

Application of Danckwerts' Expression to First-order EC' Reactions. Transient Currents at Inlaid and Recessed Microdisc Electrodes.

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Abstract

A general relationship, arising from Danckwerts' expression [P.V. Danckwerts, *Trans. Faraday Soc.*, **47** (1951) 1014], allows the computation of the transient limiting current in a system with a homogeneous first-order reaction regenerating the electroactive species (an EC' mechanism), with diffusion and convection, from the limiting currents at the same electrode when there is no homogeneous reaction. For the method to apply the boundary conditions and hydrodynamic regime must be time independent. A simple procedure (which could serve as an alternative to convolution or semi-integral methods) to determine the kinetic parameter from limiting currents obtained in an electrode of arbitrary geometry and size is suggested. An estimation of the time needed to approach steady-state is provided. Diffusion-limited transient currents at the inlaid and recessed microdisc electrode with first-order homogeneous kinetics are studied in detail, checking approximate analytical expressions and simulation data arising from Finite Element Method. If diffusion is the only transport phenomenon, all currents tend to the planar (cottrellian) behaviour when t tends to 0, regardless of the kinetic constant or the shape of the electrode.

Keywords: reaction/diffusion, EC' mechanism, chronoamperometry, microdisc, homogeneous reaction.

Introduction

In the engineering literature there is a well-known relationship, first pointed out by Danckwerts [1], which connects the transient concentrations between two systems which only differ in the presence or absence of a coupled homogeneous first-order reaction. The simplest Danckwerts' expression requires a linear time-independent operator (for instance, describing diffusion and time-independent convection) and linear time-independent boundary conditions with an initial condition of zero concentration for the product of the

electrochemical reaction [2,3]. Several extensions of Danckwerts' expression allow the inclusion of non-zero initial concentration conditions for the product of the electrochemical reaction [4,5], time-dependent boundary conditions [6,7] and a time-dependent velocity field [6,8] at the expense of the loss of some of the simplicity of the expression.

Among the many mechanisms described in electrochemistry, the EC' mechanism in which an electroactive species is regenerated by a first order homogeneous reaction [9-11], can – under certain circumstances - be treated using Danckwerts' relationship. To our knowledge, Danckwerts' expression has not been exploited in electrochemistry, except for the relation between concentrations in one-dimensional diffusion [12]. We believe that the extension of Danckwerts' expression could prove useful in the study of some EC' problems. The first order EC' scheme arises, for instance, in the particularly interesting case of an enzyme system, when there is high substrate concentration and low mediator concentration so that the conditions for pseudo first order reaction in solution are met. One existing method for determining the homogeneous kinetic parameter is to use convolution functions [13].

Inlaid disc electrodes are very often used in studies of the EC' mechanism, due to the ease of fabrication of the electrode. In this context, the EC' mechanism has previously been studied theoretically, mainly in steady-state, both analytically [14-17] and through numerical simulation [11,18-20]. More recently, the need to consider the behaviour at recessed microdisc electrodes has arisen due to the increasing application of microdisc arrays fabricated by photolithographic techniques, where the microdisc is slightly recessed beneath the overlying insulating resist. An understanding of the behaviour of such systems could lead to improved methods of measurement and analysis.

An accurate model for the transient response can help in the selection of the appropriate experimental time window. If cyclic voltammetry is to be used at the microdisc electrode, then a description of the history of the flux response is important in the selection of appropriate scan rates for the measurement. More generally, a transient simulation model is essential for any model incorporating time variable boundary conditions.

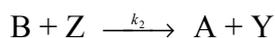
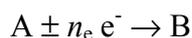
In this paper we first present a derivation of Danckwerts' expression by application of Laplace transform to the linear operator arising from the Nernst-Planck continuity equation. A

relationship, parallel to Danckwerts' expression and relating transient limiting currents, is presented for a case involving diffusion and time-independent convection. We suggest a procedure for determining the kinetic constants from measurements of the transient currents. In section 2, we deal with the inlaid disc electrode, comparing simulation results and several analytical approximations. In section 3, we follow the same development as in section 2, but now turning our attention towards the recessed disc. In section 4, we show that the initial behaviour of the EC' limiting current transient is Cottrellian at any electrode when only diffusion is present.

1. First-order EC' process

1.1 Relationship between transient concentrations

The general scheme for the catalytic regeneration of a species A is:



where Z and Y are electroinactive species and n_e is the number of electrons exchanged. In general this process exhibits second-order kinetics, but may be forced into a pseudo first order situation by making the amount of Z sufficiently large so that its concentration does not change appreciably in time or space in the course of the experiment.

Considering B to be dilute enough, so that activities can be approximated by concentrations, in an incompressible solution where electroneutrality is preserved and there is no migration, the Nernst-Planck equation can be written [21]

$$D_B \nabla^2 c_B - \mathbf{v} \cdot \nabla c_B - k_f c_B = \frac{\partial c_B}{\partial t} \quad (1)$$

where D_B is the diffusion coefficient, ∇c_B the gradient of the concentration, \mathbf{v} the velocity field and k_f the pseudo-first order kinetic constant ($k_f = k_2 c_Z$).

If, to simplify the notation, we define the linear operator \mathbf{L}

$$\mathbf{L}[c] \equiv D_B \nabla^2 c - \mathbf{v} \cdot \nabla c \quad (2)$$

we can re-write the continuity equation (1) as :

$$\mathbf{L}[c_B] - k_f c_B = \frac{\partial c_B}{\partial t} \quad (3)$$

We assume that \mathbf{L} is time-independent, which implies taking the field \mathbf{v} also as time independent (although it can be dependent on the spatial coordinates) [4,5]. As initial condition we assume that B is initially absent from the solution so that:

$$c_B = 0 \quad t = 0 \quad (4)$$

The solution is bounded by several surfaces at finite or infinite distances. We require that the boundary conditions on these surfaces are linear functions of the concentration c_B or any of its derivatives and also that these expressions do not vary with time. Thus,

$$f_1 \frac{\partial c_B}{\partial n} + f_2 c_B = f_3 \quad t > 0 \quad (5)$$

where the derivative is computed normal to the surface and f_1 , f_2 and f_3 (which are real numbers) can depend on the spatial coordinates, but are independent of time. For instance, the boundary condition $c_B = c_B^*$ at the electrode surface, would be embraced by (5) taking $f_1 = 0$, $f_2 = 1$ and $f_3 = c_B^*$. An insulating boundary can be embraced by (5) by taking f_2 and f_3 equal to 0. A Dirichlet surface (e.g. bulk conditions at infinity or positive feedback at a boundary as in a scanning electrochemical microscopy experiment [22]) is achieved by making f_1 equal to 0.

The Laplace transform of equation (3) is

$$\mathbf{L}[\bar{c}_B] = (k_f + s)\bar{c}_B \quad (6)$$

(where the overbar denotes the Laplace transform of the function), and the boundary condition (5) becomes

$$f_1 \frac{\partial \bar{c}_B}{\partial n} + f_2 \bar{c}_B = \frac{f_3}{s} \quad (7)$$

If \bar{c}_B is the solution of (6) fulfilling the boundary condition (7), the product $f_4 \bar{c}_B$ (where f_4 is a non-zero real constant) will also satisfy the differential equation (6), because (6)

is homogeneous and linear. Then on inserting $f_4 \bar{c}_B$ into equation (7) we obtain $f_4 f_3 / s$ on the righthand side because the boundary condition is also linear. This argument, which follows Lightfoot [4], indicates that the term f_3 / s in the boundary condition is the appropriate multiplying factor in the solution of the differential equation. In effect, f_3 / s "scales" the solution.

