k_E = k_E/k_C$. In the latter sequence of manipulations we have assumed that $K_A = k_1/k_{-1}$ and introduced the homogeneous rate constant k_c as follows:

$$k_C = \sqrt{\frac{D_{H^+}k_1K_A}{[A^-]_\infty}} = \sqrt{\frac{D_{H^+}k_1^2}{k_{-1}[A^-]_\infty}} = k_1\sqrt{\frac{D_{H^+}}{k_{-1}[A^-]_\infty}} = k_1\mu \tag{C13}$$

Introducing the k_c parameter into Eq. C11 and simplifying results in the following expression for the inverse reaction flux:

$$\frac{1}{j} = \frac{nFA}{i} = \frac{1}{k_D[HA]_\infty} + \frac{1}{k_C[HA]_\infty} + \frac{[A^-]_\infty}{K_Ak_E[HA]_\infty} \tag{C14}$$

which is the Koutecky-Levich equation presented in Eq. 87 in the paper.

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References

1. Bard AJ, Faulkner LR (1980) Electrochemical methods: fundamentals and applications. Wiley, New York
2. (a) Bordwell FG, Faas RH, Steiner EC (1967) J Am Chem Soc 89: 3905; (b) Bordwell FG, Matthews WS (1974) J Am Chem Soc 96: 1214; (c) Bordwell FG, Matthews WS, Vanier NR (1975) J Am Chem Soc 97: 442; (d) Bordwell FG, Bartmess JE, Pracker GE, Margolin Z, Matthews WS (1975) J Am Chem Soc 97: 3326; (e) Bordwell FG, Brucker GE (1980) J Org Chem 45: 3325
3. Dasgupta PK, Nara O (1990) Anal Chem 62: 1117
4. Fuoss RM, Kraus CA (1933) J Am Chem Soc 55: 476
5. (a) Richie CD, Mergerie GHJ (1967) J Am Chem Soc 89: 1447; (b) Richie CD, Uschold RE (1967) J Am Chem Soc 89: 1721; (c) Kolthoff IM, Bruckenstein S, Chantooni MK (1961) J Am Chem Soc 83: 3927; (d) Kolthoff IM, Chantooni MK (1963) J Am Chem Soc 85: 2195; (e) Kolthoff IM, Chantooni MK (1965) J Am Chem Soc 87: 428; (f) Kolthoff IM, Chantooni MK (1966) J Am Chem Soc 88: 5430
6. Albery WJ (1965) Trans Faraday Soc 61: 2063
7. Albery WJ (1966) Trans Faraday Soc 62: 1575
8. Barrette WC Jr, Johnson HW Jr, Sawyer DT (1984) Anal Chem 56: 1890
9. Bard AJ, Faulkner LR (1980) Electrochemical methods: fundamentals and applications, Chap 11. Wiley, New York, pp 429–487
10. Andrieux CP, Saveant JM (1986) In: Bernasconi CF (ed) Investigation of rates and mechanisms of reactions, part II, 4th edn, Chap 7. (Techniques of chemistry series, vol. VI) Wiley-Interscience, New York, pp 305–390
11. Albery WJ, Bell RP (1963) Proc Chem Soc 169
12. (a) Ciszkowska M, Stojek Z, Osteryoung JG (1992) Anal Chem 64: 2372; (b) Stojek Z, Ciszkowska M, Osteryoung JG (1994) Anal Chem 66: 1507
13. Jaworski A, Stojek Z, Osteryoung JG (1995) Anal Chem 67: 3349
14. Morris SE, Ciszkowska M, Osteryoung JG (1993) J Phys Chem 97: 10453
15. Ciszkowska M, Osteryoung JG (1994) J Phys Chem 98: 3194
16. Oldham KB (1996) Anal Chem 68: 4173
17. Lyons MEG (1994) Analyst 119: 805
18. Lyons MEG, Lyons CH, Fitzgerald CA, Bartlett PN (1994), J Electroanal Chem 365: 29
19. (a) Lyons MEG, Greer JC, Fitzgerald CA, Bannon T, Bartlett PN (1996) Analyst, 121: 715; (b) Lyons MEG (1994) Electroactive polymer electrochemistry, vol 1. Plenum Press, New York
20. Bartlett PN, Eastwick-Field V (1993), J Chem Soc Faraday Trans 89: 213
21. Saveant JM, Vianello E (1963) Electrochim Acta 8: 905
22. Koutecky J, Brdicka R (1947) Collect Czech Chem Commun 12: 337
23. Delehay P, Ora S (1960) J Am Chem Soc 82: 329
24. (a) Rice RG, Do DD (1995) Applied mathematics and modelling for chemical engineers, Chap 9. Wiley, New York, pp 331–396; (b) Spiegel MR (1965) Theory and problems of Laplace transforms. McGraw Hill, New York
25. Levich VG (1962) Physicochemical hydrodynamics, Prentice Hall, New York