Analytical formulaes and comparative analysis for linear models in chronoamperometry under conditions of diffusion and migration

Alemdar Hasanov · Şafak Hasanoglu

Abstract　Mathematical models of ion transport in a potential field are analyzed. Ion transport is regarded as the superposition of diffusion and migration. The explicit analytical formulaes are obtained for the concentration of the reduced species and the current response in the case of pure diffusive as well as diffusion–migration model, for various initial conditions. The comparitive analysis of these formulaes for current responses and deviation from the classical Cottrellian are derived. The proposed approach can predict an influence of ionic diffusivities, valences, initial and boundary concentrations to the behaviour of current response. In addition to these, the analytical formulaes obtained can also be used for numerical and digital simulation methods for Nernst-Planck equations.

Keywords　Ion transport · Chronoamperometry · Cottrell experiment · Diffusion–migration · Current response · Analytical solution

1 Introduction

In recent years there has been growth of interest in the theoretical and computational modelling of electroanalytical experiments performed under conditions of semi-infinite diffusion–migration transport (see, for example, [1,2] and references therein). Mathematical modelling of such problems in electrochemistry, in general, and in chronoamperometry, in particular, is usually based on the Nernst-Planck equations

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[3–6]. In many cases these models are quite complicated due to their nonlinearity. More realistic models, in particular, models in real time and space domains, certainly require numerical simulations [7,8]. This is one of reasons why most of the results have been obtained for simplest or/and steady state experiments. Analytical solutions obtained for these simplest models permit one to understand experiments. Moreover, some relationships obtained by this way may play a key role in finding out some distinguished features of an experiment, which can not be estimated experimentally. In chronoamperometry such a classical result has been obtained by Cottrell [9]. In 1902 Cottrell derived a linear initial-boundary value problem (IBVP) and demonstrated that, if an extreme potential is suddenly applied to an electrode in contact with a solution containing a uniform concentration of an electroreactant, then the resulting current response $\mathcal{I}_D$, defined to be as Cottrellian, is proportional to $1/\sqrt{t}$. Subsequently this result has also been confirmed experimentally. This relationship assumes that the ion transport is purely diffusive, planar and semi-infinite. Deviations from the ideal Cottrellian response provide information about complex chemical kinetics and kinetics of electron transfer. For this reason various modifications of the relationship $\mathcal{I}_D \sim 1/\sqrt{t}$ still are investigated. Thus, the transport response of electrodes under conditions of diffusion and migration was studied by Lange and Doblhofer [3]. The Nernst-Planck equation was used to derive the transport of the electroactive species with zero initial condition. The problem then was solved by digital simulation techniques. More detailed mathematical model of mass and charge transport in a controlled potential experiment were given by Pfabe [4] and Cohn et al. [5]. This model leads to the nonlocal identification problem for nonlinear parabolic equation and shows how the migration component of the the total flux gives rise to a nonlinearity in the transport equations. Moreover, the model includes the nonlocal additional condition in the form of the integral relationship between the concentration and current response. Some numerical methods for the similarity solution of the nonlocal identification problem have been given by Hasanov [10], Hasanov et al. [11], and also by Shores and Pfabe [12]. Series of modelling studies related to a hemispherical electrode immersed in a semi-infinite electrolyte have been presented by Stojek et al. [13–16]. An analytical formula and some numerical results for the potential step chronoamperometry have been obtained by Myland and Oldham [17], assuming equal diffusion coefficients of all ions. Analyzing the similarity problem, here the effect of migration on the limiting Cottrell currents was studied. For the case of unequal diffusion coefficients this model was developed by Bieniasz [6]. The effects of the diffusivity ratio D_R/D_C, as well as of the electroactive and counter-ions on the limiting chronoamperometric currents was examined. Analytical formula of the current response for diffusive–convective linear model of ion transport was given by Hasanov and Hasanoglu [18].

The above sited studies show that obtaining analytical solutions in ion transport problems is usually impossible, especially in the presence of the migration factor. This, in particular, means that computational and digital simulations for these problems are necessary (see, [10–12] and [19] and references therein). However, to make reliable computational program products and results one needs to have analytical solutions of some simple models. The aim of this work is to derive analytical solutions of some useful ion transport models, including diffusion and migration. We will analyze

also an influence of the concentration at $x = 0$ to the solution, and present some comparitive analysis of the models.