Now, we turn our attention towards the related, but simpler problem in which all the conditions of the experiment are identical except that there is now no coupled homogeneous reaction. To discriminate this new problem from the original one, we will label this case with a superscript 0. The differential equation, corresponding to (3), is

$$\mathbf{L}[c_B^0] = \frac{\partial c_B^0}{\partial t} \quad (8)$$

which upon Laplace transformation yields

$$\mathbf{L}[\bar{c}_B^0] = s \bar{c}_B^0 \quad (9)$$

with the same boundary conditions, equation (5), as before, that is

$$f_1 \frac{\partial \bar{c}_B^0}{\partial n} + f_2 \bar{c}_B^0 = \frac{f_3}{s} \quad (10)$$

The analogy between the two linear differential equations (6) and (9) can be enhanced by introducing

$$p \equiv k_f + s \quad (11)$$

and re-writing (6) as

$$\mathbf{L}[\bar{c}_B] = p \bar{c}_B \quad (12)$$

where, for both differential equations (9) and (12), p and s are just constant non-zero real parameters. Hence, both differential equations are identical except for the labelling of their parameters. Regarding the boundary conditions, (7) can be re-written as

$$f_1 \frac{\partial \bar{c}_B}{\partial n} + f_2 \bar{c}_B = \frac{f_3}{p} \left(\frac{p}{p - k_f} \right) \quad (13)$$

which simply "re-scales" the condition that (10) imposes on (9) by a factor $p / (p - k_f) = (k_f + s) / s$. Thus the solutions are related through:

$$\bar{c}_B(s) = \frac{k_f + s}{s} \bar{c}_B^0(k_f + s) = \frac{k_f}{s} \bar{c}_B^0(k_f + s) + \bar{c}_B^0(k_f + s) \quad (14)$$

which upon back-transformation (using the shift theorem) yields Danckwerts' relationship between the normalised concentrations for both problems

$$c_B(t) = k_f \int_0^t e^{-k_f u} c_B^0(u) \, du + e^{-k_f t} c_B^0(t) \quad (15)$$

Danckwerts' expression makes no assumptions about the particular size or electrode geometry. Thus, equation (15) can be used for micro- or macroelectrodes, planar electrodes (band, elliptic, irregular, etc.) or other three dimensional shapes (spherical, oblate, cylindrical, conical, or irregular) and for individual electrodes or for arrays of electrodes.

Regarding the initial condition, Danckwerts' expression (15) holds provided that the initial concentration of the product of the electrode reaction B is zero, but it can be extended for other initial concentrations by adding an additional term[4,5]. The inclusion of the migration term in the Nernst-Planck equation (1) poses no problem to the linear operator \mathbf{L} itself, but it is a problem for the realistic establishment of time independent boundary conditions compatible with (5). As a result we will present below the derivation of the relationship between currents without including migration. Experimentally this condition is met by conducting the experiments in the presence of an excess of an inert electrolyte.

1.2 A relationship between the currents.

Let us summarise the assumptions required to derive Danckwerts' relationship between concentrations (15) : i) a time-independent linear operator \mathbf{L} (see eqn. (2)), ii) zero initial concentration for B (see eqn. (4)) and iii) linear time-independent boundary conditions for c_B (see eqn. (5)). For the practical use of Danckwerts' relationship in electrochemical problems, we consider the requirement iii) to be the most restrictive constraint.

The diffusion limited condition is a particular case where equation (12) applies, given certain restrictions, and can be used to derive new and useful relationships for the current. We now analyse these restrictions. When the concentration of A is depleted to zero at the

electrode surface by the electrochemical reaction, one way of obtaining a time-independent boundary condition of the type in equation (5) for B is to assume: 1) that the operator \mathbf{L} is the same for both A and B, and 2) with the obvious exception of the conversion of A into B at the electrode surface, that A and B are confined within the solution (i.e. there is no net flux of A or B across the boundaries of the system considered, either by diffusion or by convection).

Unfortunately assumption 1) that the operator \mathbf{L} is identical for A and B imposes the restriction that the diffusion coefficients must be equal $D_A = D_B$.

A parallel expression to (3) for species A can, then, be written as

$$\mathbf{L}[c_A] + k_f c_B = \frac{\partial c_A}{\partial t} \quad (16)$$

which, upon addition to (3), yields

$$\mathbf{L}[c_A + c_B] = \frac{\partial(c_A + c_B)}{\partial t} \quad (17)$$

The initial condition according to equation (4) is that only A is present initially at a bulk concentration c_A^* . Condition 2) with $D_A = D_B$, implies that normal to any surface delimiting the system

$$\nabla c_A = -\nabla c_B \quad (18)$$

Given the previous boundary conditions, it follows that the solution to (17) is

$$c_A + c_B = c_A^* \quad (19)$$

When eqn. (19) holds, a time-independent boundary condition for B at the electrode surface is finally ensured for the diffusion limited case,

$$c_B = c_A^* \quad (20)$$

and Danckwerts' relationship (15) can be applied.

If the electroneutrality condition holds (and there is no migration)

$$I = n F D_B \int_A \nabla c_B \quad (21)$$

where integration of the concentration gradient extends over all of the electrode surface of area A . This is a linear relationship between concentration and current that allows the transformation of Danckwerts' relationship (15) into

$$I(t) = k_f \int_0^t e^{-k_f u} I^0(u) du + e^{-k_f t} I^0(t) \quad (22)$$

Equation (22) can be seen as a "shifting formula" from which we obtain $I(t)$ from the current $I^0(t)$ for the problem without homogeneous reaction. In most cases, $I^0(t)$ can be found by performing the experiment with no reactant species Z in the solution. Eqn. (22) is similar to other convolution or semi-integral expressions [13,23-28] due to their common origin in the Laplace transform method, the main difference in our expression is that the current in the integrand of (22) corresponds to that from another experiment carried out without homogeneous reaction.

The relationship given between the currents in equation (22), is wholly independent of the geometry or shape of the electrode and of the surrounding insulator. Thus the expression is appropriate, for instance, to negative feedback at a Scanning Electrochemical Microscope [29]. The condition ii) imposing no net flux of A or B through the system boundaries is satisfied by any system of finite volume (i.e. insulators and electrodes surrounding the solution), by semi-infinite diffusion, etc.

If an analytical expression (either exact or approximate) is available for $I^0(t)$ for any given problem, then equation (22) can readily yield the analytical solution for the associated first order problem. This can be verified for one dimensional problems such as planar or stationary spherical electrodes, where the exact solutions for $I^0(t)$ are known [30].

However, for most systems, analytical expressions for the transient current $I^0(t)$ have not been found. If simulated or experimental data are available, equation (22) can also be applied by performing the integration numerically. This is demonstrated in sections 2 and 3 for inlaid and recessed disc electrodes respectively.

