The influence of migration on cyclic and rotating disk voltammograms

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Abstract

Standard methods of analysis based on the dependence of current magnitudes and waveshapes on scan rate (cyclic voltammetry) and rotation rate (rotating disk electrode voltammetry) are available to interpret processes of the form \( A^{z+} + E F \rightarrow A^{(z+n)+} + ne^- \) when the migration current is negligible. Using analysis of simulated voltammograms, the present study shows that when a migration current is present, it simply acts as a scaling factor with respect to current magnitudes and introduces a small potential shift. The effects are equivalent to altering the diffusion coefficient in the fully supported case. Experimental detection of migration can be confirmed by examining the concentration dependence of a process, but not by dependence on scan rate or rotation rate.

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1. Introduction

Recently [1,2], there has been renewed interest in undertaking voltammetric studies in the absence of added supporting electrolyte (ASE) or in dilute electrolyte media such as ionic liquids, particularly when microelectrodes are employed under near steady state conditions [1–8] (minimum IR drop). However, cyclic and rotating disk electrode (RDE) voltammetry also are viable [9,10] techniques that offer some advantages relative to the microelectrode method. For example, the inherent simplicity of the interpretation of transient cyclic voltammograms at stationary electrodes with respect to electrochemical and chemical reversibility, and mechanistic evaluations of electrode processes is an obvious advantage. Consequently, this is frequently the technique preferred by experimentalists for obtaining thermodynamic and kinetic data [11,12], using simulated waves or tabulated data derived from numerical analysis of the theory as a reference. Rotation of the electrode provides hydrodynamic control of the time domain (rather than the potential scan rate), which also may be valuable in mechanistic studies [13].

In the solution phase, voltammetry is traditionally undertaken in the presence of a large excess of added supporting electrolyte (ASE). For studies on a reversible

\[
A^{z+} + E F \rightarrow A^{(z+n)+} + ne^- \tag{1}
\]

or a kinetically controlled process:

\[
A^{z+} + E F \rightarrow A^{(z+n)+} + ne^- \tag{2}
\]

(where \( E_F \) is the formal potential of the couple, \( k_s \) is the heterogeneous rate constant and \( \alpha \) is the transfer coefficient for the electrode reaction), the key to theoretical evaluation of such mechanisms is the mass transport process. In cyclic voltammetry, diffusion, as described by Eq. (3) (Fick’s second law)

\[
\frac{dc}{dt} = -D \frac{\partial^2 c}{\partial x^2} \tag{3}
\]

(where \( D \) is the diffusion coefficient and \( c \) is the concentration of the species of interest, \( t \) is the time, and \( x \) is the distance from the electrode) is the only form of mass transport. When the electrode rotates, the
diffusion–convection relationship (Eq. (4)) applies.

$$\frac{dc}{dt} = -D \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x}$$

(4)

(where $u$ is the velocity in the $x$-direction).

In studies without adequate ASE, a term representing migration has to be added to the equations to give:

$$\frac{dc}{dt} = -D \frac{\partial^2 c}{\partial x^2} - D z F \frac{\partial}{RT \partial x} \left( \frac{c \partial \phi}{\partial x} \right)$$

(5)

(where $z$ is the charge of the species, and $\phi$ is the potential, and $F$, $R$ and $T$ have their usual meanings) or with convection:

$$\frac{dc}{dt} = -D \frac{\partial^2 c}{\partial x^2} - D z F \frac{\partial}{RT \partial x} \left( \frac{c \partial \phi}{\partial x} \right) - u \frac{\partial c}{\partial x}$$

(6)

In the presence of electrolyte, there are well defined relationships that are frequently employed in analysis, for example the Randles–Sevčik equation which is used in linear sweep voltammetry at a stationary electrode:

$$I_p = 0.4463nFAc_B \left( \frac{v}{nF} \right)^{1/2} D^{1/2}$$

(7)

(where $I_p$ is the peak current, $n$ is the number of electrons transferred in the electrode reaction, $A$ is the electrode area, $c_B$ is the bulk concentration and $v$ is the scan rate) and the Levich equation in RDE voltammetry.

$$I_{\text{Lim}} = 0.62nFAc_B \omega^{1/2} V^{-1/6} D^{2/3}$$

(8)

(where $I_{\text{Lim}}$ is the limiting current, $\omega$ is the rotation rate in rad s$^{-1}$ and $V$ is the kinematic viscosity in cm$^2$ s$^{-1}$).

