A BEM model for convection-diffusion-migration problems in binary electrolytes
Z.H. Qiu, L.C. Wrobel & H. Power

Wessex Institute of Technology, University of Portsmouth, Ashurst Lodge, Ashurst, Southampton SO40 7AA, UK

INTRODUCTION

This paper presents a boundary element scheme to predict the current density distribution and, consequently, the deposition of reacting species in electrochemical systems of various natures. This is a problem of interest to many branches of the electrochemical industry, like plating, etching, anodizing, machining, etc. In all these electrochemical systems mass transport phenomena of charged species due to diffusion, convection and migration of electrical forces are strongly coupled with the electrochemical reactions at electrodes. It is therefore necessary to develop reliable numerical methods which can take into account all these effects.

In a first stage, only binary electrolytes consisting of two ions are considered. In this case, the concentrations of the two ions can be written in terms of a new concentration, and the system of equations describing the problem reduces to two equations only, one for the new concentration and one for the electrical potential [1]. Although these equations can still be manipulated in such a way that they become uncoupled, they will be solved here in coupled form since the final objective of this research is to deal with multi-ion systems.

BEM FORMULATION FOR BINARY ELECTROLYTES

This paper describes a boundary element scheme for solving the system of steady-state non-linear partial differential equations describing the current density distribution in a dilute binary electrochemical solution, given by [1], [2]:

\[ \mathbf{v} \cdot \nabla c = K_1 \nabla \cdot (c \nabla U) + \nabla \cdot (D_1 \nabla c) \]  \hspace{1cm} (1)

\[ \nabla \cdot (K_2 c \nabla U + K_3 D_2 \nabla c) = 0 \]  \hspace{1cm} (2)

in which \( c \) is the concentration, \( U \) the electrical potential, \( \mathbf{v} \) the velocity field, and \( K_1, K_2, K_3, D_1, D_2 \) are constants related to the values of charge, mechanical mobility, diffusion coefficient, and the Faraday constant [1].
For two-dimensional problems, equations (1) and (2) can be expressed in the form:

\[
D_1 \nabla^2 c - \left( v_x - K_1 \frac{\partial U}{\partial x} \right) \frac{\partial c}{\partial x} - \left( v_y - K_1 \frac{\partial U}{\partial y} \right) \frac{\partial c}{\partial y} = -K_1 \nabla^2 U \ c
\]  

Because the fundamental solution of the convection-diffusion equation with constant velocity will be used in the boundary element formulation of the problem, the velocity field in equation (3) is divided as follows:

\[
v_x(x, y) = \bar{v}_x + P_x(x, y)
\]
\[
v_y(x, y) = \bar{v}_y + P_y(x, y)
\]

where \(\bar{v}_x\) and \(\bar{v}_y\) represent the mean (constant) velocity, and \(P_x\) and \(P_y\) represent the deviation from the mean at each point. Thus, equation (3) is rewritten in the form:

\[
D_1 \nabla^2 c - \bar{v}_x \frac{\partial c}{\partial x} - \bar{v}_y \frac{\partial c}{\partial y} = P_{cx} \frac{\partial c}{\partial x} + P_{cy} \frac{\partial c}{\partial y} + C_{xy} \ c
\]  

with

\[
P_{cx}(x, y) = P_x - K_1 \frac{\partial U}{\partial x}
\]
\[
P_{cy}(x, y) = P_y - K_1 \frac{\partial U}{\partial y}
\]
\[
C_{xy}(x, y) = -K_1 \nabla^2 U
\]