1.3 Determination of the kinetic parameter

Differentiating equation (15) with respect to time, one obtains:

$$\frac{\partial c_B}{\partial t} = e^{-k_f t} \frac{\partial c_B^0}{\partial \tau} \quad (23)$$

which means that, under the conditions for which eqn. (22) holds,

$$\frac{dI(t)}{dt} = e^{-k_f t} \frac{dI^0(t)}{dt} \quad (24)$$

Equation (24) immediately suggests that one way of determining k_f is from the slope of a plot of $\ln\left(\frac{dI^0/dt}{dI/dt}\right)$ against t . As an example, data generated from the simulations described in section 2 (for the inlaid disc electrode) and section 3 (for the recessed disc electrode) have been plotted in Fig. 1 by taking

$$\frac{dI^0/dt}{dI/dt} \approx \frac{I^0(t_2) - I^0(t_1)}{I(t_2) - I(t_1)} \equiv \frac{\Delta I^0}{\Delta I} \quad (25)$$

Each value generated by (25) is plotted against the average time $t = (t_1 + t_2)/2$ taken as its abscissa. This leads to a slope in the plot equal the kinetic constant k_f

It can be seen in Fig. 1, that irrespective of the electrode (either inlaid or recessed), excellent agreement is found with the expected behaviour. Applying linear least squares regression to the data in the figure gives values of 9.87 s^{-1} for the inlaid electrode and 9.96 s^{-1} for the recessed electrode as compared to the values of $k_f = 10 \text{ s}^{-1}$ used in the simulation to generate the data. The error can be ascribed both to errors in the simulation procedure and to the approximation made in equation (25). More sophisticated ways of computing the quotient of the derivatives could be applied, but the simplest approximation given by (25) seems adequate provided that the time intervals are selected so that the experimental errors in ΔI are not dominant and that the variation of the current over the time interval is not strongly non-linear. Obvious advantages of this method are its simplicity and its general applicability regardless the electrode and insulator(s) shapes and, for this specific mechanism, the method could be an alternative to the use of convolution functions[13].

1.4 How long does it take to reach steady-state?

By letting $t \rightarrow \infty$ in equation (22), one recovers [2,31]

$$I_{SS} = k_f \int_0^{\infty} e^{-k_f u} I^0(u) du \quad (26)$$

which means that the steady state current in the kinetic problem may be seen as a Laplace transform of the transient problem without reaction. This result is also consistent with the intuitive idea that EC' system can (mathematically) reach steady state for any electrode and cell geometry, due to the non-zero value of the integral in equation (26). Thus, a steady-state is established at a planar electrode by the homogeneous chemical reaction but cannot be achieved when only diffusion is present.

A true steady-state can only be achieved at an infinite time. Nevertheless it can be useful to have an estimate of the time required to obtain a value of the (measured) transient current to be considered close enough to the (expected) steady-state value [32]. If ε denotes the fraction of error we are prepared to accept

$$\varepsilon \equiv \frac{I(t) - I_{SS}}{I_{SS}} = \frac{e^{-k_f t} I^0(t) - k_f \int_t^{\infty} e^{-k_f u} I^0(u) du}{I_{SS}} > \frac{e^{-k_f t} I^0(t)}{I_{SS}} \quad (27)$$

where we have used equation (22) twice: once for a finite time and once for infinite time. It can be easily seen that ascribing a positive sign to the currents does not imply any loss of generality in (27). Thus, if I_{SS} and some values of I^0 are known (or can be estimated), one can estimate the time t_ε needed to be within the prescribed error from

$$e^{-k_f t_\varepsilon} I^0(t_\varepsilon) = \varepsilon I_{SS} \quad (28)$$

2. The inlaid electrode

We now move on to consider the application of these results to the inlaid microdisc electrode.

2.1 Mathematical formulation

The governing reaction-diffusion equation for species B in an axi-symmetrical problem (such as the inlaid or recessed disc) is

$$\frac{\partial c_B}{\partial \tau} = \left(\frac{\partial^2 c_B}{\partial r^2} + \frac{1}{r} \frac{\partial c_B}{\partial r} + \frac{\partial^2 c_B}{\partial z^2} \right) - K c_B \quad (29)$$

where r and z are the cylindrical coordinates normalised with respect to the electrode radius a , K is the dimensionless (pseudo) first-order rate constant

$$K \equiv k_f a^2 / D_B \quad (30)$$

and τ is the dimensionless time

$$\tau \equiv D_B t / a^2 \quad (31)$$

Note that in some works [33,34] the non-dimensional time (31) is multiplied by a factor 4.

As initial condition we assume that there is no B present in solution, as in (4). Assuming $D_B = D_A$ and semi-infinite diffusion leads to $c_A + c_B = c_A^*$, as in (19). This means that we need only solve the system for c_B .

The boundary condition at the electrode surface, for the diffusion-limited current is

$$c_B(r, z, \tau) = c_A^* \quad r \leq 1 \quad z = 0 \quad \tau \geq 0 \quad (32)$$

At the insulator surrounding the electrode there is no flux

$$\frac{\partial c_B(r, z, \tau)}{\partial z} = 0 \quad r > 1 \quad z = 0 \quad \tau \geq 0 \quad (33)$$

and for reasons of symmetry

$$\frac{\partial c_B(r, z, \tau)}{\partial r} = 0 \quad r = 0 \quad z \geq 0 \quad \tau \geq 0 \quad (34)$$

Assuming semi-infinite diffusion

$$c_B(r, z, \tau) = 0 \quad r \rightarrow \infty \quad \text{or} \quad z \rightarrow \infty; \quad \tau \geq 0 \quad (35)$$

We now use ϕ to denote the normalised current or flux. For disc electrodes, this is obtained by dividing the measured current by the steady-state current [35] expected or

measured at the inlaid-microdisc with the same bulk conditions and no homogeneous reaction

$$\phi \equiv \frac{I}{4nFaD_A c_A^*} = -\frac{\pi}{2c_A^*} \int_0^1 \left(\frac{\partial c_B}{\partial z} \right)_{z=0} r dr \quad (36)$$

In terms of normalised parameters, the shifting formula (22) becomes

$$\phi(\tau) = K \int_0^\tau e^{-Ku} \phi^0(u) du + e^{-K\tau} \phi^0(\tau) \quad (37)$$

2.2 Simulation results

The transient response over a range of pseudo first-order rate constants has been modelled using the Finite Element method. The approach is essentially the same as described elsewhere [34,36] because the inclusion of first-order kinetics does not alter the linearity of the problem and no special difficulties arise. The domain was divided in a series of four node rectangular elements forming an expanding mesh similar to that also used in Finite Difference calculations [37]. In each element the unknown concentration was interpolated linearly. Fifty non-uniform expanding elements are used over the disc surface. The time part of the problem was solved using a θ -scheme with $\theta=2/3$ [38] and using a strategy of expanding time steps after an initial time-step of $\Delta\tau = 10^{-6}$ run for the first 100 iterations, the time step was increased to 10^{-4} for the next 10 iterations and then subsequently increased by a factor of 10 and run for 10 iterations each time until a final time-step of 10^5 was reached. In this way the simulation time covered 9 orders of magnitude in order to reach the steady-state region. The code was written in Fortran 77 and run on an IBM RS6000 RISC workstation with 128 Mb memory yielding a typical execution time of ca. 10 min.

The evolution of the current with time can be seen in Figure 2 for several K -values. Qualitatively the behaviour with increasing K is as expected: we see bigger values of the flux at all times due to the catalytic reaction and the asymptotic approach to steady state appears sooner as K increases. At short times, the flux values tend to the same value, regardless of K : the regeneration of species A is small at short time and so, only a small catalytic increase in flux is seen. We can ascribe this behaviour to the asymptotic collapse, for all K , of the concentration profiles to the planar diffusion regime at short times. At the other end of the time range, for any value of K , the rate of diffusion away from the electrode of species B will

become, at a certain time, comparable to the rate of the catalytic reaction in solution, at this point the concentration profiles stop spreading out as rapidly and a steady state is achieved.

