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# A NEUMANN BOUNDARY VALUE PROBLEM IN TWO-ION ELECTRO-DIFFUSION WITH UNEQUAL VALENCIES 

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#### Abstract

In prior work, a series of two-point boundary value problems have been investigated for a steady state two-ion electro-diffusion model system in which the sum of the valencies $\nu_{+}$and $\nu_{-}$is zero. In that case, reduction is obtained to the canonical Painlevé II equation for the scaled electric field. Here, a physically important Neumann boundary value problem in the generic case when $\nu_{+}+\nu_{-} \neq 0$ is investigated. The problem is novel in that the model equation for the electric field involves yet to be determined boundary values of the solution. A reduction of the Neumann boundary value problem in terms of elliptic functions is obtained for privileged valency ratios. A topological index argument is used to establish the existence of a solution in the general case, under the assumption $\nu_{+}+\nu_{-} \leq 0$.


1. Introduction. The theory of electro-diffusion originated in the liquid-junction theory of Nernst [1] and Planck [2]. It provides a macroscopic description of the transmission of charged particles through material barriers and has applications notably, in the modeling of biological membranes [3, 4] and in electrochemistry [5].

Here, it proves convenient to partition the ions into $m$ classes characterized by the same electric charge $q_{j}=q_{0} \nu_{j}$ where $q_{0}$ is the unit of charge and $\nu_{j}$ is a nonzero integral signed valency. The $m$-ion electro-diffusion model in steady régimes then reduces to the Nernst-Planck equations [6].

$$
\begin{equation*}
\frac{d n_{i}}{d x}=\nu_{i} n_{i} p-c_{i}, \quad \nu_{i} \neq 0, \quad i=1, \cdots, m \tag{1}
\end{equation*}
$$

[^1]coupled to Gauss' equation
\[

$$
\begin{equation*}
\frac{d p}{d x}=\sum_{i=1}^{m} \nu_{i} n_{i} \tag{2}
\end{equation*}
$$

\]

Here,

$$
\begin{equation*}
n_{i}=\frac{N_{i}}{N_{0}} \tag{3}
\end{equation*}
$$

and

$$
\begin{equation*}
p=\left[\frac{q_{0} \bar{\lambda}}{\kappa T}\right] E \tag{4}
\end{equation*}
$$

where $N_{i}$ are the ion densities, $N_{0}$ is an arbitrary unit of ionic density, $E$ is the electric field, $T$ the temperature, $\kappa$ the Boltzmann constant, and $\bar{\lambda}=\left[\epsilon \kappa T /\left(4 \pi q_{0}^{2} N_{0}\right)\right]^{1 / 2}$ is the Debye length where $\epsilon$ is the dielectric constant. The $c_{i}$ are arbitrary constants of integration. The Painlevé analysis of the system (1)-(2) has recently been undertaken in [7].

Attention is restricted to the two-ion case and, in the notation of [8], we set $n_{1}=n_{+}, n_{2}=n_{-}, \nu_{1}=\nu_{+}, \nu_{2}=\nu_{-}, c_{1}=c_{+}, c_{2}=c_{-}$whence (1)-(2) yield

$$
\begin{align*}
& n_{+}^{\prime}=\nu_{+} n_{+} p-c_{+}  \tag{5}\\
& n_{-}^{\prime}=\nu_{-} n_{-} p-c_{-}  \tag{6}\\
& p^{\prime}=\nu_{+} n_{+}+\nu_{-} n_{-} \tag{7}
\end{align*}
$$

The two-ion system (5)-(7) in the special case when $\nu_{+}+\nu_{-}=0$ was investigated by Grafov and Chernenko [9] and independently by Bass [10]. An analogous system was subsequently derived independently in the context of semi-conductor theory by Kudryashov [11]. In both cases, reduction to the Painlevé II equation was obtained. This integrable connection has been exploited in [12] and [13] to apply a Bäcklund transformation sequentially to generate solutions of the Bass system.

Addition of (5) and (6) together with use of (7) yields, on integration,

$$
\begin{equation*}
n_{+}+n_{-}=\frac{p^{2}}{2}-c x-k \tag{8}
\end{equation*}
$$

where $c=c_{+}+c_{-}$and $k$ is an arbitrary constant of integration. Elimination of $n_{+}$ between (7) and (8) then gives

$$
p^{\prime}=n_{-}\left(\nu_{-}-\nu_{+}\right)+\nu_{+} \frac{p^{2}}{2}-c \nu_{+} x-\nu_{+} k
$$

whence

$$
\begin{aligned}
p^{\prime \prime} & =\left(\nu_{-}-\nu_{+}\right)\left(\nu_{-} n_{-} p-c_{-}\right)+\nu_{+} p p^{\prime}-c \nu_{+} \\
& =\nu_{-} p\left[p^{\prime}-\nu_{+} \frac{p^{2}}{2}+c \nu_{+} x+k \nu_{+}\right]-c_{-}\left[\nu_{-}-\nu_{+}\right]+\nu_{+} p p^{\prime}-c \nu_{+}
\end{aligned}
$$

so that

$$
\begin{equation*}
p^{\prime \prime}=\left(\nu_{+}+\nu_{-}\right) p p^{\prime}-\left(\frac{\nu_{+} \nu_{-}}{2}\right) p^{3}+(c x+k) \nu_{+} \nu_{-} p-\left(\nu_{+} c_{+}+\nu_{-} c_{-}\right) \tag{9}
\end{equation*}
$$

The condition that there is no net current in the junction yields [8]

$$
\begin{equation*}
\nu_{+} D_{+} c_{+}+\nu_{-} D_{-} c_{-}=0 \tag{10}
\end{equation*}
$$

where $D_{ \pm}=u_{ \pm} k T$ so that

$$
\begin{equation*}
\nu_{+} u_{+} c_{+}+\nu_{-} u_{-} c_{-}=0 \tag{11}
\end{equation*}
$$

whence

$$
\begin{equation*}
\left(\nu_{+} u_{+} c_{+}+\nu_{-} u_{-} c_{-}\right)\left(\nu_{+}-\nu_{-}\right)=0 \tag{12}
\end{equation*}
$$