In the present paper, we wish to examine the influence of migration on cyclic and RDE voltammetry using the well defined relationships that apply in the absence of migration as a reference point. It will emerge from the analysis that migration acts to perturb the voltammograms in a similar manner to a change in diffusion coefficient. The implications of this conclusion are discussed.

It is important to distinguish between migration [3,14,15], the mass transport caused by the movement of ions in response to an electric field, and ohmic drop [5,11,16–18], which enhances the overpotential at the electrode surface. Although both effects derive from the presence of the electric field, their actions are different. If a high enough overpotential is applied to any solution, a limiting condition may be achieved at the electrode surface, where ohmic drop has no further discernible effect [19]. The action of migration on mass transport depends on the solution composition in the diffusion layer (and so on the bulk composition), and the exact nature of the electrode reaction. In this paper, we focus only on the effects of migration on mass transport.

2. Experimental

The simulations of cyclic voltammetry at a stationary macrodisk and the RDE were performed using a previously described finite difference technique [10], allowing the accurate reproduction of voltammograms for solutions where defined levels of supporting electrolyte are present, and the interfacial kinetics are governed by the Butler–Volmer equation. The use of an explicit finite difference method requires the use of very fine time increments to ensure the stability of the simulation, as the time step size is proportional to the square of the smallest element of the grid used. It has been the experience of the authors that a finer grid is needed for simulations where migration is a factor than for diffusion alone, and so for the simulations presented, a minimum of $10^5$ time steps were employed.

Cyclic voltammograms were simulated at stationary macrodisk electrodes as a function of scan rate, and at a rotating disk electrode (RDE) at a fixed rotation rate. The effects of migration on the shape and position of the voltammograms were determined, relative to the case where migration is negligible (with excess ASE).

An electrode of area 1 cm$^2$ was assumed. Unless otherwise stated, all species share a common diffusion coefficient of $10^{-5}$ cm$^2$ s$^{-1}$. The reversibility of a voltammogram at a stationary electrode may be gauged using the parameter $\psi$, as defined by Nicholson [20].

$$\psi = \left( \frac{D_{\text{React}}}{D_{\text{Prod}}} \right)^{n/2} \left( \frac{\pi D_{\text{React}} nF}{RT} \right)^{n} v^{-1/2}$$

(9)

(where $D_{\text{React}}$ and $D_{\text{Prod}}$ are the diffusion coefficients of the reactant and the product species, or $D_{\text{Ox}}$ and $D_{\text{Red}}$, respectively, for a reduction, and vice versa for an oxidation process).

Reversible processes were simulated using large values for $k_1$, the heterogeneous charge transfer rate constant for the electrode reaction in cm s$^{-1}$, such that $\psi \geq 20$, with quasi-reversible behaviour being expected for lower $\psi$-values [20]. In all cases presented, $\lambda$, the charge transfer coefficient, was equal to 0.5. Two cases are presented in detail, being the one electron oxidation of a species $A^+$ to $A^{2+}$, and the one electron reduction of $A^{2+}$ to $A^+$. For each case, the species $A$ is present as $A^{n+x}X^{-}$, at a concentration of 1 mM, along with a supporting electrolyte species $M^{z-}$. To achieve conditions approximating infinite support, $M^{z-}X^{-}$ concentrations of 10 M were employed in the simulations, and for low support levels where, migration is significant, $M^{z-}X^{-}$ concentrations of 0.02 mM were used (this being considered more realistic than assuming zero
concentrations of species apart from the analyte).
However, calculations performed with 0.02 mM ASE or none are almost indistinguishable, as are results for 10 M compared with 1 M ASE.

3. Results and discussion

3.1. Reversible cyclic voltammetry

3.1.1. Peak current dependence on scan rate

In linear sweep voltammetry a linear dependence of $I_p$ on $v^{1/2}$ is generally taken as proof that a process is diffusion controlled, as in Ref. [21] for example. The question arises as to whether this $v^{1/2}$ dependence is invalidated by the action of migration. Fig. 1 shows the scan rate dependence of the magnitude of the positive peak currents observed for a one electron oxidation, the negative peak currents for reduction with low support, and also the currents for either reaction with full support. As expected, the magnitude of the current is increased by migration if the magnitude of the charge of the reacting ion is decreased, and vice versa if the charge is increased.