Similarly, equation (4) is rewritten in the form:

\[
\nabla^2 U + \bar{v}_{ux} \frac{\partial U}{\partial x} + \bar{v}_{uy} \frac{\partial U}{\partial y} = P_{ux} \frac{\partial U}{\partial x} + P_{uy} \frac{\partial U}{\partial y} + U_{xy}
\]

where the coefficients of the convective terms have also been divided into an average and a perturbation:

\[
v_{ux}(x, y) = \bar{v}_{ux} + P_{ux}(x, y)
\]
\[
v_{uy}(x, y) = \bar{v}_{uy} + P_{uy}(x, y)
\]

with:

\[
v_{ux}(x, y) = -\frac{1}{c} \frac{\partial c}{\partial x}
\]
\[
v_{uy}(x, y) = -\frac{1}{c} \frac{\partial c}{\partial y}
\]
\[
U_{xy}(x, y) = \frac{K_3 D_2}{K_2} \frac{1}{c} \nabla^2 c
\]

It is important to notice that, while the terms \(\bar{v}_x\) and \(\bar{v}_y\) in equation (5) correspond to a known velocity field, the terms \(\bar{v}_{ux}\) and \(\bar{v}_{uy}\) in (6) are dependent on the unknown concentration \(c\).
The iterative scheme of solution of the system of equations (5) and (6) involves fixing an initial variation for the electrical potential $U$, and solving equation (5) for the concentration $c$ using the boundary element method. This solution provides values of $c$ and $\partial c/\partial n$ along the boundary. With these values, it is then possible to calculate, in an explicit manner, values of $c$ at internal points, first derivatives of $c$ at boundary and internal points, and second derivatives of $c$ at internal points.

Next, equation (6) is solved for $U$ using the previously calculated distribution of $c$ and its derivatives to evaluate $v_x, v_y$, and $U_y$. Initially, a boundary element scheme is used to calculate $U$ and $\partial U/\partial n$ along the boundary. Thus, values of $\partial U/\partial x$, $\partial U/\partial y$, and $\nabla^2 U$ at internal points can be evaluated explicitly. These are then used to give a better estimate of $c$ by solving equation (5) again. This procedure is repeated until convergence is achieved for both $c$ and $U$.

**SOLUTION FOR THE CONCENTRATION**

The fundamental solution of the two-dimensional steady-state convection–diffusion equation with constant velocity field

$$D \nabla^2 c - \overline{v}_x \frac{\partial c}{\partial x} - \overline{v}_y \frac{\partial c}{\partial y} = 0$$

in which $D$ is a diffusion coefficient, $\overline{v}_x$ and $\overline{v}_y$ the velocity components, is of the form [3]:

$$c^*(\xi, \chi) = \frac{1}{2\pi D} e^{-\frac{\overline{v} \cdot r}{2D}} K_0 \left( \frac{\|r\|}{2} \right)$$

where $\overline{v}$ is the velocity vector, $\xi$ and $\chi$ represent source and field points, respectively, $r$ is the modulus of $r$, the distance vector between $\xi$ and $\chi$, and $K_0$ is the Bessel function of second kind of zero order.

By employing the above fundamental solution and Green's identities, when source points are inside the domain, equation (5) can be transformed into the following integral equation

$$c(\xi) - D \int_\Gamma c^*(\xi, \chi) \frac{\partial c(\chi)}{\partial n_\chi} d\Gamma(\chi) + D \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial n_\chi} c(\chi) d\Gamma(\chi) +$$

$$\int_\Gamma c^*(\xi, \chi) \overline{v}_n(\chi) c(\chi) d\Gamma(\chi) = - \int_\Omega c^*(\xi, \chi) \left[ P_{cx}(\chi) \frac{\partial c(\chi)}{\partial x_\chi} + P_{cy}(\chi) \frac{\partial c(\chi)}{\partial y_\chi} + C_{xy}(\chi) c(\chi) \right] d\Omega(\chi) \quad (7)$$

where $\overline{v}_n = \overline{v} \cdot n$, $n$ is the unit outward normal vector. For simplification, we will denote by $b = P_{cx}(\partial c/\partial x) + P_{cy}(\partial c/\partial y) + C_{xy} c$ the term within brackets on the right-hand side of equation (7).