Accordingly,

$$
\begin{equation*}
\nu_{+} c_{+}+\nu_{-} c_{-}=\frac{\left(D_{+}-D_{-}\right) c \nu_{+} \nu_{-}}{\nu_{+} D_{+}-\nu_{-} D_{-}} \tag{13}
\end{equation*}
$$

and (9) becomes

$$
\begin{equation*}
p^{\prime \prime}-\left(\nu_{+}+\nu_{-}\right) p p^{\prime}+\nu_{+} \nu_{-}\left[\frac{p^{3}}{2}-(c x+k) p\right]+\frac{\left(D_{+}-D_{-}\right) c \nu_{+} \nu_{-}}{\nu_{+} D_{+}-\nu_{-} D_{-}}=0 \tag{14}
\end{equation*}
$$

If the junction has boundaries at $x=0$ and $x=\delta$ then, on introduction of the scalings

$$
\begin{equation*}
x=\delta x^{*}, \quad p=\frac{y}{\delta \sqrt{-\nu_{+} \nu_{-}}} \tag{15}
\end{equation*}
$$

(14) yields

$$
\begin{equation*}
y^{\prime \prime}=\left(\frac{\nu_{+}+\nu_{-}}{\sqrt{-\nu_{+} \nu_{-}}}\right) y y^{\prime}+\frac{y^{3}}{2}+\delta^{2} \nu_{+} \nu_{-}\left(c \delta x^{*}+k\right) y-c \delta^{3} D \nu_{+} \nu_{-} \tag{16}
\end{equation*}
$$

where ' now denotes the derivative with respect to $x^{*}$ and

$$
\begin{gather*}
c=n(0)-n(1)+\frac{1}{2 \delta^{2} \nu_{+} \nu_{-}}\left[y^{2}(0)-y^{2}(1)\right]  \tag{17}\\
k=\frac{y^{2}(0)}{2 \delta^{2} \nu_{+} \nu_{-}}-n(0)  \tag{18}\\
D=\frac{\sqrt{-\nu_{+} \nu_{-}}\left(D_{+}-D_{-}\right)}{\nu_{+} D_{+}-\nu_{-} D_{-}}, \quad \nu_{+} \nu_{-}<0 \tag{19}
\end{gather*}
$$

It is observed that (14) and (16) incorporate via $c$ and $k$ the boundary values $n(0)=n_{+}(0)+n_{-}(0), n(1)=n_{+}(1)+n_{-}(1)$, together with $y(0)$ and $y(1)$. It is anticipated that the interface concentrations $n_{+}(0), n_{-}(0), n_{+}(1), n_{-}(1)$ be known (Bass [10]). However, the boundary terms $y(0)$ and $y(1)$ dependent on the yet to be determined solution $y$ remain.

Insertion of (17), (18) into (16) yields

$$
\begin{aligned}
y^{\prime \prime} & =\left(\frac{\nu_{+}+\nu_{-}}{\sqrt{-\nu_{+} \nu_{-}}}\right) y y^{\prime}+\frac{y^{3}}{2}+\delta\left[\delta^{2} \nu_{+} \nu_{-}(n(0)-n(1))+\frac{1}{2}\left(y^{2}(0)-y^{2}(1)\right)\right] x^{*} y \\
& -\left[\frac{y^{2}(0)}{2}+\delta^{2} \nu_{+} \nu_{-} n(0)\right] y-\delta\left[\delta^{2} \nu_{+} \nu_{-}(n(0)-n(1))+\frac{1}{2}\left(y^{2}(0)-y^{2}(1)\right)\right] D
\end{aligned}
$$

that is, if we set $\lambda=-\delta^{2} \nu_{+} \nu_{-} n(0), l=[n(1)-n(0)] / n(0)$,

$$
\begin{align*}
y^{\prime \prime}= & \left(\frac{\nu_{+}+\nu_{-}}{\sqrt{-\nu_{+} \nu_{-}}}\right) y y^{\prime}+\frac{y^{3}}{2}+\delta\left[\lambda l+\frac{1}{2}\left(y^{2}(0)-y^{2}(1)\right)\right] x^{*} y \\
& -\left[\frac{y^{2}(0)}{2}-\lambda\right] y-\delta\left[\lambda l+\frac{1}{2}\left(y^{2}(0)-y^{2}(1)\right)\right] D \tag{20}
\end{align*}
$$

The involvement of the boundary terms $y(0)$ and $y(1)$ in (20) poses a formidable impediment to its analysis and will be addressed in the sequal. It is anticipated that analogous procedures to those presented will be applicable mutatis mutandis to the corresponding (one-point) boundary value problem on the semi-infinite domain.
2. Reduction to elliptic integral formulation for privileged valency ratios. Here, we consider the Neumann boundary value problem

$$
\begin{gather*}
p^{\prime \prime}-\left(\nu_{+}+\nu_{-}\right) p p^{\prime}+\nu_{+} \nu_{-}\left[\frac{p^{3}}{2}-(c x+k) p\right]+\frac{\left(D_{+}-D_{-}\right)\left(c_{+}+c_{-}\right) \nu_{+} \nu_{-}}{\nu_{+} D_{+}-\nu_{-} D_{-}}=0  \tag{21}\\
p^{\prime}(0)=p^{\prime}(1)=0 \tag{22}
\end{gather*}
$$

on the region $[0,1]$ It is noted that the boundary conditions (22) imply, by virtue of Gauss' equation (7) that

$$
\begin{align*}
& \nu_{+} n_{+}(0)+\nu_{-} n_{-}(0)=0,  \tag{23}\\
& \nu_{+} n_{+}(1)+\nu_{-} n_{-}(1)=0, \tag{24}
\end{align*}
$$

