

# Relationship between current response and time in ion transport problem including diffusion and convection.

## 2. Numerical approach

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The mathematical model related to controlled potential experiments in electrochemistry is studied. Ion transport is regarded as the superposition of diffusion and migration under the influence of an electric field. Modeling of the experiment leads to the nonlocal identification problem for nonlinear parabolic equation. It is shown that in some cases the nonlocal identification problem can be transformed to an initial value problem for nonlinear parabolic equation. The finite difference approximation of this problem, with the appropriate iteration algorithm, is derived. Based on these algorithms the solution of the identification problem is presented. The obtained results permits one to derive the behaviour of the current response  $\mathcal{I}_c(t)$ , depending on time, also the relationship between the current response  $\mathcal{I}_c(t)$  and Cottrellian  $\mathcal{I}_G$  is obtained in explicit form. An influence of the valences oxidised and reduced species is also analyzed.

**KEY WORDS:** ion transport, identification, current response, migration

**AMS(MOS) subject classifications:** 35K15, 76R05, 80A30

### 1. Introduction

Mathematical modeling of kinetics and mass-transfer in electrochemical events, even in their simplest statement, generally consists of dealing with various physico-chemical parameters, as well as complicated mathematical problems. In this study we analyse the mathematical and numerical models of mass and charge transport in a controlled potential experiment in electrochemistry, called

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chronoamperometry [1–14]. In the case of two-species (oxidized and reduced species) migrating under the influence of the electric field, the mathematical model and governing equations are derived in [1]. This model assumes that the charge flux arises from diffusion and migration of ions under the influence of the electric field. The scaled model with respect to the concentration  $u(x, t)$  of the reduced species leads to the following identification problem for the nonlinear parabolic equation with the unknown coefficient  $q(t)$  [1]:

$$\begin{cases} u_t = (g(u)u_x)_x + q'(t)h(u)_x, & (x, t) \in R_+ \times R_+, \quad R_+ := (0, +\infty), \\ u(x, 0) = 0, & x \in R_+, \\ u(0, t) = 1, & t \in R_+, \\ q(t) = \int_0^\infty u(x, t)dx, & t \geq 0. \end{cases} \quad (1)$$

To the best of our knowledge, this problem, interesting also from the point of view nonlocal inverse optimal control problems, is not still solved neither mathematically, nor numerically. The only similarity solution of this problem is studied in [1]. A variational approach with the conservative finite difference scheme for the similarity solution was presented in [15, 16]. In the case of charge flux arising only from diffusion, the model reduces to initial-boundary value problem for parabolic equation. The analytical formula for classical Cottrellian  $\mathcal{I}_G$ , corresponding to pure diffusive model has also been obtained in [1]. Extending this approach for the diffusion-convection model the explicit analytical formula for the current response  $\mathcal{I}_c$  was obtained in [17]. Obtained relationship between the current response  $\mathcal{I}_c$  and the classical Cottrellian  $\mathcal{I}_G$  shows the degree of influence of the convection factor to the current response  $\mathcal{I}_c$ .

The present work is aimed to analyze the nonlinear model (1) by taking into account the migration component, assuming that the nonlinear term  $h(u)_x$  of the parabolic equation has the form  $h(u)_x := u/z_r$ . Physically this linearization is possible when  $z_r D_r = z_0 D_0$ , where  $z_r, z_0$  are the valences, and  $D_r, D_0$  are the diffusivity of the reduced and oxidizes species. Although the second assumption makes some restrictions, it permits to analyze the nonlinear model (1) for some real class of materials. In particular, we reduce the nonlocal identification problem (1) to the nonlinear parabolic problem, and construct an iteration algorithm for the numerical solution. Note that the mathematical and numerical analysis of the considered problem were given only for similarity solution (see, [1, 15, 16]).

In the next section the derive some important aspects of the physico-chemical and mathematical models derived in [1]. An analysis of the identification problem is given section 3. The finite-difference approximation and iteration algorithms for obtained nonlinear discrete problem is derived in section 4. In the final section 5 the results of numerical experiments and their interpretations are presented.

Table 1  
The values of valences and the diffusivity ratio.