Significantly, the peak current for both the oxidative and reductive processes display a linear dependence on the square root of the scan rate with or without migration, with the oxidative and reductive currents being scaled by factors of 0.815 and 1.136, respectively, when only low levels of support are used. The data in Eq. (1) show that a linear dependence $I_p$ on $v^{1/2}$ actually indicates that a process is under mass transport control (diffusion with or without migration), and not that the process is solely diffusion controlled. The implication is that the Randles–Sevčik equation holds in a phenomenological sense even when a migration current is present. It follows that if the level of supporting electrolyte is unknown, as can be the case with ionic liquids, but is falsely assumed to be adequate to be the purposes of analysis, incorrect conclusions will be arrived at using any method of interpretation based on diffusion-only theory.

3.1.2. Analysis of peak positions

Section 3.1.1 concerns linear sweep voltammetry, whereas in the present section, the influence of migration on cyclic voltammetry is considered. Fig. 2(a) shows a cyclic voltammogram for the oxidation of $A^+$ to $A^{2+}$, with and without adequate support, for a scan rate of 25.69 mV s$^{-1}$ (so that $v = RT/F$) for the reversible case. As expected, the current is diminished by the action of migration relative to that observed with full support. The difference in the positions of the voltammograms is more readily observed by normalising both voltammograms to the oxidative peak, to give the result shown in Fig. 2(b). The net effect of migration in this case is to

![Fig. 1. Scan rate dependence of voltammetric peak currents observed for cyclic voltammetry for a one electron oxidation of $A^+$ to $A^{2+}$ and reduction $A^{2+}$ to $A^+$ under conditions of full support (diffusion only) and minimal support (diffusion plus migration).](image)

![Fig. 2. (a) Comparison of cyclic voltammograms with and without supporting electrolyte for the oxidation of $A^+$ to $A^{2+}$ process. (b) shows the same data as (a) but normalised to the oxidative peak current.](image)
shift the whole voltammmogram to negative potentials. For the corresponding A$^{2+}$ to A$^+$ reduction a negative potential shift is also observed. Negative shifts are always observed where both reactant and product are positively charged and positive shifts are observed where both reactant and product are negatively charged.

For the fully supported case, and if the switching potential is sufficiently removed from the peak potential [12,20], the following relations hold:

\[
\frac{E_{p}^{\text{ox}} + E_{p}^{\text{red}}}{2} = E_{av} = E_{1/2}
\]

(10)

\[
E_{1/2} = E_{f}^{i} + \frac{RT}{nF} \ln \left( \frac{D_{\text{Red}}}{D_{\text{Ox}}} \right)^{1/2}
\]

(11)

\[
P_{p}^{\text{ox}} = E_{1/2} - 1.109 \frac{RT}{nF}
\]

(12)

\[
P_{p}^{\text{red}} = E_{1/2} + 1.109 \frac{RT}{nF}
\]

(13)

\[
\Delta E_{p} = \left| P_{p}^{\text{ox}} - P_{p}^{\text{red}} \right| = 2.218 \frac{RT}{nF}
\]

(14)

(where, $D_{\text{ox}}$ and $D_{\text{red}}$ are the diffusion coefficients of the oxidised and reduced species, $E_{p}^{\text{ox}}$ and $E_{p}^{\text{red}}$ are the potentials of the oxidation and reduction peaks, $E_{1/2}$ is the reversible half-wave potential and $E_{f}^{i}$ is the formal potential).

Examination of Eq. (11) shows that for equal diffusion coefficients, $E_{1/2} = E_{f}^{i}$, and considering Eq. (10) it follows that for the fully supported case $E_{av} = E_{f}^{i}$. In the absence of support the peak potentials shift so that for the A$^{+}$/A$^{2+}$ oxidation $E_{av} - E_{f}^{i} = -7.2$ mV and for the A$^{2+}$/A$^{+}$ reduction $E_{av} - E_{f}^{i} = -5.3$ mV. Thus migration causes a small shift in peak potentials, relative to the fully supported case.