The latter conditions correspond to charge neutrality at the boundaries and can be imposed at the outset. These imply the necessary requirements

$$
\begin{equation*}
\frac{n_{+}(0)}{n_{-}(0)}=-\frac{\nu_{-}}{\nu_{+}}=\frac{n_{+}(1)}{n_{-}(1)} \tag{25}
\end{equation*}
$$

on the interface concentration data. In particular, if, as in $[8,10,11], \nu_{+}+\nu_{-}=0$, it is seen that

$$
\begin{equation*}
\frac{n_{+}(0)}{n_{-}(0)}=\frac{n_{+}(1)}{n_{-}(1)}=1 \tag{26}
\end{equation*}
$$

Here, we proceed with the generic case

$$
\nu_{+}+\nu_{-} \neq 0
$$

On introduction of the ansatz

$$
\begin{equation*}
p=\frac{a w^{\prime}}{w} \tag{27}
\end{equation*}
$$

where

$$
\begin{equation*}
\left(\frac{w^{\prime}}{w}\right)^{2}=A w^{-2}+B w^{-1}+C+D w+E w^{2} \tag{28}
\end{equation*}
$$

into the model equation (21) for the scaled electric field $p$, it is seen that,

$$
c_{+}+c_{-}=0, \quad \nu_{+} c_{+}+v_{-} c_{-}=0
$$

so that

$$
\begin{equation*}
c_{+}=c_{-}=0 \quad\left(\nu_{+} \neq \nu_{-}\right)^{\dagger} \tag{29}
\end{equation*}
$$

whence $c=0$. Moreover,

$$
\begin{equation*}
C=\frac{2 k}{a^{2}} \tag{30}
\end{equation*}
$$

and

$$
\begin{array}{ll}
\text { I } & A\left(a \nu_{+}+2\right)\left(a \nu_{-}+2\right)=0 \\
\text { II } & B\left(a \nu_{+}+1\right)\left(a \nu_{-}+1\right)=0 \\
\text { III } & D\left(a \nu_{+}-1\right)\left(a \nu_{-}-1\right)=0 \\
\text { IV } & E\left(a \nu_{+}-2\right)\left(a \nu_{-}-2\right)=0 . \tag{34}
\end{array}
$$

[^2]The Specializations with $\nu_{+} \nu_{-}<0, \quad \nu_{+}+\nu_{-} \neq \mathbf{0}$
These are

$$
\begin{array}{rrrrr}
A \neq 0 & \nu_{+}=-\frac{2}{a} & \text { or } & \nu_{-}=-\frac{2}{a} & \\
& \Downarrow & & \Downarrow & , \quad B=E=0  \tag{35}\\
D \neq 0 & \nu_{-} & =\frac{1}{a} & \text { or } & \nu_{+}=\frac{1}{a}
\end{array}
$$

or

$$
\begin{array}{rrrrr}
B \neq 0 & \nu_{+}=-\frac{1}{a} & \text { or } & \nu_{-}=-\frac{1}{a} & \\
& \Downarrow & & \Downarrow & , \quad A=D=0  \tag{36}\\
E \neq 0 & \nu_{-}=\frac{2}{a} & \text { or } & \nu_{+}=\frac{2}{a} &
\end{array}
$$

In the two canonical cases with valencies

$$
\begin{array}{ll}
\nu_{+}=\frac{1}{a}, & \nu_{-}=-\frac{2}{a} \\
\nu_{+}=\frac{2}{a}, & \nu_{-}=-\frac{1}{a} \tag{38}
\end{array}
$$

the electric field equation becomes, in turn

$$
\begin{equation*}
a^{2} p^{\prime \prime}+a p p^{\prime}-p^{3}+2 k p=0 \tag{39}
\end{equation*}
$$

or

$$
\begin{equation*}
a^{2} p^{\prime \prime}-a p p^{\prime}-p^{3}+2 k p=0 \tag{40}
\end{equation*}
$$

with general solution (27) where $w$ is given in terms of elliptic integrals via

$$
\begin{equation*}
w^{\prime}= \pm \sqrt{A+2 k w^{2} / a^{2}+D w^{3}} \tag{41}
\end{equation*}
$$

or

$$
\begin{equation*}
w^{\prime}= \pm \sqrt{B w+2 k w^{2} / a^{2}+E w^{4}} \tag{42}
\end{equation*}
$$

respectively. The positive sign is taken in the sequel.

## Case I

Here, we proceed with the case (37) with $\nu_{+}: \nu_{-}=1:-2$ as obtained via Painlevé analysis in [7]. Insertion of (27) into (5) and (6) with $c_{+}=c_{-}=0$ on integration yields

$$
\begin{gather*}
n_{+}=k_{+} w^{a \nu_{+}}=k_{+} w  \tag{43}\\
n_{-}=k_{-} w^{a \nu_{-}}=k_{-} w^{-2} \tag{44}
\end{gather*}
$$

where the Gauss equation (7) shows that

$$
\begin{aligned}
& k_{+}=\frac{a D}{2 \nu_{+}}=\frac{a^{2} D}{2} \\
& k_{-}=-\frac{a A}{\nu_{-}}=\frac{a^{2} A}{2}
\end{aligned}
$$

whence, the concentrations are given by

$$
\begin{align*}
& n_{+}=\frac{a^{2} D w}{2}  \tag{45}\\
& n_{-}=\frac{a^{2} A}{2 w^{2}} \tag{46}
\end{align*}
$$

The Neumann boundary conditions (22) require that

$$
-2 A w(0)^{-2}+D w(0)=0, \quad-2 A w(1)^{-2}+D w(1)=0
$$

so that

$$
\begin{equation*}
w(0)=w(1)=\left(\frac{2 A}{D}\right)^{1 / 3} \tag{47}
\end{equation*}
$$