2.3 Application of the shift expression

To our knowledge, no rigorous analytical solution for the transient current towards an inlaid disc electrode has been reported. Many workers have made contributions to the current understanding of the asymptotic behaviour at short time [33,39-41], the most recent being by Phillips [42]

$$\phi^0(\tau) = \frac{1}{4} \left(\sqrt{\frac{\pi}{\tau}} + \pi + \frac{\sqrt{\pi\tau}}{2} \right) \quad (38)$$

where ϕ^0 refers to the normalised current given by (36) for the system without coupled reaction. Upon application of the shifting formula, equation (37) to eqn. (38), we obtain

$$\phi(\tau) = \frac{\pi}{4} \left(1 + \left(\sqrt{K} + \frac{1}{4\sqrt{K}} \right) \operatorname{erf}(\sqrt{K\tau}) + \frac{e^{-K\tau}}{\sqrt{\pi\tau}} \right) \quad (39)$$

Fig. 3 shows, in continuous line, the decay of the current, computed with the Finite Element simulation, towards the steady state value. Also shown in the figure, by the various symbols, are the results for different approximations. These are discussed below. It can be seen in Fig. 3 that, for $K=10$, the asymptotic analytical expression (39) (represented by the symbol \times) reproduces very well (less than 0.6 % difference with respect to the simulated values) the whole τ range. The errors increase with decreasing K ; for example the maximum percentage difference is below 5.1 % when $K=1$ and below 0.2% when $K=100$. The decreasing of the error with increasing K can be understood from equation (40) because for large values of K the main contribution comes from the short time region in the integral term, where (38) is very accurate.

By reference to equation (39) it is now easy to see that the asymptotic collapse of the currents, regardless of the value of K , onto the planar diffusion regime for low τ discussed above. As τ tends towards zero in eqn. (39), we just recover, as the leading term, the first term in eqn. (38), which is the Cottrell expression for planar diffusion.

In order to facilitate a direct comparison between the different approximate expressions (such as expression (39) and the others discussed below) for $\phi(\tau)$, the percentage difference between the simulated data (for $K=1$) and the values predicted according to the different expressions are plotted in Fig. 4. If we knew the exact values of the current at different times we could assess the absolute error. In the absence of an exact analytical solution we must content ourselves with an indication of the error associated with this difference with respect to the simulated values. In fact, we can estimate the accuracy of the Finite Element simulation to be around -0.42%, which is the maximum difference observed between the steady state simulation value and the exact value [43] computed for steady-state using the dual integral method [44]). It can be seen in figures 3 and 4, that the agreement between the Finite Element simulation and expression (39) is excellent except when K is small and τ is large. In Fig 4 it can be seen that the expression is accurate to 1% up to $\tau=0.1$ when $K=1$

Other closed-form approximate expressions [33,45] are not easily integrated and so we resort to numerical integration. In particular, using the *de facto* expression [33], one obtains

$$\phi(\tau) = 0.7854(1 - e^{-K\tau}) + 0.4431\sqrt{K\pi} \operatorname{erf} \sqrt{K\tau} + 0.2146 K \int_0^\tau e^{-\frac{0.39115}{\sqrt{u}} - Ku} du + e^{-K\tau} \left\{ 0.7854 + 0.2146 e^{-\frac{0.39115}{\sqrt{\tau}}} + \frac{0.4431}{\sqrt{\tau}} \right\} \quad (40)$$

For $K=10$, the difference between (40) and the simulated results remains under 0.17% (see Fig.3). For $K=1$ the limit is 0.81% and for $K=100$ the maximum difference is 0.03%. It is seen in Fig. 4, that the differences with (40) follow a slight oscillation: for low τ the differences are negative and then become positive. The discrepancy is largest at long time.

As pointed out above, the shifting expression (22) (or its dimensionless counterpart (37)) can also be used to relate values obtained from simulation. In this case the numerical integration for a specified non-zero value of K can be performed within the program that runs the simulation for $K=0$. However, once the simulated current values for $K=0$ have been generated, Danckwerts' expression can be used to obtain the current for any value of K using just a spreadsheet. This latter option, which is more similar to the approach for handling

experimental data, has been used in this work. Which ever approach is used an interpolation formula is needed to compute the integral term in equation (37). The accuracy of the procedure obviously depends on the spacing of the original data for ϕ^0 . We have used 10 equally spaced values of τ within each decade, starting from $\tau=0.001$, according to the time stepping strategy described in section 2.2. Linear interpolation over estimates the current, as seen in Fig 3, by around 1%, which can be understood because the linearly interpolated current for $K=0$ between consecutive data points will always over estimate the actual current and because this over estimate is carried through by the Danckwerts' expression. It is seen in Fig 4 that the error usually increases smoothly except when changing decade (e.g. from $\tau=0.1$ to $\tau=0.2$ or from $\tau=1$ to $\tau=2$) due to the spread of the original data for $K=0$.

To improve the results, we have used what can be called “cottrellian interpolation”, that is the current for each interval is approximated by

$$\phi^0(\tau) \approx a_0 + \frac{a_1}{\sqrt{\tau}} \quad (41)$$

where a_0 and a_1 are chosen so that the interpolated current passes through the extremes of the interval (arising from each pair of time-contiguous data collected from the simulation). This option is consistent [24] with the leading terms of the asymptotic expressions (which are valid regardless of the shape of the electrode) for the normalised current at both time limits: very short τ (see eqn. (44) below, derived in ref. [42]) and long τ (see eqn. 18 in ref. [46]). The suggested “cottrellian interpolation” is simple to implement and is more accurate than linear interpolation, as can be verified by checking the accuracy of the interpolation with data generated for $K=0$. Using the shifting expression (37), the differences decrease to a level similar to the shifted *de facto* solution: under 0.19% difference for $K=10$ and under 0.74% difference for $K=1$.

3. Recessed microdisc

We now consider the case of the recessed microdisc.

3.1 Mathematical formulation

The modelling of diffusion in the recessed electrode [36] follows the same differential equation (29) as the inlaid electrode. The same initial value $c_B=0$ and boundary condition

equations (32), (34) and (35) apply. For the recessed microdisc the insulator forms a well whose depth, normalised with respect to the electrode radius a , is L . As a consequence we have

$$\frac{\partial c_B(r, z, \tau)}{\partial z} = 0 \quad r > 1 \quad z = L \quad \tau \geq 0 \quad (42)$$

$$\frac{\partial c_B(r, z, \tau)}{\partial r} = 0 \quad r = 1 \quad 0 \leq z \leq L \quad \tau \geq 0 \quad (43)$$

3.2 Simulation results

Modelling the recessed microdisc under pseudo first-order kinetics was carried out using the program described in our previous work [36] with the modifications needed to incorporate the EC' kinetics. Calculation details are analogous to those given in section 2.2 except that the mesh varied exponentially within the recess region as fully described elsewhere [36]. To our knowledge there are no previous results for this case in the literature, thus the use of the shift formula is a useful check on the correct behaviour of the simulation (see next section).