$z_0$	-1	-2	-3	2	3
$z_r$	-2	-3	-4	1	2
$k := D_r/D_0$	1/2	2/3	3/4	2	3/2

**2. The mathematical model of nonlinear ion transport problem**

To briefly discuss here the scaled mathematical model given by (1). The functions  $g(u)$  and  $h(u)$  express an influence of the diffusion and migration in the ion transport and have the forms:

$$g(u) := \frac{z_0 + (z_r - z_0)u}{z_0 + (z_r k - z_0)u}, \quad h(u) := \frac{ku}{z_0 + (z_r k - z_0)u}.$$

The valences  $z_r, z_0$  are assumed to have the same sign and their admissible values are given in table 1. The dimensionless parameter  $k := D_r/D_0$  is the diffusivity ratio.

In the view of the dimensionless parameters, the function  $q(t) \geq 0, \forall t \geq 0$ , on the left hand side of the nonlocal condition (1), is defined via the total charge

$$Q(t) = \int_0^t \mathcal{I}(\tau) d\tau, \quad t \geq 0, \tag{2}$$

carried out by ions of reduced species, as follows:

$$q(t) = \frac{z_r}{nS_e F \delta C^*} Q(t), \quad t \geq 0.$$

Here  $\mathcal{I}$  is the current response,  $n$  is the number of electrons gained by an ion upon reduction,  $F$  is Faraday’s constant,  $S_e$  is the surface of the electrode and the constant  $C^* > 0$  is the bulk concentration of exchange sites. According to the nonlocal condition (1), the total charge is proportional to the amount of reduced species produced during the experiment. Since the concentration  $u(x, t)$  of the reduced species is initially zero, we have  $q(0) = 0$ .

Let us summarize some properties of the functions  $g(u)$  and  $h(u)$ . Since

$$g'(u) = \frac{z_0 z_r (1 - k)}{[z_0 + (z_r k - z_0)u]^2}$$

and  $g(0) = 1, g(1) = 1/k$ , we conclude that  $g(u)$  is a monotonically increasing function of  $u$ , if  $0 < k < 1$ , and  $g(u)$  is a monotonically decreasing function, if  $k > 1$ . In the first case  $\max g(u) = 1/k$ , and in the second case  $\max g(u) = 1$ . Further,

$$h'(u) = \frac{kz_0}{[z_0 + (z_r k - z_0)u]^2}$$

and  $h(0) = 0$ ,  $h(1) = 1/z_r$ . Hence  $h(u)$  is a monotonically increasing function of  $u$ , if  $z_0 > 0$ , and  $h(u)$  is a monotonically decreasing function, if  $z_0 < 0$ . Note that the valences  $z_r$ ,  $z_0$  are assumed to be integers of the same sign, and  $z_r \neq -1$ ,  $z_0 \neq 1$ , since one electron must be gained in reduction. In practice,  $-4 < z_r < z_0 \leq -1$  and  $1 < z_r < z_0 \leq 3$  (table 1).

We assume that  $z_r D_r = z_0 D_0$ . This, with the definition of the diffusivity ratio  $k := D_r/D_0$ , means that  $z_r k - z_0 = 0$ . Then the above functions  $g(u)$  and  $h(u)$  have the form

$$g(u) := 1 + \left(\frac{z_r}{z_0} - 1\right)u, \quad h(u) := \frac{1}{z_r}u.$$

It is shown in [1] that for fixed  $t \in (0, \infty)$  the function  $u(x, t)$  (scaled concentration) and its partial derivative  $u_x(x, t)$  decreases rapidly to 0 as  $x \rightarrow \infty$ . Moreover, this function assumes the values in  $[0, 1]$ , i.e.,  $0 \leq u(x, t) \leq 1$ .

Taking into account these properties of the solution, and the form of the function  $g(u)$  with its values between 1 and  $1/k$ , we will replace the coefficient  $g(u)$  in the parabolic equation (1) by the coefficient  $D := D(x, t)$ , and consider the following reduced model in the bounded domain  $\Omega_T := (0, l) \times (0, T)$ .