Moreover,

$$
\begin{aligned}
& n_{+}(0)=\frac{a^{2} D w(0)}{2}=\frac{a^{2} D}{2}\left(\frac{2 A}{D}\right)^{1 / 3}=n_{+}(1) \\
& n_{-}(0)=\frac{a^{2} A w^{-2}(0)}{2}=\frac{a^{2} A}{2}\left(\frac{2 A}{D}\right)^{-2 / 3}=n_{-}(1)
\end{aligned}
$$

so that

$$
\begin{equation*}
A D^{2}=\frac{4 n_{+}^{3}(0)}{a^{6}}=\frac{32 n_{-}^{3}(0)}{a^{6}} \tag{48}
\end{equation*}
$$

If we denote

$$
\begin{align*}
& \left.n_{+}\right|_{x=0}=\left.n_{+}\right|_{x=1}=n^{+}  \tag{49}\\
& \left.n_{-}\right|_{x=0}=\left.n_{-}\right|_{x=0}=n^{-} \tag{50}
\end{align*}
$$

so that

$$
\begin{equation*}
n_{+}=\frac{n^{+} w}{w(0)}, \quad n_{-}=n^{-}\left(\frac{w}{w(0)}\right)^{-2} \tag{51}
\end{equation*}
$$

and

$$
\begin{equation*}
p=\sqrt{2\left(n^{+} w / w(0)+n^{-}(w / w(0))^{-2}+k\right)} \tag{52}
\end{equation*}
$$

so that

$$
\begin{equation*}
\left.p\right|_{x=0}=\sqrt{2\left(n^{+}+n^{-}+k\right)}=\left.p\right|_{x=1} . \tag{53}
\end{equation*}
$$

It is noted that the requirement (25) shows that the constants $n^{+}$and $n^{-}$are related by

$$
\begin{equation*}
\frac{n^{+}}{n^{-}}=-\frac{\nu_{-}}{\nu_{+}}=2 \tag{54}
\end{equation*}
$$

In the above, $w$ is given via

$$
\begin{align*}
w^{\prime} & = \pm \frac{1}{a} \sqrt{2\left(\frac{n^{+} w^{3}}{w(0)}+k w^{2}+n^{-} w^{2}(0)\right)}  \tag{55}\\
& = \pm \sqrt{A+2 k w^{2} / a^{2}+D w^{3}}
\end{align*}
$$

where it is required that the constants $A, D$ and $k$ be specified.

## Case II

Here, we consider the case (38) with $\nu_{+}: \nu_{-}=2:-1$ so that, in relations (43), (44) for the concentrations,

$$
\begin{gather*}
k_{+}=\frac{a E}{\nu_{+}}=\frac{a^{2} E}{2}  \tag{56}\\
k_{-}=-\frac{a B}{2 \nu_{-}}=\frac{a^{2} B}{2} \tag{57}
\end{gather*}
$$

whence

$$
\begin{gather*}
n_{+}=\frac{a^{2} E w^{2}}{2}  \tag{58}\\
n_{-}=\frac{a^{2} B}{2 w} \tag{59}
\end{gather*}
$$

The Neumann boundary conditions (43) require that

$$
\begin{equation*}
w(0)=w(1)=-\left(\frac{B}{2 E}\right)^{1 / 3} \tag{60}
\end{equation*}
$$

be applied to

$$
\begin{equation*}
w^{\prime}=\sqrt{B w+\frac{2 k w^{2}}{a^{2}}+E w^{4}} \tag{61}
\end{equation*}
$$

## Illustration

Here, we set

$$
\begin{equation*}
w(0)=w(1)=1 \tag{62}
\end{equation*}
$$

together with $A=1$ so that, from (47), $D=2$. The corresponding class of solutions of the two-ion system is then given by

$$
\begin{align*}
n_{+} & =a^{2} w, \quad n_{-}=\frac{a^{2} w^{-2}}{2}  \tag{63}\\
p & =a \sqrt{w^{-2}+\frac{2 k}{a^{2}}+2 w} \tag{64}
\end{align*}
$$

where

$$
\begin{equation*}
w^{\prime}=\sqrt{1+\frac{2 k w^{2}}{a^{2}}+2 w^{3}} \tag{65}
\end{equation*}
$$

In the sequel, we apply an exact shooting method to a Neumann boundary value problem for the nonlinear equation (20) when reduction to an elliptic integral formalism is not available.
3. The case $\nu_{+}+\nu_{-} \leq 0$. Here, we consider (20) under Neumann conditions, namely the problem

$$
\begin{gather*}
y^{\prime \prime}=\left(\frac{\nu_{+}+\nu_{-}}{\sqrt{-\nu_{+} \nu_{-}}}\right) y y^{\prime}+\frac{y^{3}}{2}+\delta\left[\lambda l+\frac{1}{2}\left(y^{2}(0)-y^{2}(1)\right)\right] x y \\
-\left[\frac{y^{2}(0)}{2}-\lambda\right] y-\delta\left[\lambda l+\frac{1}{2}\left(y^{2}(0)-y^{2}(1)\right)\right] D  \tag{66}\\
y^{\prime}(0)=y^{\prime}(1)=0, \tag{67}
\end{gather*}
$$

without the assumption of any privileged valency ratio, except requiring $\nu_{+}+\nu_{-} \leq 0$.
We shall show the existence of solutions. It proves convenient to set

$$
C:=\frac{\nu_{+}+\nu_{-}}{\sqrt{-\nu_{+} \nu_{-}}}
$$

and it is noted that $\lambda=-\delta^{2} \nu_{+} \nu_{-} n(0)>0$.
The main result of this section reads as follows:
Theorem 3.1. Assume that $\nu_{+}+\nu_{-} \leq 0, \delta \leq 1$ and $l>0$. Then problem (66)-(67) admits at least one solution, provided that $0<D<1+\frac{1}{l}$.

The above extends our previous result proved in [15] for the case $\nu_{+}+\nu_{-}=0$ and $\delta=1$.