The transient responses have been modelled for $L = 0$ to 1, because this range is encountered in microdisc arrays commonly fabricated by photolithographic techniques. Figure 5 shows the behaviour of current for a shallow recess. The pattern of behaviour is analogous to that of the inlaid electrode, as can be seen by comparison of Fig 5 with Fig. 2. Consequently the comments made in section 2.2 also apply here for the recessed electrode. In particular, we notice the collapse of all the currents as τ tends towards zero. A similar collapse at low t , for any L , has already been shown elsewhere [36]. The main difference between Fig 5 and Fig. 2 is the global decrease in all currents due to the enhanced difficulty for the mass transport towards the electrode at the bottom of the well.

3.3 Application of the shift expression

Expression (37) with $K=10$ has been applied to data obtained from a simulation with $K=0$ [36] and $L=0.1$. As already seen for the inlaid electrode, Fig. 6 shows that ‘‘cottrellian

interpolation" (41) works much better in reproducing the directly simulated values (with $K=10$) than linear interpolation. Values from both simulations match very well, furnishing an independent internal check on the coherence of the simulations.

4. The diffusion start of EC' is cottrellian

The observed asymptotic trend towards cottrellian behaviour at short times for the inlaid and recessed disc can be shown to be generally applicable for any electrode geometry when diffusion is the only transport phenomenon present. Phillips and Jansons have shown [42] that

$$I^0(t) = n_e F c^* D \left[\frac{A}{\sqrt{\pi D t}} + M \right] + O(t^{1/2}) \quad (44)$$

where M is a constant depending on the geometric characteristics of the electrode and insulator in contact with it. Using the shift expression (22), one obtains

$$I(t) = n_e F A c^* \sqrt{\frac{D}{\pi t}} + n_e F D c^* M + O(t^{1/2}) \quad (45)$$

for the current with a coupled first order homogeneous reaction. It is worth noticing that the leading term of the asymptotic expression (45) for the current does not contain the kinetic constant. This cottrellian behaviour can be physically understood because the current is insensitive to the regeneration of the reactant through the kinetic step at sufficiently short times.

Conclusions

Danckwerts' expression relates the transient concentrations c_B in a first-order EC' reaction with the concentrations found for c_B in the same problem but with no reaction. Conditions for the application of Danckwerts' expression are: a time-independent linear operator \mathbf{L} (equation (2)), zero initial concentration for B (equation (4)) and linear time-independent boundary conditions (equation (5)). Although migration is just another linear term in the global linear operator along side those for diffusion and convection, the need of time independent boundary conditions on the surfaces bounding the solution impedes

its inclusion when applying Danckwerts' expression to limiting currents. Assuming equal diffusion coefficients for A and B and no flux of A or B across the boundaries, we have derived expression (22), which allows the computation of transient currents through a "shifting" of the currents obtained when there is no coupled reaction. The shifting can be applied to (exact or approximate) analytical expressions for the transients or arrays of (simulated or experimental) data. The value of K (or k_f) can be determined by exploiting the relationship in equation (24) in a logarithmic plot of derivatives (or increments) of the transient currents for a wide range of experimental conditions. It has been shown that "cottrellian interpolation" (equation (41)) is a very convenient method for interpolating the current when there is no coupled homogeneous reaction. An estimation of the time needed to achieve a certain proximity to the steady-state, equation (28), has also been provided.

Using the Finite Element Method we have obtained transient currents for the inlaid and recessed electrodes. In both cases, the shifting expression arising from Danckwerts' expression allows a satisfactory assessment of the quality of the simulation. The currents exhibit a catalytic increase with increasing homogeneous reaction rate, K , and a decrease with increasing recess depth, L .

For short times, low τ , the behaviour of all transient currents (regardless of K or L) collapse to cottrellian behaviour (which can be ascribed to planar diffusion with $K=0$) at any shape of electrode where diffusion is the only transport phenomenon.

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Figure legends:

Figure 1. Determination of the kinetic constant (k_f) from a plot of the natural logarithm of the quotient of increments in current against time. The approximate expression given in equation (25) has been used together with data from the Finite Element simulations with $k_f = 10 \text{ s}^{-1}$ for the inlaid electrode (marker o) and for the recessed electrode ($L=0.1$; marker Δ). The solid line corresponds to the expected values given by $k_f t$.

Figure 2. Simulated dimensionless currents (ϕ given by equation (36)) at the inlaid microdisc as a function of the dimensionless time (τ given by equation (31)) calculated using the Finite Element simulation for pseudo-first order EC' kinetics, using the different values for the dimensionless rate constant, K (given by equation (30)), shown.

Figure 3. Plot of the normalised current ϕ as a function of the dimensionless time τ for $K=10$. The solid line was calculated by Finite Element simulation of the homogeneous reaction. The various symbols show the results obtained by application of the “shifting formula” (37) to different approximations for ϕ^0 : \times represents the results obtained from the shifted asymptotic short time expression (39); Δ represents the results obtained from the shifted *de facto* expression (40); \bullet represents the results calculated from the Finite Element simulation for $K=0$ and using linear interpolation; \square represents the results calculated from the same Finite Element simulation for $K=0$ but with using “cottrellian” interpolation (41). The broken horizontal line indicates the steady-state value as computed exactly [43].

Figure 4. Plot of the percentage differences of various expressions with respect to the results of the Finite Element simulation for $K=1$. \times represents the results obtained from the shifted asymptotic short time expression (39); Δ represents the results obtained from the shifted *de facto* expression (40); \bullet represents the results calculated from the Finite Element simulation for $K=0$ and using linear interpolation; \square represents the results calculated from the same Finite Element simulation for $K=0$ but with using “cottrellian interpolation” (41).

Figure 5.: Simulated dimensionless currents (ϕ) at the recessed microdisc ($L=0.1$) as a function of the dimensionless time (τ) calculated using Finite Element for pseudo-first order EC' kinetics, corresponding to different values for the dimensionless rate constant, K , shown.

Figure 6. Currents obtained through direct Finite Element simulation of recessed microdisc ($L=0.025$) for $K=10$ (o) and application of the shift formula (37) to data from the simulation $K=0$ (• linear interpolation, “cottrellian interpolation” (41)).