It is important to notice that only the fundamental solution depends on the position of the source point; all other terms are only related to field points. Based on this, it is possible to take derivatives with respect to coordinates of the source point directly on the above equation.
When source point $\xi$ is inside domain $\Omega$

Rewriting equation (7) by introducing the expression of $b$ defined above gives

$$
\begin{align*}
\alpha(\xi) c(\xi) & - D \int_\Gamma c^*(\xi, \chi) q(\chi) d\Gamma(\chi) + D \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial n_\chi} c(\chi) d\Gamma(\chi) + \\
\int_\Gamma c^*(\xi, \chi) \vec{n}(\chi) c(\chi) d\Gamma(\chi) &= - \int_\Omega c^*(\xi, \chi) b(\chi) d\Omega(\chi)
\end{align*}
$$

with $q(\chi) = \partial c(\chi)/\partial n_\chi$.

The first derivatives of function $c$ with respect to coordinates $x$ and $y$ of the source point are obtained by differentiating equation (8)

$$
\begin{align*}
\frac{\partial c(\xi)}{\partial x_\xi} &= - D \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial x_\xi} q(\chi) d\Gamma(\chi) + D \int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial n_\chi \partial x_\xi} c(\chi) d\Gamma(\chi) + \\
\int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial x_\xi} \vec{n}(\chi) c(\chi) d\Gamma(\chi) &= - \int_\Omega \frac{\partial c^*(\xi, \chi)}{\partial x_\xi} b(\chi) d\Omega(\chi)
\end{align*}
$$

$$
\begin{align*}
\frac{\partial c(\xi)}{\partial y_\xi} &= - D \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial y_\xi} q(\chi) d\Gamma(\chi) + D \int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial n_\chi \partial y_\xi} c(\chi) d\Gamma(\chi) + \\
\int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial y_\xi} \vec{n}(\chi) c(\chi) d\Gamma(\chi) &= - \int_\Omega \frac{\partial c^*(\xi, \chi)}{\partial y_\xi} b(\chi) d\Omega(\chi)
\end{align*}
$$

The second derivatives of function $c$ with respect to the coordinates $x$ and $y$ of the source point are obtained by differentiating equations (9) and (10). In this case, however, care must be taken when differentiating the domain integrals because of the strong singularity of their kernel. This has to be carried out using Leibnitz’ rule, and the final result are the expressions:

$$
\begin{align*}
\frac{\partial^2 c(\xi)}{\partial x_\xi^2} &= - D \int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial x_\xi^2} q(\chi) d\Gamma(\chi) + D \int_\Gamma \frac{\partial^3 c^*(\xi, \chi)}{\partial n_\chi \partial x_\xi^2} c(\chi) d\Gamma(\chi) + \\
\int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial x_\xi^2} \vec{n}(\chi) c(\chi) d\Gamma(\chi) &= - \int_\Omega \frac{\partial^2 c^*(\xi, \chi)}{\partial x_\xi^2} b(\chi) d\Omega(\chi) + \frac{1}{2D} b(\xi)
\end{align*}
$$

$$
\begin{align*}
\frac{\partial^2 c(\xi)}{\partial y_\xi^2} &= - D \int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial y_\xi^2} q(\chi) d\Gamma(\chi) + D \int_\Gamma \frac{\partial^3 c^*(\xi, \chi)}{\partial n_\chi \partial y_\xi^2} c(\chi) d\Gamma(\chi) + \\
\int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial y_\xi^2} \vec{n}(\chi) c(\chi) d\Gamma(\chi) &= - \int_\Omega \frac{\partial^2 c^*(\xi, \chi)}{\partial y_\xi^2} b(\chi) d\Omega(\chi) + \frac{1}{2D} b(\xi)
\end{align*}
$$

where the last term in the above equations results from a jump of the domain integral at the source point.