In the view of the above assumptions the nonlinear problem (1) has the following form:

$$\begin{cases} u_t = (D(x, t)u_x)_x + \frac{1}{z_r}q'(t)u_x, & (x, t) \in \Omega_T := (0, l) \times (0, T], \\ u(x, 0) = 0, & x \in (0, l), \\ u(0, t) = 1, \quad u_x(l, t) = 0, & t \in (0, T], \\ q(t) = \int_0^l u(x, t)dx, & t \in [0, T]. \end{cases} \tag{3}$$

### 3. Some properties of the solution

Let us use the nonlocal condition to transform the considered problem (3). We have

$$q'(t) = \int_0^l u_t(x, t)dx.$$

Substituting this in the parabolic equation we have

$$q'(t) = \int_0^l (D(x, t)u_x)_x dx + \frac{1}{z_r}q'(t) \int_0^l u_x dx.$$

Since  $l > 0$  is large enough, due to rapid decay  $u(x, t)$  and  $u_x(x, t)$  as  $x \rightarrow \infty$  we get  $(u(l, t) = u_x(l, t) = 0)$

$$q'(t) = -D(0, t)u_x(0, t) - \frac{1}{z_r}q'(t)u(0, t).$$

Hence

$$q'(t) = -\frac{z_r}{1+z_r} D(0, t) u_x(0, t) \tag{4}$$

and

$$q(t) = -\frac{z_r}{1+z_r} \int_0^t D(0, \tau) u_x(0, \tau) d\tau. \tag{5}$$

Denoting by  $\lambda = z_r/(nS_e F \delta C^*) > 0$  and using (2) we can express the current response  $\mathcal{I}(t)$  via the flux:

$$\mathcal{I}(t) = -\frac{z_r}{\lambda(1+z_r)} D(0, t) u_x(0, t). \tag{6}$$

Let us use now (4) to transform the considered problem (3). We have

$$\begin{cases} u_t = (D(x, t)u_x)_x - \frac{1}{1+z_r} D(0, t) u_x(0, t) u_x, & (x, t) \in \Omega_T := (0, l) \times (0, T], \\ u(x, 0) = 0, & x \in (0, l), \\ u(0, t) = 1, \quad u_x(l, t) = 0, & t \in (0, T]. \end{cases} \tag{7}$$

The nonlinear initial-boundary value problem (7) is the reduced form of the considered identification problem (3), without the nonlocal condition (1). This problem, is most convenient for numerical implementation, as we will show below.

Let us denote by  $v(t) = q'(t)/z_r$  and assume for the first time that  $v(t)$  is the given function. Then we have the following initial value problem

$$\begin{cases} u_t = (D(x, t)u_x)_x + v(t)u_x, & (x, t) \in \Omega_T := (0, l) \times (0, T], \\ u(x, 0) = 0, & x \in (0, l), \\ u(0, t) = 1, \quad u_x(l, t) = 0, & t \in (0, T]. \end{cases} \tag{8}$$

As shows table 1 and formula (4),  $v(t) > 0$  if  $z_r > 0$ , and  $v(t) < 0$  if  $z_r < 0$ . Hence the sign of the convection term  $v(t)u_x$  in the parabolic equation (8) depends on the sign of the valence  $z_r$ . We are going to prove that the sign of the flux  $\Phi(x, t) = -D(x, t)u_x(x, t)$  at any point  $x \in (0, l)$  is determined by the sign of the flux  $\Phi(0, t) = -D(0, t)u_x(0, t)$  at the initial point  $x = 0$ .

**Lemma 1.** Let  $u(x, t) \in C^2(\Omega) \cap C^1(\overline{\Omega})$  be the solution of the parabolic problem (2). If  $\Phi(0, t) = -D(0, t)u_x(0, t) > 0, \forall t \in (0, T]$ , then  $\Phi(x, t) = -D(x, t)u_x(x, t) \geq 0$  for all  $x \in (0, l)$ .

*Proof.* Let  $\varphi(x, t) \in C_0^\infty(R^2)$  be an arbitrary smooth function with compact support  $D_\varphi$  in  $\Omega_T$ . Then we obtain the following integral identity:

$$\int \int_{\Omega_T} [u_t - (Du_x)_x - v(t)u_x] \varphi_x dx dt.$$

Integrating by parts we get

$$\int_0^l (u\varphi_x)_{t=0}^{t=T} dx - \int \int_{\Omega_T} u\varphi_{xt} dx dt - \int_0^T (Du_x\varphi_x)_{x=0}^{x=l} dt + \int \int_{\Omega_T} Du_x\varphi_{xx} dx dt - \int \int_{\Omega_T} v(t)u_x\varphi_x dx dt = 0.$$