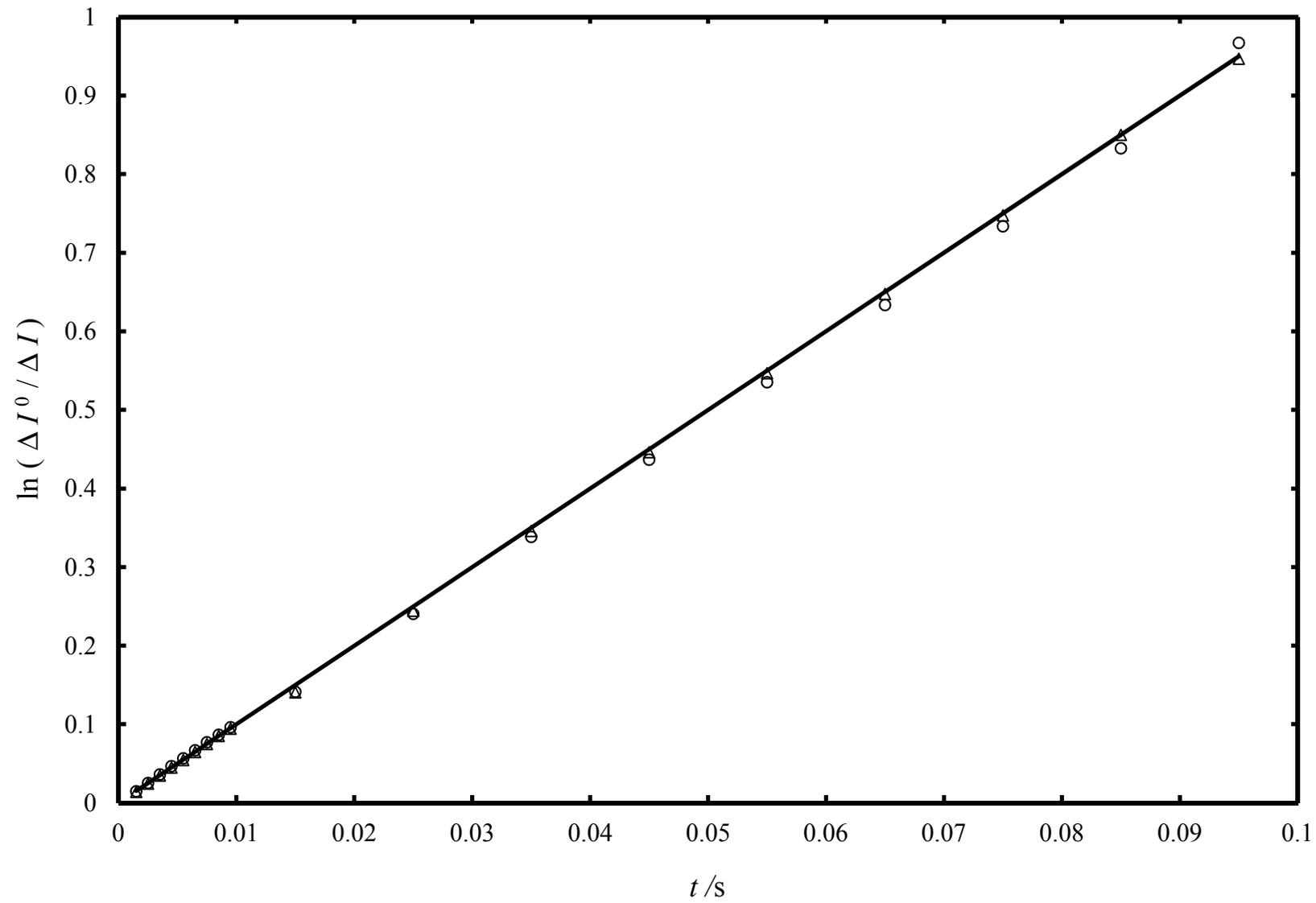


Fig 1

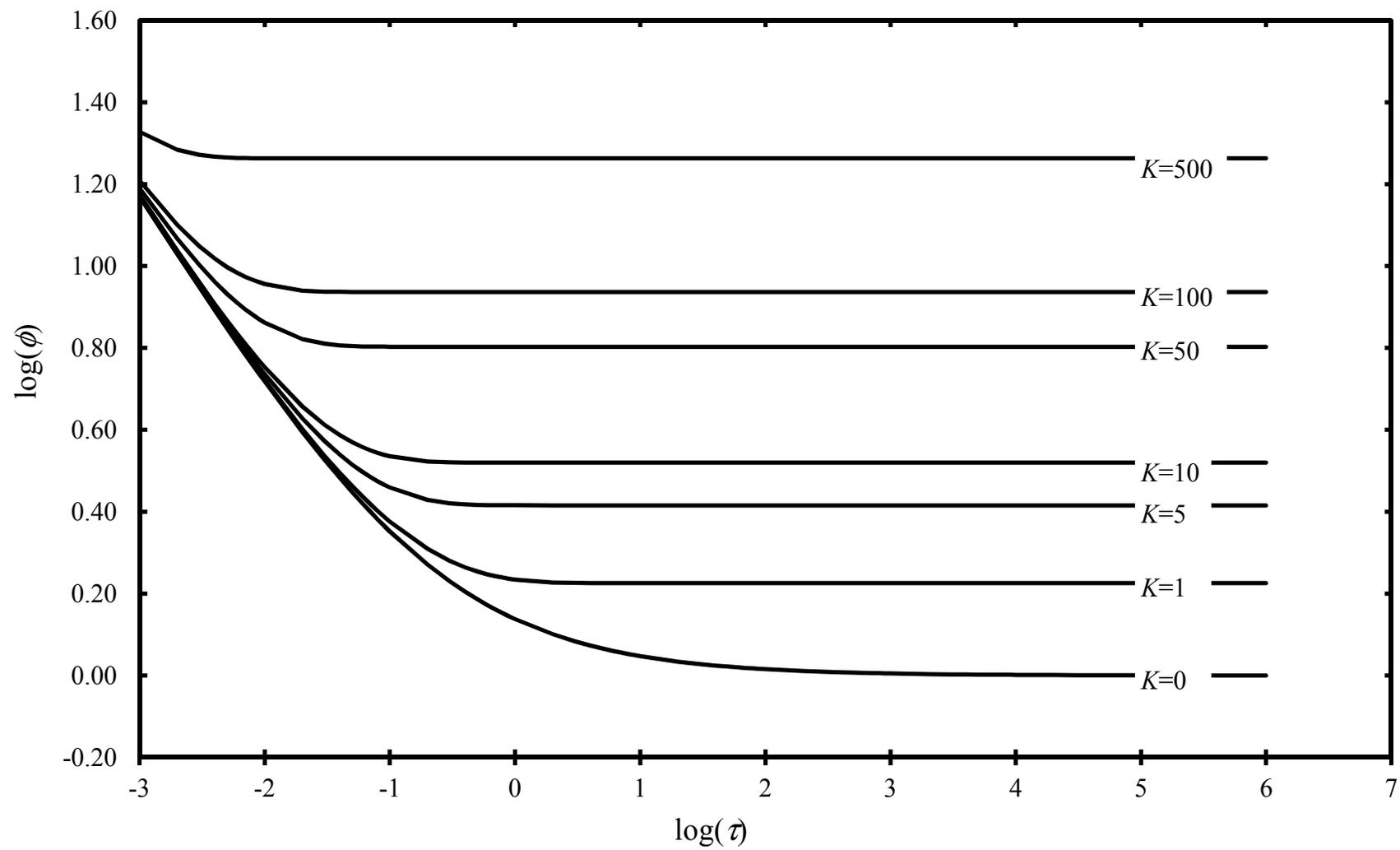


Fig 2