When source point $\xi$ is on boundary $\Gamma$

By taking the limit when the source point $\xi$ approaches the boundary $\Gamma$ in equation (8), the following is obtained:

$$
\begin{align*}
\alpha(\xi) c(\xi) & - D \int_\Gamma c^*(\xi, \chi) q(\chi) d\Gamma(\chi) + D \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial n_\chi} c(\chi) d\Gamma(\chi) + \\
\int_\Gamma c^*(\xi, \chi) \vec{n}(\chi) c(\chi) d\Gamma(\chi) &= - \int_\Omega c^*(\xi, \chi) b(\chi) d\Omega(\chi)
\end{align*}
$$
where $\alpha(\xi)$ is a function of the internal angle subtended at point $\xi$. In particular, $\alpha = 1/2$ on a smooth boundary.

In order to get the derivatives of function $c$ with respect to the coordinates $x$ and $y$ of the source point, we take the limit when the source point in equations (9) and (10) approaches the boundary. Taking into account the jumps that appear because of the strong singularity of the kernels, the final expressions are of the form:

$$\frac{1}{2D} \frac{\partial c(\xi)}{\partial x} - D \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial x} q(\chi) d\Gamma + D \int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial n_x \partial x} c(\chi) d\Gamma + \frac{1}{2D} \nu_n(\xi) n_x(\xi) c(\xi) + \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial x} \nu_n(\chi)c(\chi)d\Gamma = - \int_\Omega \frac{\partial c^*(\xi, \chi)}{\partial x} b(\chi) d\Omega \quad (14)$$

$$\frac{1}{2D} \frac{\partial c(\xi)}{\partial y} - D \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial y} q(\chi) d\Gamma + D \int_\Gamma \frac{\partial^2 c^*(\xi, \chi)}{\partial n_y \partial y} c(\chi) d\Gamma + \frac{1}{2D} \nu_n(\xi) n_y(\xi) c(\xi) + \int_\Gamma \frac{\partial c^*(\xi, \chi)}{\partial y} \nu_n(\chi)c(\chi)d\Gamma = - \int_\Omega \frac{\partial c^*(\xi, \chi)}{\partial y} b(\chi) d\Omega \quad (15)$$

**Matricial system**

Discretizing the boundary $\Gamma$ into linear boundary elements and the domain $\Omega$ into linear triangular cells, applying equations (8), (9), (10), (11) and (12) to internal nodes and equations (13), (14) and (15) to boundary nodes, the following matricial equations are obtained:

$$C_i + H_c C_b - G_c Q_c = - E_c B_c \quad (16)$$

$$\frac{\partial C_i}{\partial x} + H_{cx fd} C_b - G_{cx fd} Q_c = - E_{cx fd} B_c \quad (17)$$

$$\frac{\partial C_i}{\partial y} + H_{cy fd} C_b - G_{cy fd} Q_c = - E_{cy fd} B_c \quad (18)$$

$$\frac{\partial^2 C_i}{\partial x^2} + H_{cx sd} C_b - G_{cx sd} Q_c = - E_{cx sd} B_c \quad (19)$$

$$\frac{\partial^2 C_i}{\partial y^2} + H_{cy sd} C_b - G_{cy sd} Q_c = - E_{cy sd} B_c \quad (20)$$

$$H_{cb} C_b - G_{cb} Q_c = - E_{cb} B_c \quad (21)$$

$$\frac{\partial C_b}{\partial x} + H_{xb fd} C_b - G_{xb fd} Q_c = - E_{xb fd} B_c \quad (22)$$

$$\frac{\partial C_b}{\partial y} + H_{yb fd} C_b - G_{yb fd} Q_c = - E_{yb fd} B_c \quad (23)$$