2 Analytical formulaes for pure diffusive models

Consider one-dimensional model of mass and charge transport in a controlled potential experiment, i.e. in chronoamperometry, given by Pfabe [4] and Cohn et al. [5]. We assume that there is an electrode at $x = 0$, and a medium containing mobile ions and electroactive species in the one-dimensional motion from the electrode to $x = \infty$. A potential $E = E(x, t)$ introduced at the initial time $t = 0$ causes a *reduced fraction* of the *oxidized species* at the surface of the electrode. As oxidized species are reduced at the surface of the electrode, its concentration decreases, and the concentration $C_R = C_R(x, t)$ of the reduced species at the electrode increases. As a result there arises two diffusion processes: oxidized species diffuse in toward $x = 0$, and the reduced species, out into the medium. Hence ion transport here can be regarded as a superposition of diffusion and migration. Exchange of electrons between the surface of the electrode and electroactive species in the time $t > 0$ gives rise to the *current response* $\mathcal{I} = \mathcal{I}(t)$, which is related to the concentration of reduced species by the equation

$$\int_0^\infty C_R(x, t)dx = \frac{1}{nFS_e} \int_0^t \mathcal{I}(\tau)d\tau. \tag{1}$$

Here n is the number of electrons gained by an ion upon reduction, F is Faraday's constant and S_e is the surface of the electrode. The total charge carried by the reduced species is

$$Q(t) = \int_0^t \mathcal{I}(\tau)d\tau. \tag{2}$$

Definitions (1), (2) permit one to define the total charge $Q(t)$ and the current response $\mathcal{I}(t)$ via the concentration $C_R(x, t)$ of the reduced species as follows:

$$Q(t) = nFS_e \int_0^\infty C_R(x, t)dx, \quad \mathcal{I}(t) = nFS_e \int_0^\infty \frac{\partial C_R(x, t)}{\partial t}dx. \tag{3}$$

We denote by $J_R(x, t)$ and D_R the flux and diffusivity of the reduced species. According to the Nernst-Planck equation [20]

$$J_R(x, t) = -D_R \left(\frac{\partial C_R(x, t)}{\partial x} - \frac{F}{RT} z_R C_R(x, t) E(x, t) \right), \tag{4}$$

where $E(x, t)$ denotes the electric field, and R and T denote the gas constant and the temperature, respectively, and z_R denotes the valence of the reduced species.

Let us assume first that the migration flux is negligable, i.e. $(F/RT)z_R C_R E(x, t) = 0$. Then the balance equation $\partial C_R/\partial t + \partial J_R/\partial x = 0$ with the above Nernst-Planck equation implies the diffusion equation $\partial C_R/\partial t = D_R \partial^2 C_R/\partial x^2$, $x > 0$, $t > 0$.

To derive the initial (at $t = 0$) and boundary (at $x = 0$) conditions we use the electroneutrality condition, and also the relationship between the potential and concentrations species [20]. The electroneutrality condition at the boundary $x = 0$ implies:

$$z_O C_O(0, t) + z_R C_R(0, t) = C^*. \tag{5}$$

Here z_O denotes the valence of the oxidized reduced species, and the constant $C^* \geq 0$ is the characteristic concentration of the medium and may not be zero. The relationship between the potential E and the concentrations C_R and C_O of the reduced and oxidized species, at $t = 0$, is given by the formulae [21]

$$\exp\left\{\frac{nF}{RT}(E(t) - E^{0'})\right\} = \frac{C_O(0, t)}{C_R(0, t)}. \tag{6}$$

Here $E(t)$ and $E^{0'}$ denote the applied electric potential step, and the conditional potential that is characteristic of the considered chemical reaction.

Solving Eqs. (5) and (6) with respect to $C_R(0, t)$ we find $C_R(0, t) = \mu_0(t)$, where

$$\mu_0(t) = \frac{C^*}{z_R + z_O \exp\left\{\frac{nF}{RT}(E(t) - E^{0'})\right\}}. \tag{7}$$

If $E(t) \ll E^{0'}$ (for a reduction) then the exponential term in Eq. (7) is negligable and the equation reduces to $C_R(0, t) = C^*/z_R$. Since the concentration of the reduced species is initially zero, at $t = 0$ the have the initial condition $C_R(x, 0) = 0$. Hence, if $E(t) \ll E^{0'}$, in absence of migration the IBVP describing the above experiment can be modelled by the following IBVP:

$$\begin{cases} \frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}, & x > 0, \quad t > 0; \\ C_R(x, 0) = 0, & x > 0; \\ C_R(0, t) = C^*/z_R, & t > 0. \end{cases} \tag{8}$$