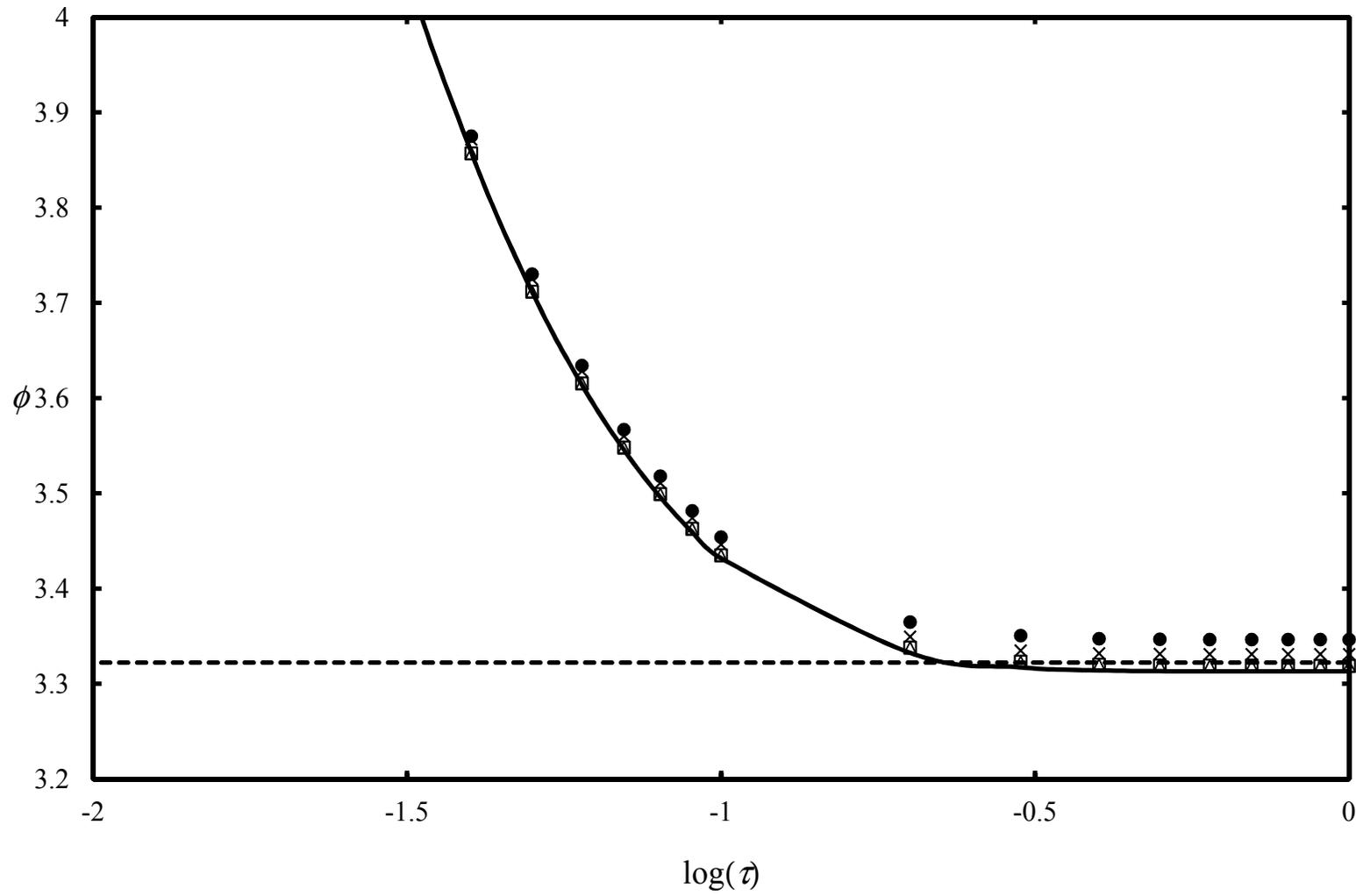


Fig 3

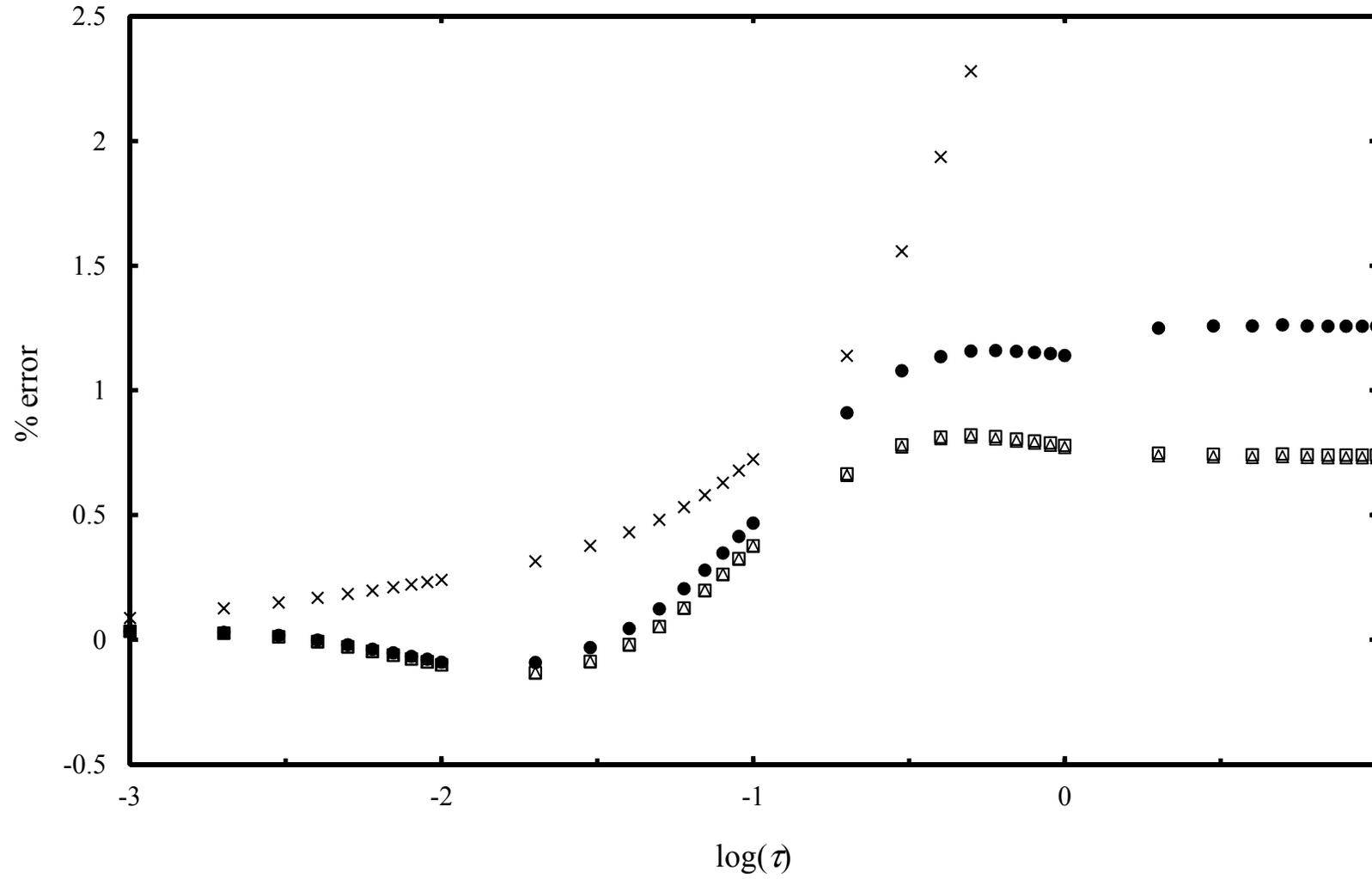


Fig 4