The vectors $C_b$ and $Q_c$ comprise the values of the concentration and its normal derivative, respectively, at boundary nodes; vectors $C_i$ and $B_c$ comprise the values of the concentration and the term $b$, respectively, at internal points. All matrices $H$, $G$ and $E$ are influence matrices resulting from boundary or domain integrals.
In order to eliminate the domain variable $b$ from the system of equations (21), we start by multiplying equation (16) by $C_{xy}$, multiplying equation (17) by $P_{cx}$, multiplying equation (18) by $P_{cy}$, and adding the resulting equations to give

$$C_{xy}(C + H_c B - G_c Q_c) + P_{cx}\left(\frac{\partial C_i}{\partial x} + H_{cx} C_b - G_{cx} Q_c\right) + P_{cy}\left(\frac{\partial C_i}{\partial y} + H_{cy} C_b - G_{cy} Q_c\right) = -(C_{xy} E_c + P_{cx} E_{cx} + P_{cy} E_{cy}) B_c$$  (24)

Recalling the definition of the variable $b$, equation (24) can be rewritten as

$$IB_c + H_c B - G_c Q_c = -E_c B_c$$  (25)

Here, $I$ is the unit matrix and:

$$H_c = C_{xy} H_c + P_{cx} H_{cx} + P_{cy} H_{cy}$$

$$G_c = C_{xy} G_c + P_{cx} G_{cx} + P_{cy} G_{cy}$$

$$E_c = C_{xy} E_c + P_{cx} E_{cx} + P_{cy} E_{cy}$$

These definitions are extremely useful for the iteration process, as explained in the next section.

Eliminating the variable $b$ from equations (21) and (25), another matrix system is constructed,

$$[H_{cb} - E_{cb}(E_c + I)^{-1} H_c] C_b = [G_{cb} - E_{cb}(E_c + I)^{-1} G_c] Q_c$$  (26)

which is only related to boundary values. With it, all the boundary unknowns can be evaluated. This step is completed implicitly, by solving a system of equations. Once all nodal boundary values are obtained, the system of equations (25) is also solved implicitly to provide the domain terms $b$. After this, the values of concentration at internal points, and derivatives at boundary and internal points, can be calculated explicitly by using the relevant matrix equation.

**SOLUTION FOR THE ELECTRICAL POTENTIAL**

The set of matrix equations for calculating the electrical potential $U$ is obtained following the same ideas as for the concentration $c$. These matrices are of the form:

$$H_{ub} U_b - G_{ub} Q_u = -E_{ub} B_u$$  (27)

$$\frac{\partial U_i}{\partial x} + H_{ux} U_b - G_{ux} Q_u = -E_{ux} B_u$$  (28)

$$\frac{\partial U_i}{\partial y} + H_{uy} U_b - G_{uy} Q_u = -E_{uy} B_u$$  (29)

$$\frac{\partial^2 U_i}{\partial x^2} + H_{ux} U_b - G_{ux} Q_u = -E_{ux} B_u$$  (30)
\[ \frac{\partial^2 U_i}{\partial y^2} + H_{uyyd} U_b - G_{uyyd} Q_u = -E_{uyyd} B_u \]  

(31)

\[ I B_u - I U_{xy} + H_{ui} U_b - G_{ui} Q_u = -E_{ui} B_u \]  

(32)

In the above, vectors \( U_b \) and \( Q_u \) comprise the values of the electrical potential and its normal derivative, respectively, at boundary nodes; vectors \( U_i \) and \( B_u \) comprise the values of \( U \) and the term \( b \), respectively, at internal points. The domain variable \( b \) for the electrical potential equation is defined in the form

\[ b_u = P_{ux} \frac{\partial U_i}{\partial x} + P_{uy} \frac{\partial U_i}{\partial y} + U_{xy} \]

The final set of equations for the unknown values of \( U \) and \( \partial U/\partial n \) on the boundary is obtained by substituting the vector \( B_u \) in equation (27) by its expression in terms of \( U_b \) and \( Q_u \), given by (32). The final result is of the form:

\[ \begin{bmatrix} H_{ub} - E_{ub}(E_{ui} + I)^{-1} H_{ui} \\ G_{ub} - E_{ub}(E_{ui} + I)^{-1} G_{ui} \end{bmatrix} U_b = \begin{bmatrix} Q_u - E_{ub}(E_{ui} + I)^{-1} U_{xy} \end{bmatrix} \]