The proof will follow from a series of lemmas.
First, we observe that, on searching for positive solutions, if we set $z=y / \gamma$, where $\gamma=y(0)$, then (66)-(67) is equivalent to

$$
\begin{equation*}
z^{\prime \prime}(x)-C \gamma z(x) z^{\prime}(x)=\left[\lambda-\frac{\gamma^{2}}{2}\left(1-z(x)^{2}\right)+\gamma \alpha x\right] z(x)-\alpha D \tag{68}
\end{equation*}
$$

with conditions

$$
\begin{equation*}
z(0)=1, \quad z^{\prime}(0)=z^{\prime}(1)=0 \tag{69}
\end{equation*}
$$

where

$$
\begin{equation*}
\alpha=\frac{\delta}{\gamma}\left(l \lambda+\frac{\gamma^{2}}{2}\left(1-z(1)^{2}\right)\right) \tag{70}
\end{equation*}
$$

In the original problem, the parameter $l$ together with the other parameters, $\lambda$, $D$, and $\delta$, are given, and we seek a solution $y$ of (66) which satisfies the boundary conditions (67). As noted before, the fact that the differential equation (66) contains the unknown boundary values $y(0)$ and $y(1)$ makes the problem unconventional and cannot be adequately solved by traditional methods. To circumvent this difficulty, we consider the new problem (68) and (69). Here the parameter $l$ is no longer given beforehand. Instead, we prescribe the parameters $\alpha$ and $\gamma$ and proceed to solve the initial value problem (68) with the first two conditions in (69). By adjusting $\alpha$ appropriately, we can coerce the third condition in (69) to hold also, and then we recover $l$ from the solution by solving (70). If the calculated $l$ coincides with the given value of the parameter, we have our desired solution.

Thus, it suffices to find a pair $(\alpha, \gamma)$ such that the corresponding solution of the initial value problem satisfies $z^{\prime}(1)=0$ and

$$
l=\frac{2 \alpha \gamma-\delta \gamma^{2}\left(1-z(1)^{2}\right)}{2 \delta \lambda}
$$

However, it is observed that an impediment arises on the fact that $z$ may or may not be 'properly' defined throughout the entire interval $[0,1]$. One situation is that $z(t)$ can blow up to infinity before $t$ reaches the endpoint 1 of the interval. Another possibility is that $z(t)$ can hit the $t$-axis somewhere inside $[0,1]$ and then becomes negative subsequently. Let us define an 'endpoint' $\sigma \in(0,1]$ of the solution $z$ in the following way:

Case 1: If $0<z<2$ on $\left[0, t_{0}\right) \subset[0,1]$ and $z\left(t_{0}\right)=0$, then $\sigma:=t_{0}$.
Case 2: If $0<z<2$ on $\left[0, t_{0}\right) \subset[0,1]$ and $z\left(t_{0}\right)=2$, then $\sigma:=t_{0}$.
Case 3: If $0<z<2$ on $[0,1]$ then $\sigma:=1$.
Thus, we are able to define a two-dimensional shooting operator $T$ given by

$$
T(\alpha, \gamma):=\left(z^{\prime}(\sigma), L\right)
$$

where $L$ is given by

$$
\begin{equation*}
L=L(\alpha, \gamma):=\frac{2 \alpha \gamma-\delta \gamma^{2}\left(1-z(\sigma)^{2}\right)}{2 \delta \lambda} \tag{71}
\end{equation*}
$$

Although physical considerations mean that we are interested only in those ( $\alpha, \gamma$ ) in the (open) first quadrant, we note parenthetically that $T$ is defined also for $\gamma=0$. We seek a pair $(\alpha, \gamma)$ such that $T(\alpha, \gamma)=(0, l)$ : in that case it shall be seen that $\sigma=1$ and $\gamma>0$, and hence the corresponding $z$ is a positive solution of (68)-(69) with $\alpha$ as in (70).

We shall make use of two comparison lemmas. The first is well known (see, for example, [16]) and the second is specific to our equation.

Lemma 3.2. Let $Z, W:[0, a] \rightarrow \mathbb{R}$ satisfy

$$
Z^{\prime \prime}(x) \geq F(x, Z(x))
$$

and

$$
W^{\prime \prime}(x)=F(x, W(x))
$$

for $x \in[0, a]$, where $F$ is continuous and non-decreasing in the second variable for each fixed $x \in[0, a]$. If, in addition, it is assumed that

$$
Z(0) \geq W(0), \quad Z^{\prime}(0) \geq W^{\prime}(0)
$$

then

$$
Z(x) \geq W(x), \quad Z^{\prime}(x) \geq W^{\prime}(x)
$$

for all $x \in[0, a]$.
Lemma 3.3. Let $z$ be a solution of (68) with $\alpha>0$, and either $\gamma>0$, or $\gamma=0$ but $\lambda \neq \alpha D$. Assume that $0 \leq z\left(x_{0}\right) \leq z\left(x_{1}\right)$ and $z^{\prime \prime}\left(x_{0}\right) \geq C \gamma z\left(x_{0}\right) z^{\prime}\left(x_{0}\right)$ for some $x_{0}<x_{1}$.

Then

$$
\begin{equation*}
z^{\prime \prime}\left(x_{0}\right)-C \gamma z\left(x_{0}\right) z^{\prime}\left(x_{0}\right)<z^{\prime \prime}\left(x_{1}\right)-C \gamma z\left(x_{1}\right) z^{\prime}\left(x_{1}\right) \tag{72}
\end{equation*}
$$

Proof. First assume that $\gamma>0$. As $z^{\prime \prime}\left(x_{0}\right) \geq C \gamma z\left(x_{0}\right) z^{\prime}\left(x_{0}\right)$, it follows that

$$
\left[\lambda-\frac{\gamma^{2}}{2}\left(1-z\left(x_{0}\right)^{2}\right)+\gamma \alpha x_{0}\right] z\left(x_{0}\right) \geq \alpha D>0
$$

This implies that the righthand side term of (68) has positive $z$-derivative for $z \geq$ $z\left(x_{0}\right)$. As it is also an increasing function of $x$, the result obviously follows.