Applying again integration by parts to the second integral we have

$$\int_0^l (u\varphi_x)_{t=0}^{t=T} dx - \int_0^T (u\varphi_t)_{x=0}^{x=l} dt + \int \int_{\Omega_T} u_x\varphi_t dx dt - \int_0^T (Du_x\varphi_x)_{x=0}^{x=l} dt + \int \int_{\Omega_T} Du_x\varphi_{xx} dx dt - \int \int_{\Omega_T} v(t)u_x\varphi_x dx dt = 0.$$

Hence

$$\int \int_{\Omega_T} [\varphi_t + D(x, t)\varphi_{xx} - v(t)\varphi_x]u_x dx dt = \int_0^T (u\varphi_t)_{x=0}^{x=l} dt + \int_0^T (D(x, t)u_x\varphi_x)_{x=0}^{x=l} dt - \int_0^l (u\varphi_x)_{t=0}^{t=T} dx. \tag{9}$$

We require that the function  $\varphi(x, t)$  is chosen to be the solution of the following backward parabolic problem:

$$\begin{cases} \varphi_t + D(x, t)\varphi_{xx} - v(t)\varphi_x = F(x, t), & (x, t) \in \Omega_T := (0, l) \times (0, T], \\ \varphi(x, T) = 0, & x \in (0, l), \\ \varphi(0, t) = \varphi(l, t) = 0, & t \in (0, T], \end{cases} \tag{10}$$

where  $F(x, t)$  is an arbitrary function and will be defined below. Evidently the backward problem (10) is well-defined due to the given final condition  $\varphi(x, T) = 0$ .

Let us calculate the right hand side terms of (10). Due to the boundary condition  $\varphi(0, t) = 0, t \in (0, T]$  we have  $\varphi_t(0, t) = 0$  Taking into account the initial and boundary condition in (8) and (10) the integral identity (9) becomes to the following identity:

$$\int \int_{\Omega_T} F(x, t)u_x dx dt = - \int_0^T (D(0, t)u_x(0, t)\varphi_x(0, t))dt. \tag{11}$$

According to maximum principle for parabolic equations, if  $F(x, t) > 0$  then  $\varphi(x, t) < 0, \forall (x, t) \in \Omega_T$ . Hence

$$\varphi_x(0, t) = \lim_{x \rightarrow 0} \frac{\varphi(x, t) - \varphi(0, t)}{x} \leq 0.$$

Using this inequality with the assumption  $-D(0, t)u_x(0, t) > 0$  of the lemma in (11) we get

$$\int \int_{\Omega_T} F(x, t)u_x dx dt \leq 0, \quad \forall F(x, t) > 0.$$

Hence  $u_x(x, t) \leq 0, \quad \forall (x, t) \in \Omega_T$ . This implies the proof. □

The Lemma 1 has a precise physical meaning and asserts that if the flux  $\Phi(x, t) := -D(x, t)u_x(x, t)$  is positive at the initial point  $x = 0$ , then it is non-negative at any point  $x \in (0, l)$ .

**4. The discrete problem and verification of the iteration algorithm on the analytical solution**

Consider the nonlinear problem (7). Let us define the uniform meshes  $w_h := x_i \in (0, l) : x_i = ih; h = l/N, w_\tau := t_j \in (0, T] : t_j = j\tau; \tau = T/M$ . By using the standard finite difference approximation [18]

$$u_{x,ij} := \frac{u_{i+1,j} - u_{i,j}}{h}, u_{t,ij} := \frac{u_{i,j+1} - u_{i,j}}{\tau}, u_{i,j} := u(x_i, t_j), i = \overline{1, N}, j = \overline{1, M}$$

of the partial derivatives  $\partial u/\partial x, \partial u/\partial t$ , first approximate the problem on the piecewise uniform mesh  $w_{h\tau} := w_h \times w_\tau$  as follows:

$$\left\{ \begin{array}{l} \frac{u_{i,j+1} - u_{i,j}}{\tau} - \frac{1}{h} \left[ D_{i+1/2,j} \frac{u_{i+1,j+1} - u_{i,j+1}}{h} - D_{i-1/2,j} \frac{u_{i,j+1} - u_{i-1,j+1}}{h} \right] \\ + \frac{1}{1+z_r} D_{1/2,j} \frac{u_{2,j} - u_{1,j}}{h} \frac{u_{i+1,j+1} - u_{i-1,j+1}}{2h} = 0, \quad i = \overline{1, N-1}, \quad j = \overline{2, M}; \\ u_{i,1} = 0, \quad i = \overline{1, N} \\ u_{1,j} = 1, \quad \frac{u_{N,j+1} - u_{N-1,j+1}}{h} = 0, \quad j = \overline{2, M}. \end{array} \right. \tag{12}$$

This scheme assumes that the flux  $-D(0, t)u_x(0, t)$  in the nonlinear term is linearized by taking its value from previous time layer  $j$ .