Otherwise, for the given by (7) data $\mu_0(t)$, the general IBVP is:

$$\begin{cases} \frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}, & x > 0, \quad t > 0; \\ C_R(x, 0) = 0, & x > 0; \\ C_R(0, t) = \mu_0(t), & t > 0. \end{cases} \tag{9}$$

Problem (8) corresponds to the classical Cottrell's model, which analytical solution and the corresponding current response $\mathcal{I}_C(t)$ (Cottrellian) has been obtained by Cohn in [5]:

$$C_R(x, t) = \frac{C^*}{z_R} erfc\left(\frac{x}{2\sqrt{D_R t}}\right), \quad \mathcal{I}_C(t) = \frac{nFS_e C^*}{z_R}\sqrt{\frac{D_R}{\pi t}}. \tag{10}$$

Table 1 Models and analytical solutions

Models/IBVPs	Current response
Pure diffusion	$\mathcal{I}_D(t)$
Cottrell's model (8)	$\mathcal{I}_C(t) = \frac{nFS_eC^*}{z_R}\sqrt{\frac{D_R}{\pi t}}$
$C_R(0,t) = C^*/z_R$	(Cottrellian)
General IBVP (9)	
$C_R(0,t) = \mu_0(t)$	$\frac{z_R}{C^*}\mu_0(0)\mathcal{I}_C(t) + nFS_e\sqrt{\frac{D_R}{\pi}}\int_0^t \frac{\partial\mu_0(\tau)}{\partial\tau}\frac{d\tau}{\sqrt{t-\tau}}$ (F_1)
Diffusion–migration	$\mathcal{I}_{DM}(t)$
Model (12) (Limiting case)	
$C_R(0,t) = C^*/z_R$	$\exp\left(-\frac{v^2}{4D_R}t\right)\mathcal{I}_C(t) + \frac{nFS_eC^*v}{2z_R}\left[1 + erf\left(\frac{v}{2}\sqrt{\frac{t}{D_R}}\right)\right]$ (F_2)
Model (15) (with data (7))	$\frac{z_R}{C^*}\mu_0(0)\exp\left(-\frac{v^2}{4D_R}t\right)\mathcal{I}_C(t) + nFS_e\{\frac{v}{2}\mu_0(t) +$
$C_R(0,t) = \mu_0(t)$	$\sqrt{\frac{D_R}{\pi}}\int_0^t \exp\left(-\frac{v^2(t-\tau)}{4D_R}\right)[\mu_0'(\tau) + \frac{v^2}{4D_R}\mu_0(\tau)]\frac{d\tau}{\sqrt{t-\tau}}\}$ (F_3)

where $erfc(z) = 1 - erf(z)$, and $erf(z)$ is the error function.

The solution of the general problem (9) has the following integral representation [22]:

$$C_R(x,t) = \int_0^t \mu_0(\tau)\frac{\partial}{\partial t}erfc\left(\frac{x}{2\sqrt{D_R(t-\tau)}}\right)d\tau. \tag{11}$$

Substituting Eq. (12) in Eq. (4), after elementary calculations we find the formulae (F_1) given in Table 1, for the current response $\mathcal{I}_D(t)$. Comparing Eq. (10) with Eq. (11) and (F_1) we conclude that formulaes (10) are the special case of these general formulaes. Furthermore, $\mathcal{I}_D(t) = \mathcal{I}_C(t)$, when $\mu_0(\tau) = C^*/z_R$, and formulae (F_1) preserve the characteristic Cottrellian current dependence $\mathcal{I}_D(t) \sim t^{-1/2}$ [9].

3 The model including diffusion and migration

Let us denote by $v(x,t) = (F/RT)E(x,t)D_Rz_R$ the coefficient (migration parameter) on the right hand side of Eq. (4), related to the migration. We assume that $v(x,t) = v = const$, and the concentration $C_R(x,t)$ of the reduced species at the electrode $(x = 0)$ is made to jump from zero to C^*/z_r. This experiment corresponds to the following IBVP:

$$\begin{cases} \frac{\partial C_R}{\partial t} = D_R\frac{\partial^2 C_R}{\partial x^2} - v\frac{\partial C_R}{\partial x}, & x > 0, \quad t > 0; \\ C_R(x,0) = 0, & x > 0; \\ C_R(0,t) = C^*/z_R, & t > 0. \end{cases} \tag{12}$$