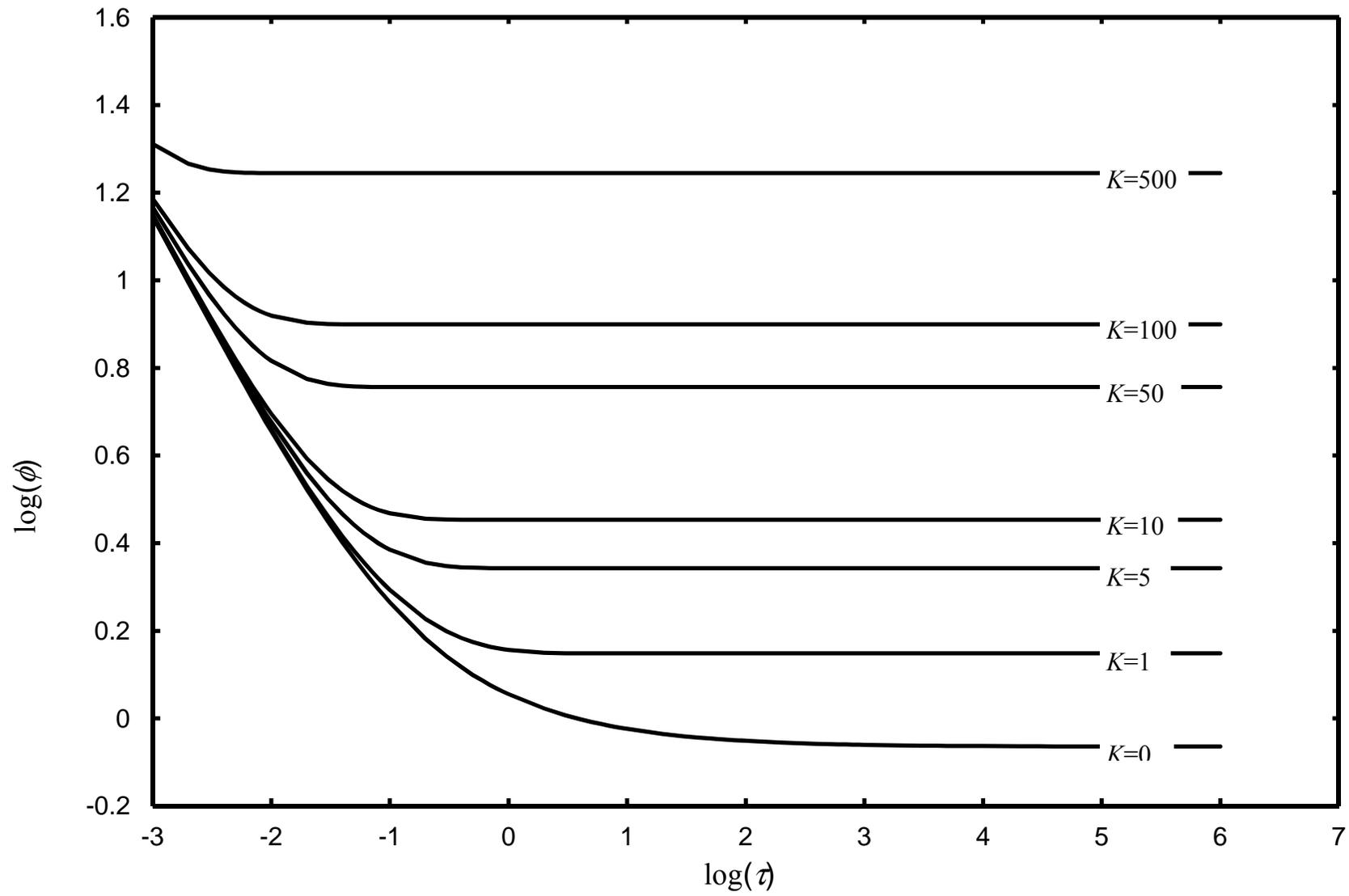


Fig 5

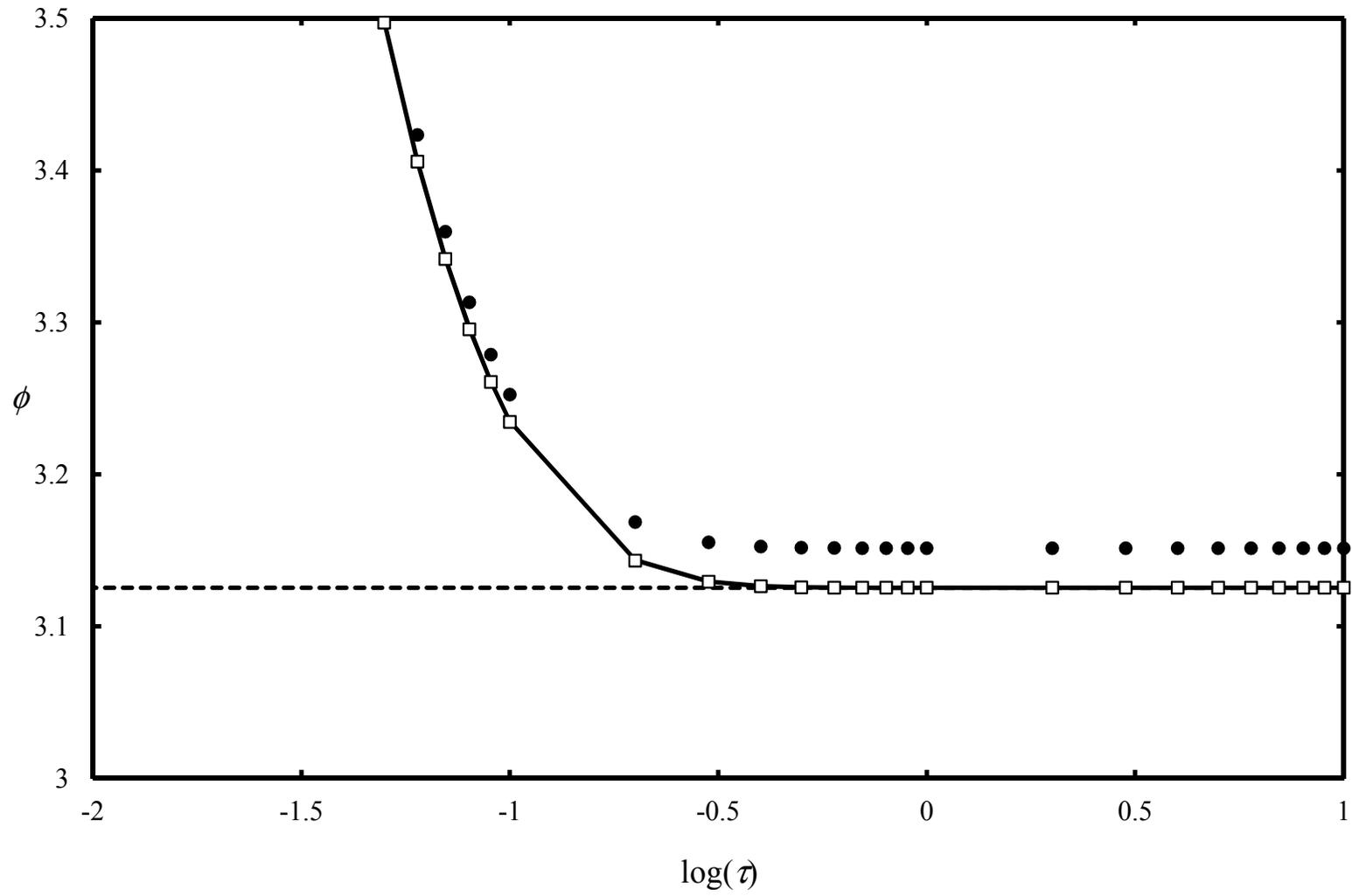


Fig 6