When $\gamma=0$ and $\lambda \neq \alpha D$, (68) becomes $z^{\prime \prime}=\lambda z-\alpha D$. A direct computation gives

$$
\begin{equation*}
z(x)=\frac{\alpha D}{\lambda}+\frac{1}{2}\left(1-\frac{\alpha D}{\lambda}\right)\left(e^{\sqrt{\lambda} x}+e^{-\sqrt{\lambda} x}\right) \tag{73}
\end{equation*}
$$

The conclusion of the Lemma can then be verified directly.
Note that if $\gamma=0$, and $\lambda=\alpha D$, then (68) has the constant solution $z \equiv 1$, and (72) does not hold.

Lemma 2 allows us to establish two fundamental facts about the shooting operator $T$. These are set down below:
Lemma 3.4. $T$ is continuous. Moreover, if $T(\alpha, \gamma)=(0, l)$ with $\gamma>0$ then $y:=\gamma z$ is a solution of the original problem (66)-(67).
Proof. We start by proving the following claim: if $z^{\prime}(\sigma)=0$, then $0<z<2$ on $[0,1]$.

In other words, $z^{\prime}(\sigma)=0$ precludes Cases 1 and 2 and we must have $\sigma=1$.
Suppose first that Case 1 holds. Then $\sigma$ is the global minimum of $z$ on $[0, \sigma]$, which implies $z^{\prime \prime}(\sigma) \geq 0$. But from (68) we have $z^{\prime \prime}(\sigma)=-\alpha D<0$, a contradiction.

Next, suppose that Case 2 holds. Let $x_{0}$ be the global minimum of $z$ in $[0, \sigma]$. Then $0<z\left(x_{0}\right)<z(\sigma)$ and $z^{\prime \prime}\left(x_{0}\right) \geq 0$. As $z^{\prime}\left(x_{0}\right)=z^{\prime}(\sigma)=0$, from Lemma 3.3, we obtain $z^{\prime \prime}(\sigma)>0$, a contradiction, except when $\gamma=0$ and $\lambda=\alpha D$. For the exceptional case, the claim is trivially true.

Continuity of $T$ now follows from the standard continuous dependence result for ordinary differential equations.

Finally, if $T(\alpha, \gamma)=(0, l)$ then from the above claim, $\sigma=1$ and the equality $L=l$ implies that $\alpha$ satisfies (70), and $y$ is therefore a solution of the original problem.

In order to prove the existence of a pair $(\alpha, \gamma)$ such that $T(\alpha, \gamma)=(0, l)$, we shall find a bounded domain $\mathcal{C} \subset(0,+\infty) \times[0,+\infty)$ such that the topological index $I$ of the curve $T \circ \partial \mathcal{C}$, which is the image of the boundary of $\mathcal{C}$ under $T$, satisfies

$$
I(T \circ \partial \mathcal{C},(0, l)) \neq 0
$$

From the standard topological index theory, this implies that the equation $T=(0, l)$ has at least one solution in $\mathcal{C}$. More specifically, $\mathcal{C}$ shall be defined as the rectangle $P Q R S$ given by the vertices

$$
\begin{aligned}
S:=\left(\frac{\lambda}{D}, \gamma^{*}\right), & R:=\left(\alpha^{*}, \gamma^{*}\right) \\
P & :=\left(\frac{\lambda}{D}, 0\right),
\end{aligned} \quad Q:=\left(\alpha^{*}, 0\right)
$$

where $\alpha^{*}$ and $\gamma^{*}$ are suitable constants to be chosen later.
Lemma 3.5. Let $\gamma>0$. If $z$ attains a local minimum at $x_{0}<\sigma$, then $z^{\prime}(x)>0$ for $x>x_{0}$ (in particular, $z^{\prime}(\sigma)>0$ ). If furthermore $\alpha D \geq \lambda$, then $L>0$.

Proof. If $z^{\prime}\left(x_{1}\right)=0$ for some $x_{1}>x_{0}$, then either $z\left(x_{1}\right)<z\left(x_{0}\right)$ or else from Lemma 3.3 we obtain $z^{\prime \prime}\left(x_{1}\right)>0$ and $x_{1}$ is a local minimum. In both cases, $z$ attains a local maximum at some $x_{2} \in\left(x_{0}, x_{1}\right)$ with $z\left(x_{2}\right) \geq z\left(x_{0}\right)$, and again we obtain $z^{\prime \prime}\left(x_{2}\right)>0$, a contradiction. Thus $z^{\prime}$ does not vanish after $x_{0}$, and then $z^{\prime}(x)>0$ for $x>x_{0}$. It is observed that, in particular, Case 1 cannot hold.

Note that If Case $\mathbf{2}$ holds, or if Case $\mathbf{3}$ holds and $z(1) \geq 1$, then (from the definition of $L$ ) $L>0$, regardless of whether $\alpha D \geq \lambda$. or not. For the remaining case, when $\sigma=1$ and $z(1)<1$, we have

$$
\begin{aligned}
0 & <z^{\prime \prime}(1)-C \gamma z(1) z^{\prime}(1) \\
& =z(1)\left(\lambda(1+L)+\gamma \alpha\left(1-\frac{1}{\delta}\right)\right)-\alpha D \\
& <\lambda(1+L)-\lambda .
\end{aligned}
$$

The first inequality follows from Lemma 3.3, the equality in the second line from the differential equation (68) and the definition (71), and the inequality in the third line from the assumptions $\delta \leq 1, z(1)<1$, and $\alpha D \geq \lambda$. Hence, we have $L>0$.

The following lemmas provide a picture of the image of $\partial \mathcal{C}$.
Lemma 3.6. The segment $P Q$ is mapped one-to-one onto the segment $P^{\prime} Q^{\prime}$, where $P^{\prime}=(0,0)$ and $Q^{\prime}=(-r, 0)$ for some $r>0$.