(33)

where

\[ H_{ui} = P_{ux} H_{uxfd} + P_{uy} H_{uyfd} \]

\[ G_{ui} = P_{ux} G_{uxfd} + P_{uy} G_{uyfd} \]

\[ E_{ui} = P_{ux} E_{uxfd} + P_{uy} E_{uyfd} \]

After solving system (33) implicitly and calculating the values of \( B_u \) using (32), also implicitly, it is possible to calculate first and second derivatives at internal points, explicitly, using equations (28) to (31).

**ITERATION PROCEDURE**

The iteration procedure is carried out with the following steps:

1. With an initial estimate of the electrical potential distribution (which can be a null field) calculate \( P_{cx}, P_{cy} \) and \( C_{xy} \).

2. Solve equation (26) for the boundary values of \( c_b \) and \( q_c = \partial c_b / \partial n \) (subscript \( b \) means that the source point is on the boundary).

3. Calculate implicitly the values of \( b_c \) at internal points using equation (25).

4. Calculate explicitly the values of \( \partial c_b / \partial x \) and \( \partial c_b / \partial y \) using equations (22) and (23).

5. Calculate explicitly the values of \( c_i, \partial c_i / \partial x, \partial c_i / \partial y, \partial^2 c_i / \partial x^2 \) and \( \partial^2 c_i / \partial y^2 \) (subscript \( i \) means that the source point is on the domain), using equations (16) to (20).
6. Using the above values, calculate the values of $v_{ux}, v_{uy}$ and $U_{xy}$ and solve the system of equations (33) to provide a new distribution of $U_b$ and $q_u$.

7. Calculate implicitly the values of $b_u$ at internal points using equation (32).

8. Calculate explicitly the values of $\partial U_i/\partial x$, $\partial U_i/\partial y$, $\partial^2 U_i/\partial x^2$ and $\partial^2 U_i/\partial y^2$ using equations (28) to (31).

9. Update the values of $P_{cx}, P_{cy}$ and $C_{xy}$, and go to step 2.

Convergence of the solution is verified for both the concentration and the electrical potential. Thus, it is possible (and likely) that one of the variables will converge faster than the other. In this case, the iteration loop proceeds until convergence of the remaining variable is achieved.

In spite of the large number of matrix equations involved in the iteration process, its efficiency is very reasonable. This is because all the matrices depend only on geometry, the diffusion coefficient (which is constant) and the convection coefficients. For the concentration equation (5), it is recalled that the terms $\overline{v}_x$ and $\overline{v}_y$ correspond to a known velocity field which is constant throughout the iteration steps. However, for the electrical potential equation (6), the terms $v_{ux}$ and $v_{uy}$ depend on $c$. The procedure adopted was to maintain the mean values $\overline{v}_{ux}$ and $\overline{v}_{uy}$ from the first iteration constant throughout the process, and only updating the perturbation terms $P_{ux}$ and $P_{uy}$.

It is important to notice that by grouping matrices in the form:

$$
H_{ci} = C_{xy}H_c + P_{cx}H_{cxf} + P_{cy}H_{cyf}
$$

$$
G_{ci} = C_{xy}G_c + P_{cx}G_{cxf} + P_{cy}G_{cyf}
$$

$$
E_{ci} = C_{xy}E_c + P_{cx}E_{cxf} + P_{cy}E_{cyf}
$$

it becomes very simple to update them since all the matrices on the right-hand sides of above expressions, which are computed by integration, do not change during the iteration loop. Only the values of the parameters $C_{xy}, P_{cx}$ and $P_{cy}$ are updated. The same is valid for the iteration loop for function $U$.