In addition to the discrete model (12) we will use also the following iteration scheme:

$$\left\{ \begin{aligned} & \frac{u_{i,j+1}^{(n)} - u_{i,j}^{(n)}}{\tau} - \frac{1}{h} \left[ D_{i+1/2,j} \frac{u_{i+1,j+1}^{(n)} - u_{i,j+1}^{(n)}}{h} - D_{i-1/2,j} \frac{u_{i,j+1}^{(n)} - u_{i-1,j+1}^{(n)}}{h} \right] \\ & + \frac{1}{1+z_r} D_{1/2,j} \frac{u_{2,j+1}^{(n-1)} - u_{1,j+1}^{(n-1)}}{h} \frac{u_{i+1,j+1}^{(n)} - u_{i-1,j+1}^{(n)}}{2h} = 0, \quad i = \overline{1, N-1}, \quad j = \overline{2, M}; \quad (13) \\ & u_{i,1} = 0, \quad i = \overline{1, N} \\ & u_{1,j} = 1, \quad \frac{u_{N,j+1} - u_{N-1,j+1}}{h} = 0, \quad j = \overline{2, M}. \end{aligned} \right.$$

In this nonlinear scheme the parameter  $n = 1, 2, 3, \dots$  shows the number of iterations. This scheme assumes that the flux  $-D(0, t)u_x(0, t)$  in the nonlinear term is linearized by taking its value from previous iteration.

### 5. Numerical experiments

In this section we discuss results of computational experiments related to the numerical solution of the nonlinear problem (1) by using schemes (12), (13). In the first series of the computational experiments, the convergence and accuracy of the numerical solution of the problem (1) are analyzed. For this aim we consider the analytical solution

$$u(x, t) = \exp(-x/\sqrt{t}), \quad x \in [0, 10], \quad t \in (0, 1]$$

of problem (1), with  $g(u) = 1, \quad h(u) = 1 - 2g(u) + (2g(u) - 1 - \ln u)u$ .

For the above given function  $u(x, t)$  we can calculate  $q(t)$ , by the following formula:

$$q(t) = \int_0^\infty u(x, t) dx. \tag{14}$$

Then we have  $q(t) = \sqrt{t}$ , and  $q'(t) = 1/(2\sqrt{t})$ .

Therefore  $q'(t) \sim 1/\sqrt{t}$ , which means that  $q'(t)$  is proportional to the classical Gottrelian  $\mathcal{I}_G$  [1, 17].

Denote by  $u_h$  and  $u_h^{(n)}$  be the numerical solutions of the nonlinear problem (1), obtained by schemes (12) and (13), respectively. The computational experiments performed on the mesh  $40 \times 40$ , for the above test example show that the absolute sup-norm errors  $\varepsilon_h := \|u - u_h\|_\infty, \varepsilon_h^{(n)} := \|u - u_h^{(n)}\|_\infty$  of concentrations are  $2.9 \times 10^{-2}$  and  $2.7 \times 10^{-2}$ , respectively.

The values of the exact (analytical) charge, given by the function  $q(t) = \sqrt{t}$ , and the values this function, calculated by applying the numerical integration



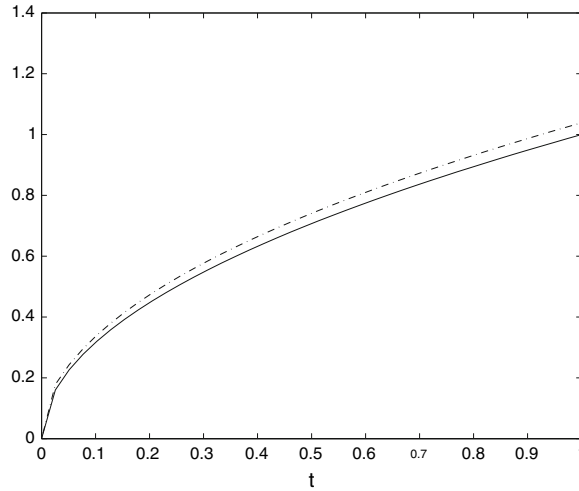


Figure 1. The function  $q(t) = \sqrt{t}$  (solid line) and the found from formula (14) (by numerical integration formula function)  $q_h(t)$  (the broken line).