Introducing the new function

$$w(x,t) = \exp\left(-\frac{v}{2D_R}x + \frac{v^2}{4D}t\right)C_R(x,t), \tag{13}$$

we can easily show that the function $w = w(x, t)$ satisfies the IBVP

$$\begin{cases} w_t = D_R w_{xx}, & x > 0, \quad t > 0; \\ w(x, 0) = 0, & x > 0; \\ w(0, t) = \mu_1(t), & t > 0, \end{cases} \tag{14}$$

with the time dependent concentration at $x = 0$ $\mu_1(t) = C^*/z_r \exp(v^2/4Dt)$. For many purely diffusional problems auxiliary problem (14) with the given boundary concentration $\mu_1(t)$ at $x = 0$ can be hanled seperately (see, [20,23] and references therein). This model corresponds to the exponentially increasing concentration of reduced species at $x = 0$. The solution of this problem can be obtained from formulae (11) by subsituting here $\mu_0(t) = \mu_1(t)$. The analytical formulaes for the current responses corresponding to problems (12) and (14) are obtained in [18]. The current response corresponding to the model (12) is given in Table 1 by formulae (F_2).

We consider here the general diffusion–migration model with the real data $\mu_0(t)$, given by Eq. (7):

$$\begin{cases} \frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} - v \frac{\partial C_R}{\partial x}, & x > 0, \quad t > 0; \\ C_R(x, 0) = 0, & x > 0; \\ C_R(0, t) = \mu_0(t), & t > 0. \end{cases} \tag{15}$$

Solution of this problem can be obtained by using the solution $w(x, t)$ of the auxiliary problem (14), with $\mu_1(t) = \mu_0(t)$:

$$C_R(x, t) = \frac{x}{2\sqrt{\pi D_R}} \exp\left(\frac{vx}{2D_R} - \frac{v^2 t}{4D_R}\right) \int_0^t \exp\left(\frac{v^2 \tau}{4D_R} - \frac{x^2}{4D_R(t - \tau)}\right)$$
$$\times \frac{\mu_0(\tau)}{\sqrt{(t - \tau)^3}} d\tau. \tag{16}$$

The formulae for the current response $\mathcal{I}_{DM}(t)$ corresponding to the general diffusion–migration model (15) is given by formulae (F_3) in Table 1. It can be verified that all the above formulas for the current response can be obtained from this formulae. This formula convenient and useful for testing various numerical methods for diffusion–migration models.

The analytical formulaes for the current responses, given in Table 1 and corresponding to the above considered models with the given initial concentrations, precisely show deviations from the Cottrellian as well as dependence of these deviations from the physico-chemical parameters. Specifically, all the formulaes $(F_1) - (F_3)$ contain the Cottrellian $\mathcal{I}_C(t)$. Further, the formulae (F_2) is the limit case of the formulae (F_3), when $E(t) - E^{0'} \to -\infty$, which means in practce $E(t) \ll E^{0'}$. The case $E(t) \gg E^{0'}$ means that the initial concentration $C_R(0, t)$ at $x = 0$ is too small. The formulae (F_3) also show the charter of dependence of the current response on migration parameter $v > 0$.
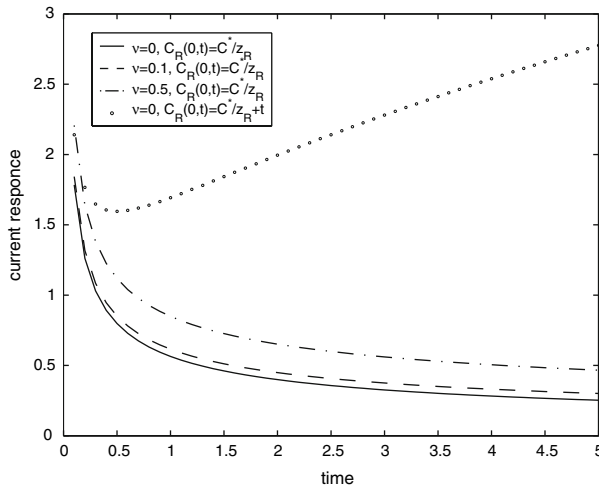
Fig. 1 Current responses corresponding to pure diffusion and diffusion–migration models, and constant initial concentration $C_R(0, t) = C^*/z_R (D_R = 1, C^* = 1, (z_R, z_O) = (1, 3))$.(**a**) initial concentration $C_R(0, t) = C^*/z_R$ (**b**) $C_R(0, t) = \mu_0(t)$