Proof. Along the segment $P Q, \gamma=0$ and $z(x)$ is given by (73). Hence, $T(P)=$ $(0,0)$. The injectiveness property of $T$ on $P Q$ is actually not needed in the proof of Theorem 1. To prove it, we have to consider two cases. As we increase $\alpha$ from $\lambda / D$, initially we have Case 3, in which $\sigma=1$. We can then use (73) to get

$$
\frac{\partial}{\partial \alpha} z^{\prime}(1)=\frac{-D}{2 \sqrt{\lambda}}\left(e^{\sqrt{\lambda}}-e^{-\sqrt{\lambda}}\right)<0
$$

to see that $z^{\prime}(\sigma)$ is decreasing in $\alpha$. However, after $\alpha$ reaches a critical value $\alpha_{0}$, i.e. for $\alpha>\alpha_{0}$, Case 1 prevails. In this case, we multiply the differential equation $z^{\prime \prime}=\lambda z-\alpha D$ by $z^{\prime}$ and integrate from $x=0$ to $x=\sigma$ to obtain

$$
\frac{z^{\prime 2}(\sigma)}{2}=\frac{\lambda z^{2}(\sigma)}{2}-\alpha D z(\sigma)-\frac{\lambda}{2}+\alpha D=-\frac{\lambda}{2}+\alpha D
$$

Hence, $z^{\prime 2}(\sigma)$ is an increasing function of $\alpha$. However, $z^{\prime}(\sigma)$ is negative. Thus $z^{\prime}(\sigma)$ is a decreasing function of $\alpha$.

The next lemma shows that, except for the point $P$, the image of the segment $P S$ lies in the first quadrant:

Lemma 3.7. If $\alpha=\lambda / D$ and $\gamma>0$ then $z^{\prime}(\sigma)>0$ and $L>0$.
Proof. If $z$ is initially increasing, then 0 is a local minimum and Lemma 3.5 applies.
If $z$ is initially decreasing, then as $C \leq 0$ and $z^{\prime} \leq 0$ in $[0, \varepsilon]$ for some $\varepsilon>0$, we obtain:

$$
z^{\prime \prime} \geq\left[\lambda-\frac{\gamma^{2}}{2}\left(1-z^{2}\right)\right] z-\lambda
$$

on $[0, \varepsilon]$. Applying Lemma 3.2 with $W \equiv 1$, we deduce that $z \geq 1$ on $[0, \varepsilon]$, a contradiction.

Finally, if neither of the previous situations occurs, $z$ would have more than one local minimum, and this contradicts Lemma 3.5.

The remaining two lemmas concern a convenient choice of $\alpha^{*}$ and $\gamma^{*}$.
Lemma 3.8. Let $\alpha>\lambda(1+l) / D$ and $\gamma \geq 0$. If $z^{\prime}(\sigma)=0$, then $L>l$.
Proof. As $z^{\prime}(\sigma)=0$, we are in Case 3 and it is readily seen that $\gamma>0$. From Lemma 3.5, $z$ cannot have a local minimum in $[0,1)$. Hence the global minimum of $z$ is attained at the endpoint $\sigma=1$, and we deduce that $z^{\prime \prime}(1) \geq 0$ and $z$ is nonincreasing. From (68), we also deduce that $z \not \equiv 1$, then $z(1)<1$ and

$$
\begin{aligned}
0 & \leq z^{\prime \prime}(1) \\
& =z(1)\left(\lambda(1+L)+\gamma \alpha\left(1-\frac{1}{\delta}\right)\right)-\alpha D \\
& <\lambda(1+L)-\lambda(1+l),
\end{aligned}
$$

which implies $L>l$. Again, the equality in the second line follows from (68) and (71).

In view of the preceding result, we fix a constant $\alpha^{*}$ such that

$$
\begin{equation*}
\alpha^{*}>\frac{\lambda(1+l)}{D} \tag{74}
\end{equation*}
$$

and proceed with the last lemma.
Lemma 3.9. If $\gamma^{*}$ is large enough, then the image of the segment $R S$ lies on the first quadrant.

Proof. We already know that $T(S)$ lies on the first quadrant, so we may assume that $\alpha>\lambda / D$. Then $z^{\prime \prime}<0$ in a neighborhood of 0 and $z$ is initially decreasing. If $z$ attains a local minimum at some point $x_{0}<\sigma$, then Lemma 3.5 applies. Thus, it suffices to prove that $z$ cannot be strictly decreasing all the time.

Suppose, on the contrary, that $z$ decreases strictly on $[0, \sigma]$, then the term $-C \gamma z(x) z^{\prime}(x)$ is nonnegative. Also, as $z \leq 1$, we have that $\left(1-z^{2}\right) z \leq 2(1-z)$, and hence from (68) we obtain:

$$
z^{\prime \prime} \geq-\gamma^{* 2}(1-z)+\left(\lambda+\gamma^{*} \alpha x\right) z-\alpha D .
$$

Next, fix a constant $m$ such that $\alpha^{*} D /\left(\alpha^{*}+\lambda\right)<m<1$. This can be done since $D<1+\frac{1}{l}$, and the value of $\alpha^{*}$ can be modified if necessary, as far as it satisfies (74).

Finally, define $W$ as the solution of the linear problem

$$
\begin{gathered}
W^{\prime \prime}(x)=-\gamma^{* 2}(1-W)+\left(\lambda+\gamma^{*} \alpha x\right) m-\alpha D \\
W(0)=1, \quad W^{\prime}(0)=0
\end{gathered}
$$

Direct computation shows that

$$
W(x)=1+C_{1} e^{\gamma^{*} x}+C_{2} e^{-\gamma^{*} x}-R(x)
$$

where

$$
C_{1}=\frac{(\lambda+\alpha) m-\alpha D}{2 \gamma^{* 2}}, \quad C_{2}=\frac{(\lambda-\alpha) m-\alpha D}{2 \gamma^{* 2}}
$$

and

$$
R(x)=\frac{1}{\gamma^{*}}\left(\alpha m x+\frac{\lambda m-\alpha D}{\gamma^{*}}\right)
$$