formula (Trapezoidal rule) to (14), are plotted in figure 1. The maximum relative error, calculated by the formula

$$\varepsilon_q = \frac{\max_t |q(t) - q_h(t)|}{\max_t |q(t)|} \times 100\% \tag{15}$$

is obtained  $\varepsilon_q = 3.9\%$ . This shows high accuracy of the presented schemes (12) and (13).

In the second series of the computational experiments, we consider the non-linear problem (7). As it was shown above, this problem is the reduced (transformed) form of the identification problem (1). The numerical solutions obtained by schemes (12) and (13) for the given data  $D(x, t) = 1$  and  $z_r = 1$  are plotted in figure 2(a) and (b), respectively. The solid lines on the left surfaces in the both figures show decay of the solution  $u(x, t)$  with respect to the variable  $x > 0$ .

The cross-sections at the times  $t = 0.5; 0.9$  of these solutions are plotted in figure 3. As show the figures, the numerical solutions of the nonlinear problem (7), obtained by the schemes (12) and (13), are almost identical.

To study the dependence of the monotonicity the solution  $u(x, t)$  on the values  $z_r$  of the valences we consider the same problem with the given data  $D(x, t) = 1$  and  $z_r = -2$ . The results are plotted in figure 4(a) and (b). Comparing figures 2 and 4 we observe that the rate of the decay of the solution  $u(x, t)$  with respect to the variable  $x > 0$  increases by increasing the value of the valence  $z_r$  of the reduced species.

The next series of the computational experiments are related to the values of the total charge  $Q(t)$ , defined by (2). To compare the original model (1) with

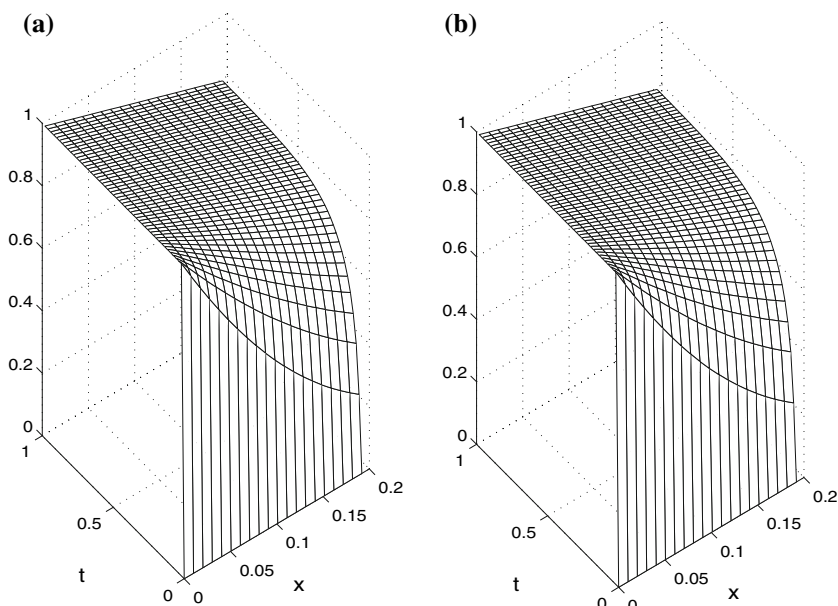


Figure 2. (a) Numerical solutions of problem (7) by schemes (12) (left figure) and (13) (right figure) [ $D(x, t) = 1, z_r = 1$ ].