It was noted in Section 3.1.1 that the change in peak current associated with the presence of migration mirrors that caused by a change in diffusion coefficient in the absence of migration. An analogous situation applies when considering the location of peak potentials. As the peak current for a linear sweep voltammogram is proportional to the square root of the diffusion coefficient of the species of interest, and the shift in peak position is equal to $RTnF \ln (D_{\text{Red}}/D_{\text{Ox}})^{1/2}$ it is possible to find a pair of values for $D_{\text{Red}}$ and $D_{\text{Ox}}$ that will mimic the effect of migration on the linear sweep voltammogram. For example, the one electron oxidation of A$^+$ to A$^{2+}$ with low support gives a peak current 0.815 times that of the fully supported case, and with $E_{p}^{\text{ox}}$ offset by -7.2 mV. Clearly, the fully supported oxidation of some species B$^+$ to B$^{2+}$ will give an identical peak height to the fully supported oxidation of A$^+$ to A$^{2+}$ if $D_{b}^{*} = 0.815^{2}D_{A}^{*}$ (and other properties remain unchanged). Furthermore the linear sweep voltammograms for the two cases may overlie each other if either the formal potential is shifted, or if $D_{b}^{*}/D_{A}^{*}$ is set to be equal to $(\exp(0.072nF/RT))^2 = 1.751$. The almost exact equivalence of the oxidative components for cyclic voltammograms when constructed in this manner is shown in Fig. 3, as is the close equivalence for the reductive component.

An analogous set of $D$-values may be chosen for the A$^{2+}$ to A$^+$ reduction to achieve a similar outcome. This method of treating the influence of migration by considering fully supported experiments with artificially modified (and possibly unequal) coefficients reproduces the linear sweep voltammogram almost exactly with respect to the peak potential and current. In the case of cyclic voltammetry only very small differences on the reverse peak are observed when this treatment is employed in cyclic voltammetry.

3.1.3. $I_{p}^{\text{ox}}/I_{p}^{\text{red}}$ ratios

For the fully supported case it is well established that the ratio $[I_{p}^{\text{ox}}/I_{p}^{\text{red}}] = 1.0$ [21]. In cyclic voltammetry, the presence of migration produces only minor departures from this equivalence, as shown in Fig. 2(b), with $[I_{p}^{\text{ox}}/I_{p}^{\text{red}}]$ for the oxidation process being 1.060. A similar result is found for the reduction of A$^{2+}$ to A$^+$, with $[I_{p}^{\text{red}}/I_{p}^{\text{ox}}]$ being 0.946. From an experimental perspective, the changes caused by migration are very small and conclusions based on the chemical reversibility of the process (as indicated by a ratio close to unity) are only marginally altered with respect to the fully supported case.

3.1.4. Current decay after peaks

As would be expected on the basis of the above discussion, and Myland and Oldham’s examination of potential step transients [19], migration acts simply as a scaling factor with respect to the current decay that
occurs after a peak. Thus the Cottrellian dependence of \( I \) on \( i^{-1/2} \) is maintained in the presence of migration.

### 3.2. Reversible rotating disk electrode voltammetry

In a steady state RDE experiment, the mass transport properties of the product do not have the same significance as in cyclic voltammetry. However, by analogy with linear sweep voltammetry, it would be reasonable to assume that migration will appear to act in the same way to a modification of the diffusion coefficient relative to the case of mass transport by diffusion and convection only. In the fully supported case, the Levich equation predicts a linear dependence on the square root of the rotation rate \([21]\). Simulations confirm that this linear relationship still holds both with and without migration. For the oxidation of \( \text{A}^+ \) to \( \text{A}^{2+} \) the ratio of the limiting currents is scaled by a factor 0.822 when migration is present, and for the reduction of \( \text{A}^{2+} \) to \( \text{A}^+ \), a factor of 1.295 was obtained. In a study by Oldham \([22]\) employing analytical solutions to the theory, it was shown that these ratios are 0.820 and 1.298 for the completely unsupported case. The excellent agreement supports the validity of the simulations employed in the study. The dependence of \( I_{\text{lim}} / \omega^{1/2} \) is usually taken as proof that a process is controlled by convection (and diffusion). Our studies and those of Oldham \([22]\) confirm that this linear dependence only provides proof of mass transport control (diffusion plus convection plus migration).

The analytical theory of Oldham is restricted to the limiting current plateau and is not applicable to the rising part of the voltammogram. In contrast, simulations afford the entire voltammetric response. Thus we are now in a position to analyse the effect of migration on the RDE waveshape and position. Fig. 4 shows a comparison of simulated voltammograms for the supported and unsupported oxidation of \( \text{A}^+ \) to \( \text{A}^{2+} \).