**NUMERICAL EXAMPLES**

Two examples are analysed to assess the numerical approach described. Both are simple one-dimensional problems with constant velocity, in order that the numerical solutions can be compared with analytical ones. They are analysed, however, considering a two-dimensional geometry of cross-section $10 \times 1$. The two problems involve diffusion, convection and migration effects, the main difference being in the boundary conditions. The first example has only Dirichlet and Neumann, while the second also has a Robin condition which couples the two variables $c$ and $U$. In both cases, discretizations are carried out using discontinuous linear boundary elements and semi-discontinuous triangular internal cells.
In the first test, the following boundary conditions are imposed:

\[ x = 0 \rightarrow c = 1 ; \quad U = 0 \]
\[ x = 10 \rightarrow c = 2 ; \quad U = 1 \]
\[ y = 0 \rightarrow \frac{\partial c}{\partial n} = 0 ; \quad \frac{\partial U}{\partial n} = 0 \]
\[ y = 1 \rightarrow \frac{\partial c}{\partial n} = 0 ; \quad \frac{\partial U}{\partial n} = 0 \]

The constants of the problem are as follows:

\[ v_x = D_2 = K_2 = K_3 = 1 \]
\[ D_1 = 1.1 \quad K_1 = 0.1 \]

The analytical solutions are given by:

\[ c = \frac{e^x + e^{10} - 2}{e^{10} - 1} \]
\[ U = 0.181925 \ln \left| 1 - \left( \frac{e^{10} - 2}{e^{10} - 2} \right) \frac{1}{c} \right| - \ln c + 1.81925 \]

The discretization uses 22 boundary elements of the same length, while the domain is subdivided into 10 cells. Results for the concentration and electrical potential are presented in table 1.

In the second test:

\[ x = 0 \rightarrow \frac{\partial c}{\partial n} = 2c \frac{\partial U}{\partial n} ; \quad U = 0 \]
\[ x = 10 \rightarrow c = 1 ; \quad U = 1 \]
\[ y = 0 \rightarrow \frac{\partial c}{\partial n} = 0 ; \quad \frac{\partial U}{\partial n} = 0 \]
\[ y = 1 \rightarrow \frac{\partial c}{\partial n} = 0 ; \quad \frac{\partial U}{\partial n} = 0 \]

It can be seen that the boundary condition at \( x = 0 \) couples the two variables \( c \) and \( U \). In the iteration process, this is treated as a Robin condition for \( c \), with the value of \( \partial U/\partial n \) updated at each iteration.

The constants of the problem are as follows:

\[ K_1 = D_1 = K_3 = 1 \]
\[ K_2 = -2 ; \quad D_2 = 0.5 ; \quad v_x = 0.0125 \]

The analytical solutions are given by:

\[ c = 8.265098e^{0.01x} - 8.131346 \]
\[ U = -0.2540185(0.01x - \ln c) + \ln c/4 + 1.025402 \]

The discretization uses 28 boundary elements, 22 along the \( x \)-direction and 6 on the \( y \)-direction. The domain is discretized with 22 cells. Results are shown in table 2.
## Table 1: Example 1: Variation of concentration and electrical potential

<table>
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<th>$x$</th>
<th>$c$</th>
<th>analy-c</th>
<th>err-c %</th>
<th>$U$</th>
<th>analy-$U$</th>
<th>err-$U$ %</th>
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## Table 2: Example 2: Variation of concentration and electrical potential

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CONCLUSIONS

The work reported in this paper represents the first attempt to model the complete mass transport equations for electrochemical systems, including convection, diffusion and migration effects, using the boundary element method. The iterative scheme of solution developed was shown to work well for simple one-dimensional problems with linear (although coupled) boundary conditions.

Extension of this research will include nonlinear boundary conditions and multi-ion systems. Another important consideration will be the inclusion of realistic flow fields in which turbulent effects may be significant.

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References