As $\alpha \leq \alpha^{*}$, it follows from the choice of $m$ that $C_{1}>0$, and for $\gamma^{*}$ large enough we also have that $\left|C_{2} e^{-\gamma^{*} x}-R(x)\right| \leq 1-m$ for every $x \in[0,1]$, which, in turn, implies $W>m$ on $[0,1]$. Now, suppose that $z\left(x_{0}\right)=m$, then

$$
z^{\prime \prime} \geq-\gamma^{* 2}(1-z)+\left(\lambda+\gamma^{*} \alpha x\right) m-\alpha D
$$

on $\left[0, x_{0}\right]$. From Lemma 3.2, we deduce that $z \geq W>m$ on $\left[0, x_{0}\right]$, a contradiction. Thus, $z>m$ and the previous inequality holds on $[0,1]$. Applying Lemma 3.2 again, it follows that $z \geq W$ on $[0,1]$. Since $C_{1} e^{\gamma^{*}} \rightarrow+\infty$ as $\gamma^{*} \rightarrow+\infty$, for $\gamma^{*}$ large enough, we get $W(1)>1$, and this contradicts the fact that $z \leq 1$.

Proof of Theorem 3.1. From the previous lemmas we conclude that the index of the curve $T \circ \partial \mathcal{C}$ relative to the point $(0, l)$ is -1 , and hence $T(\alpha, \gamma)=(0, l)$ for some $(\alpha, \gamma) \in \mathcal{C}$.


Figure 1. Image of $P Q R S$ under the mapping $T$

To help us to visualize the proof, we plot the image $P^{\prime} Q^{\prime} R^{\prime} S^{\prime}$ of the rectangle $P Q R S$ under the mapping $T$ in Figure 1, for a special case in which the physical parameters have been chosen to be $\lambda=1, D=1$, and $\delta=1$, and the constants
$\alpha^{*}$ and $\gamma^{*}$ in the definition of the rectangle $P Q R S$ have been chosen to be 6 and 4 respectively. The numerical experiment is done with the help of MATLAB.

The two distinctive kinks, one on the curve $Q^{\prime} R^{\prime}$ and the other on $R^{\prime} S^{\prime}$ represent the locations where there is a switch of case of the nature of the endpoint $\sigma$ (between the three cases listed before Lemma 1). Let $O$ denote the origin and $A$ where the curve $Q^{\prime} R^{\prime}$ intersects the $L$-axis. Then the topological index of $P^{\prime} Q^{\prime} R^{\prime} S^{\prime}$ is 1 for every point that lies on the line segment $O A$. Hence, the original Neumann problem has a solution for these values of $L$. By increasing $\alpha^{*}$ and $\gamma^{*}$, more values of $L$ will be covered (Lemmas 7 and 8).

If we reduce $\gamma^{*}$ to 3 , the image of the side $R S$ becomes $R^{\prime \prime} S^{\prime \prime}$. As shown in the figure, it does not lie entire in the first quadrant. This attests the fact that Lemma 8 only holds if $\gamma^{*}$ is sufficiently large.

## REFERENCES

[1] W. Nernst, Zur Kinetik der in Lösung befindlichen Körper: I Theorie der Diffusion, Z. Phys. Chem., 2 (1882), 613-637.
[2] M. Planck, Über die Erregung von Elektricität und Wärme in Electrolyten, Ann. Phys. Chem., 39 (1890), 161-186.
[3] K. S. Cole, "Membranes, Ions and Impulses," University of California Press, Berkeley, 1968.
[4] T. L. Schwarz, "Biophysics and Physiology of Excitable Membranes" (ed. W. J. Adelman, Jr.), Van Rostrand, New York, 1971.
[5] J. O'M Bokris and A. K. N. Reddy, "Modern Electrochemistry," Plenum, New York, 1971.
[6] H. R. Leuchtag, A family of differential equations arising from multi-ion electrodiffusion, J. Mathematical Phys., 22 (1981), 1317-1320.
[7] R. Conte, C. Rogers and W. K. Schief, Painlevé structure of a multi-ion electrodiffusion system, J. Phys. A, 40 (2007), F1031-F1040.
[8] H. B. Thompson, Existence for two-point boundary value problems in two-ion electrodiffusion, J. Math. Anal. Appl, 184 (1994), 82-94.
[9] B. M. Grafov and A. A. Chernenko, Theory of the passage of a constant current through a solution of a binary electrolyte, Dokl. Akad. Nauk. SSR, 146 (1962), 135-138.
[10] L. Bass, Electrical structures of interfaces in steady electrolysis, Trans. Faraday Soc., 60 (1964), 1655-1663.
[11] N. A. Kudryashov, The second Painlevé equation as a model for the electric field in a semiconductor, Phys. Lett. A, 233 (1997), 397-400.
[12] C. Rogers, A. Bassom and W. K. Schief, On a Painlevé II model in steady electrolysis: Application of a Bäcklund transformation, J. Math. Anal. Appl., 240 (1999), 367-381.
[13] L. Bass, J. Nimmo, C. Rogers and W. K. Schief, Enhanced structures of interfaces: A Painlevé II model, Proc. Roy. Soc. London Ser. A Math. Phys. Eng. Sci., 466 (2010), 2117-2136.
[14] L. Bass, Irreversible interactions between metals and electrolytes, Proc. Roy. Soc. London A, 277 (1964), 125-136.
[15] P. Amster, M. K. Kwong and C. Rogers, On a Neumann boundary value problem for Painlevé II in two-ion electro-diffusion, Nonlinear Analysis, Theory, Methods and Applications, in press.
[16] C. De Coster and P. Habets, Upper and lower solutions in the theory of ODE boundary value problems: Classical and recent results, in "Nonlinear Analysis and Boundary Value Problems for ODEs," CISM Courses and Lectures, 371, Springer, Vienna, (1996), 1-78.

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[^2]:    ${ }^{\dagger}$ It is noted that the corresponding arbitrary constants in the 3-ion case are required to be zero in Bass [14].