For the reversible case at an RDE, the entire wave is shifted by \(-6.09 \text{ mV}\) for the oxidation of \( \text{A}^+ \) to \( \text{A}^{2+} \), and by \(-5.94 \text{ mV}\) for the reduction of \( \text{A}^{2+} \) to \( \text{A}^+ \). However, the wave shape is unaltered by migration as indicated by plots of \( \ln(I_{\text{lim}}/I-1) \) versus \( E-E_r \), which have slopes of \( nF/RT \) \([12]\), where \( I \) is the current at potential \( E \).

For a reversible process under full support, well known voltammetric equations include \([23]\).

\[
E_{1/2} = E_r + \frac{RT}{nF} \ln \left( \frac{D_{\text{Red}}}{D_{\text{Ox}}} \right)^{2/3}
\]

\[
E = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{I_{\text{lim}}}{I} - 1 \right)
\]

In the presence of migration, the apparent shift in wave position again mirrors that caused by the action of unequal diffusion coefficients.

### 3.3. Quasi-reversible cyclic voltammetry

The influence of migration on quasi-reversible voltammetry can be conveniently discussed with reference to Eq. \((9)\). Thus we shall look at the effect of varying \( \psi \) on the voltammetric response with and without migration.

#### 3.3.1. \( \Delta E_p \) analysis

Traditionally for quasi-reversible cases, analysis of \( \Delta E_p \) as a function of scan rate is used to gauge the reversibility of the electrode process. Nicholson’s normalised parameter \( \psi \) \([20]\), as defined in Eq. \((9)\), expresses the reversibility of a cyclic voltammogram as...
a function of the scan rate and the rate of interfacial electron transfer. For fully supported cyclic voltamograms the expected peak splitting, $\Delta E_P$ is found to be a function of $\psi$, and to be constant provided that the switching potential $E_s$ is at least $90/n$ mV beyond $E_{1/2}$. Following Nicholson’s practice of setting $E_s$ to be $E_{1/2} + 141$ mV, Fig. 5 shows a family of cyclic voltamograms resulting from setting $\psi$ to 0.1, 0.25, 0.35, 0.5, 0.75, 1, 2, 3, 4, 6 and 20 along with those obtained by setting $E_s$ to be $E^{\text{eq}}_p + 110$ mV, for the one electron oxidation of $A^+$ with low support. For all the voltamograms shown, the scan rate was set to $RT/F$ (V s$^{-1}$), and $k_s$ was varied to achieve the desired $\psi$-value.

Simulations for the one electron reduction of $A^+$ and its supporting electrolyte, and for constant or variable $E_s$ have also been undertaken with and without support, and the $\Delta E_P$ values found are shown in Table 1. It may be observed that where the charge of the product is larger than that of the reactant, the $\Delta E_P$ values obtained with low support are reduced compared with the fully supported case, and vice versa. It is notable that the influence of migration on the $\Delta E_P$ values remains minimal for quasi-reversible systems. This indicates that the analysis of such voltamgrams using Nicholson’s method [20], valid for the diffusion only case, would remain reasonably accurate under this circumstance.

As before, the influence of migration on the position of the voltammetric waves is more readily revealed by examining normalised voltamograms, as in Fig. 6(b). This form of presentation shows that a similar offset in potential applies for quasi-reversible voltamgrams as found for the reversible case.

This offset may be characterised by examination of $E_{\text{av}}$, as defined in Eq. (10). Table 2 shows the shift in $E_{\text{av}}$ relative to $E_f^\psi$ as a function of $\psi$ for both supported and unsupported cases. The shift in potential identified previously for the reversible case is essentially additive with that caused by the quasi-reversible kinetics. The magnitude of the shift would be difficult to detect experimentally. Thus, the average peak position may still be assumed to give $E_{\text{av}}$ to within 10 mV for $\psi > 0.25$. Note that for the fully supported case, the value for the average of the peaks tends to zero only when the reversal potential is well removed from the formal potential.