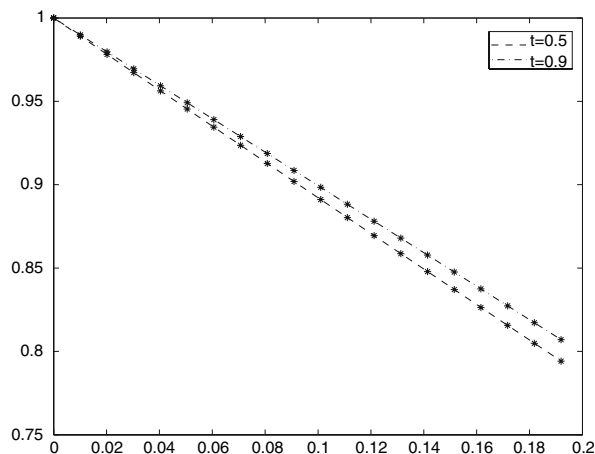


Figure 3. Cross-sections of the numerical solutions from figure 2(a) and (b) at the times  $t = 0.5; 0.9$  (the results obtained by schemes (12) and (13) are plotted by the lines – and \*, respectively).

the reduced (transformed) model (7), the dimensionless total charge  $q(t)$  was calculated by the both formulas (14) and (5). The numerical results for the values  $z_r = 1$  and  $z_r = -2$  of valences are resented in figure 5. The absolute sup-norm errors  $\delta_q := \|q_h - \tilde{q}_h\|_\infty$  were obtained  $\delta_q = 3.0\%$  and  $\delta_q = 2.7\%$ . Here the values of the dimensionless total charge  $q(t)$ , calculated by the formulas (14) and (5),

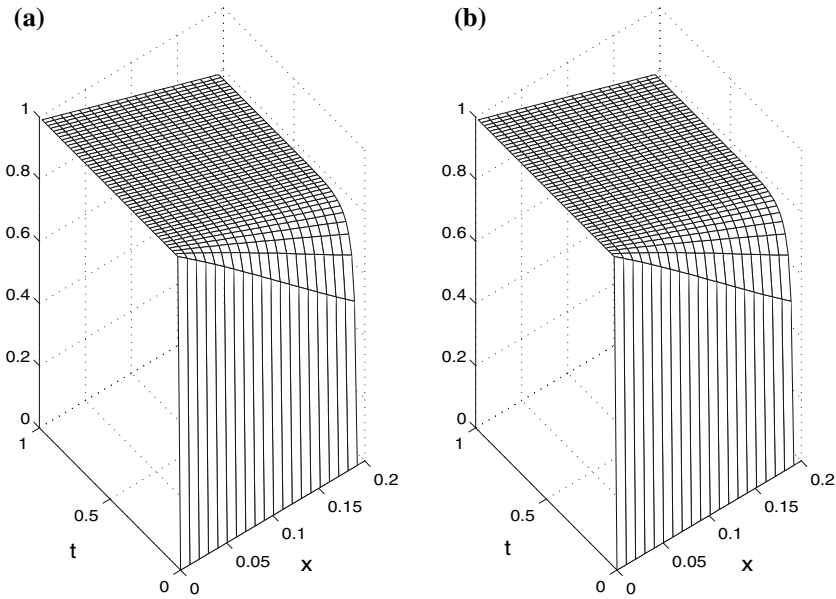


Figure 4. (a) Numerical solutions of problem (7) by schemes (12) (left figure) and (13) (right figure) ( $D(x, t) = 1, z_r = -2$ ).

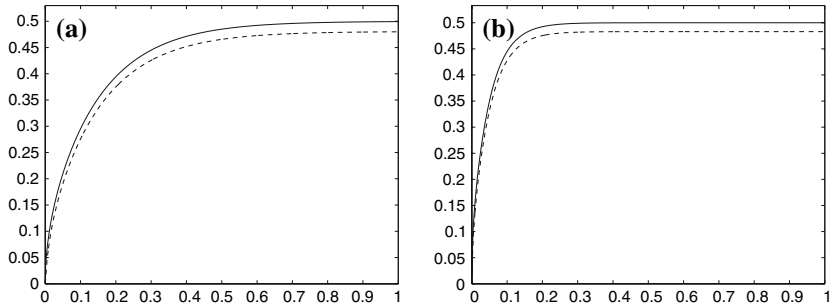


Figure 5. The values of the dimensionless total charge  $q(t)$  calculated by (14) (solid line) and by (5) (the broken line):  $z_r = 1$  (left figure) and  $z_r = -2$  (right figure).

are denoted by  $q_h$  (solid lines in figure 5) and  $\tilde{q}_h$  (broken lines in figure 5), correspondingly.

These results show that the initial model (1) can successfully be replaced by the reduced (transformed) model (7), which easy for computational experiments.

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