4 Computational experiments

Analytical formulaes presented in Table 1 show the relationship between the classical Cottrellian $\mathcal{I}_C$ and the current responses for different models. These formulaes also show the dependence of the current responses on the diffusion–migration parameters. We will analyze here these dependencies on the numerical solutions of these models. The valences z_R and z_O of the reduced and oxidized species are assumed to be integers of the same sign, and $z_R \neq -1, z_O \neq 1$, since one electron must be gained in reduction. In our computations, $-4 < z_R < z_O \leq -1$ and $1 < z_R < z_O \leq 3$. The value of the parameter $\kappa = nF/(RT)$ is assumed to be [20] as $\kappa = 0.0592 \log e$. For simplicity we will use the normalized diffusion coefficient $D_R = 1$ and characteristic concentration $C^* = 1$.

In the first series of computational experiments demonstrate the comparison of current responses corresponding to different models. Figure 1a visualizes an influence of the migration parameter $\nu > 0$ (normalized by $RT/(FE)$) to the current response. The solid line here is the classical Cottrelian $\mathcal{I}_C$, and other lines are the current responses corresponding to the general diffusion–migration model, given by Eq. (15). Except the line ◦ ◦ ◦, here all lines, which have the same charcter of decay, correspond to the constant concentration $C_R(0, t) = C^*/z_R$ at $x = 0$, and only the upper line ◦ ◦ ◦ corresponds to the non-constant concentration at $x = 0 : C_R(0, t) = C^*/z_R + t$. Figure 1b demonstrates the behaviour of the current response for the positive and negative values of valences of the reduced and oxidized species.

To study the dependence of the current response and the concentration profile of the reduced species on the difference $\Delta E = E(t) - E^{0'}$ of the applied electrode potential step and the conditional potential of the considered electrochemical reaction in Eq. (7), series of computational experiment were realized for the general
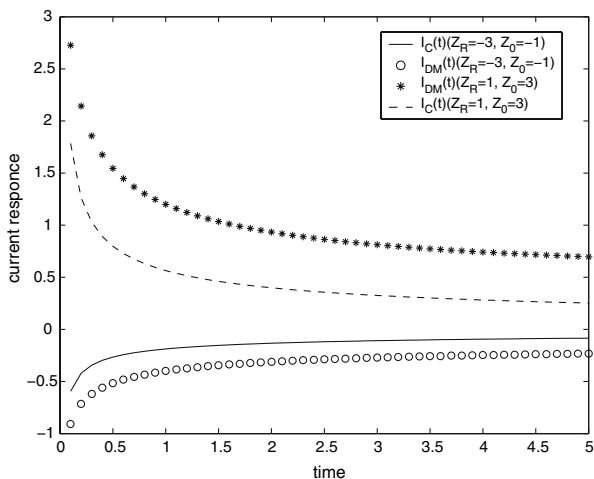
Fig. 2 An influence of the applied electrode potential step $\Delta E(t)$ to the character of the current response and concentration profiles at $t = 4(D_R = 1, \nu = 1)$. (**a**) Current responses $\mathcal{I}_C$ and $\mathcal{I}_{DM}$ (**b**) Concentration profiles $((z_R, z_O) = (1, 2))$

diffusion–migration model (15). The solid line in Fig. 2a corresponds to the limiting case when the concentration at $x = 0$ is constant: $C_R(0, t) = C^*/z_R$, when $(z_R, z_O) = (1, 2)$. Other lines show the behaviour of the current response when ΔE changes from -10^2 to 10^2. The case $\Delta E = -10^2$ evidently close to the limiting case $C_R(0, t) = C^*/z_R$, and the case $\Delta E \geq 10^2$ corresponds to almost zero values of the concentration.

Note that in chronoamperometry, concentration of the reduced species is made jump from zero to C^*/z_R at time $t = 0$. Reassessment of this phenomenon is illustrated in Fig. 2b. For extremely high voltage perturbation, the concentration of oxidized species at the electrode drops immediately to zero, as was established experimentally [20]. This expectation is seen from the profiles $C_R(x, t = 4)$ of the concentration in Fig. 2b. To show an influence of the valence z_O of the oxidized species the case $(z_R, z_O) = (1, 3)$ is also illustrated here (the second line . . . from below).

5 Conclusions

Analytical solutions of diffusion–migration model arising in ion transport problem has been derived based on the Nernst-Planck equation. The presented general solution can generate all well known analytical solutions with various type of concentrations at the initial point. The comparitive analysis of the formulaes for current responses and deviation from the classical Cottrellian are deived. The presented analytical solutions can also be used as an important tool in numerical simulations.

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