### Table 1

<table>
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<th>Low support</th>
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<td>Oxidation of $A^-$</td>
<td>Reduction of $A^{3-}$</td>
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3.3.3. Quasi-reversible rotating disk electrode voltammetry

The limiting current at an RDE is always independent of \( k_e \) and thus the discussion of the invariant behaviour of \( I_{\text{lim}} \) for the reversible case (Section 3.2) also applies to the quasi-reversible case. However, the shape of the voltammograms will be altered by slow electron transfer. To describe such changes in the shape of RDE voltammograms, the position of the potential at which the current reaches 1/4, 1/2, and 3/4 of the limiting current \( (E_{1/4}^\text{p}, E_{1/2}^\text{p}, E_{3/4}^\text{p}) \) may be examined. Figs. 8 and 9 show the variation of these parameters with \( k_e \) (the rate of electron transfer) for the supported and unsupported cases.

Figs. 8 and 9 show that the position of the waves obtained moves in the presence of migration, but by an almost constant offset so that the shape of the voltammograms obtained is not altered. The shift of the voltammogram by a small offset is entirely analogous to that seen in transient voltammetry, where the offset is nulled in analysis of \( \Delta E_p \) values \( (E_p^\text{QV} - E_p^\text{Red}) \). For RDE voltammograms the value of \( E_{1/4}^\text{p} - E_{1/4}^\text{p} \) is used for kinetic analysis, and again the offset in \( E_{1/4}^\text{p} \) and \( E_{3/4}^\text{p} \) is almost constant so that the differences are substantially unaltered by migration. Consequently, the simpler theory for the fully supported case may be employed without noticeable errors. It also follows that it is not, therefore, possible to tell by examining a single voltammogram obtained at an RDE whether it is influenced by migration or not.

4. Conclusions

Calculations in this paper show that diagnostic tests to establish diffusion only (transient voltammetry at

![Graph](image)

Table 2

\[
\begin{array}{ccc|ccc|ccc|ccc}
\hline
\psi & Full support & & & Low support & & & \\
& Oxidation of A^+ & Reduction of A^{2+} & & Oxidation of A^- & Reduction of A^{2-} & \\
\hline
20 & -0.92 & -0.94 & 0.92 & 0.92 & -7.02 & -7.08 & -5.29 & -5.34 \\
7 & -0.80 & -0.80 & 0.80 & 0.78 & -6.89 & -6.94 & -5.41 & -5.47 \\
6 & -0.77 & -0.77 & 0.77 & 0.75 & -6.86 & -6.91 & -5.44 & -5.51 \\
5 & -0.72 & -0.72 & 0.72 & 0.70 & -6.81 & -6.86 & -5.49 & -5.56 \\
4 & -0.66 & -0.65 & 0.65 & 0.63 & -6.74 & -6.78 & -5.55 & -5.63 \\
3 & -0.54 & -0.52 & 0.54 & 0.51 & -6.63 & -6.66 & -5.67 & -5.76 \\
2 & -0.32 & -0.28 & 0.32 & 0.27 & -6.41 & -6.42 & -5.9 & -6.01 \\
1 & -0.37 & 0.44 & -0.37 & -0.44 & -5.74 & -5.73 & -6.62 & -6.76 \\
0.75 & 0.83 & 0.91 & -0.83 & -0.91 & -5.30 & -5.28 & -7.11 & -7.25 \\
0.5 & 1.72 & 1.80 & -1.72 & -1.80 & -4.42 & -4.44 & -8.04 & -8.18 \\
0.35 & 2.80 & 2.82 & -2.80 & -2.83 & -3.36 & -3.46 & -9.14 & -9.21 \\
0.25 & 4.04 & 3.93 & -4.04 & -3.97 & -2.09 & -2.38 & -10.36 & -10.28 \\
0.1 & 7.48 & 6.42 & -7.48 & -6.60 & 1.70 & 0.21 & -13.35 & -12.31 \\
\hline
\end{array}
\]
macrodisks) or diffusion–convection (RDE voltammetry) behaviour are not invalidated by the presence of migration. It is not, therefore, as easy as might be imagined to distinguish whether migration is or is not influencing a voltammogram without any prior knowledge of the system under study. Thus tests based on
parameter interrelationships derived from the Randles–Sevčik or Levich equations can only show whether or not a process is mass transport controlled, and not whether mass transport by migration is absent.

Experimental detection of migration should be made by examining the interrelationship between currents and the ratio of analyte to supporting electrolyte concentrations. All the calculations and discussion in the present paper assume the absence of uncompensated resistance effects and charging current. In any real experiment, these terms must be considered, making the influence of migration even harder to detect.

References