Journal of Dynamics and Differential Equations
https://doi.org/10.1007/s10884-021-10118-x

Flux Ratios for Effects of Permanent Charges on Ionic Flows with Three Ion Species: New Phenomena from a Case Study

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Received: 13 August 2021 / Revised: 2 December 2021 / Accepted: 7 December 2021

Abstract
In this work, for ionic flows through ion channels involving three ion species (two cations with different valences and one anion), we examine how channel structure (permanent charge distribution) interacts with boundary conditions to affect individual fluxes. This is analyzed via a quasi-one-dimensional classical Poisson–Nernst–Planck model and, as an early step, the focus is on finding of new phenomena presented by the biological settings with three ion species (comparing to two ion species). Permanent charges are taken to be piecewise constant with three regions: zeros over two end regions of the channel including the baths and a constant over the middle region. For ionic flows involving two ion species (one cation and one anion), the topic has been recently examined and important phenomena, some counterintuitive, were revealed. For ionic flows involving three ion species treated in this work, even for small permanent charges and for a special case of boundary conditions, several striking phenomena are discovered and the study also immediately leads to a number of questions. We hope and believe the rich behavior revealed in this work for the special case will stimulate a great deal of research along this line in the near future.

Keywords Ionic flux · Permanent charge · Flux ratio

Mathematics Subject Classification 34B16 · 37N25 · 92C35

1 Introduction

The electrodiffusion process of ions (charged particles) plays a critical role for living organisms. The basic units where migration of ions take place are membrane proteins (ion

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Published online: 24 January 2022

channels) that provide major channels for cells to communicate and coordinate with other cells for major biological functions [22–26,52,59]. Ion channels are nano valves for life [7,12,13,15,31,32,36]. There are many different types of ion channels defined mainly by their protein structures or permanent charges. Ionic flow properties are major concerns of physiological ion channels and are controlled by the nonlinear interplay between permanent charges and transmembrane electric potential as well as boundary concentrations. Ionic flow through ion channels is a special electrodiffusion process with a number of specifics. It is a problem with multiple interacting physical parameters and presents multi-scales too (see [1,14,16,17,39,40,51,54,55,60]).

The structure of many ion channels is now known thanks to the revolutionary advances of cryo-electron microscopy, recognized in the 2018 Nobel Prize. This work greatly enhances the study of permanent charge effects on ionic flow toward a comprehensive understanding of ion channel properties. On the other hand, great challenges are still present. Due to the limitation of present experimental techniques, the major experimental measurement of ionic flows is the I-V relation defined in (1.5) below [4,6,11], which is an input-output type information of an average effect of physical parameters on ionic flows; in particular, it is still not possible to “measure/observe” internal dynamical behaviors of ionic flows. Those features make it difficult for researchers to extract quantitative information or identify characteristics from experimental data that are critical for classifying general behavior of ionic flows and for identifying possible effect of permanent charges on ionic flows. Measurements of I-V relations however can determine some characteristics of ion channels quite well, using well established methods of the theory of inverse problems [9,10].

The aforementioned challenges strongly suggest the importance of mathematical models and analysis and numerical simulations as complementary tools to the physiological theory and experiments. Mathematical study could provide deep correspondences from the multiple parameters involved to the internal dynamics and to properties of ion channels, at least for the simplified settings used in many biological experiments. The basic primitive models for ionic flows are the Poisson–Nernst–Planck (PNP) type models and have been analyzed and simulated extensively [2,3,17,30,48]. The geometric singular perturbation theory relies on special structures of the PNP models developed in [17,34,38–40,44] that allow a systematical study of several ion channel problems in [18,29,35,41,45,46,62,63].

To measure permanent charge effects on fluxes, a flux ratio was introduced in [41] (see (1.6) below). This flux ratio measures effects on fluxes of permanent charges relative to zero permanent charge. It is an important characteristic for roles of permanent charges, as demonstrated by a number of phenomena, some counterintuitive, revealed in [29,35,41,63] for ionic flows involving two ion species (one cation and one anion). We remark that the choice of zero permanent charge as a reference in the definition of the flux ratio is actually not a restriction, in particular, one can include large permanent charges in the study of flux ratios. In fact, one can express the ratio between fluxes of any two permanent charges in terms this flux ratio. Nevertheless there are a number of merits for a direct examination of ratios between fluxes of any two permanent charges, for example, one may study properties of a mutant protein of an ion channel by studying ratios between fluxes associated to the mutated permanent charge and those of the original permanent charge. Furthermore, there are properties of ratios between fluxes of two permanent charges that could not be derived from properties of flux ratios relative to zero permanent charge. This general flux ratio is currently under investigation by the authors. We also remark that this flux ratio measuring permanent charge effects is different from Ussing’s flux ratio [58] and from Hodgkin-Keynes’ flux ratio exponent [27]. The latter two measure fluxes with the same permanent charges under different setups of boundary conditions. We refer interested readers to [33] for a detailed mathematical treatment of Ussing's flux ratio and Hodgkin-Keynes' flux ratio exponent.

In this work, for ionic flows through ion channels involving three ion species (two cations with different valences and one anion), we examine roles of permanent charges in ion channel properties by comparing permanent charge effect on fluxes of different ion species. This is analyzed via a quasi-one-dimensional classical PNP model and based on the flux ratio for permanent charge effects introduced in [41] and mentionedx above. By including some essential physical laws and biological specifics, with the rather idealized PNP model, our purpose for this paper is, taking the advantage of mathematical (explicit or implicit) formulas for the central quantities, to discover new phenomena and to formulate new characteristics/quantities that are directly related to biology, hoping these will be observed experimentally and useful in general. We will take permanent charges to be piecewise constant with three regions: zeros over two end regions of the channel including the baths and a constant over the middle region. It turns out the phenomena are extremely rich—even for a case study carried out in this paper with the classical PNP model. The rich behavior reflects the presence of multiple parameters—they all are relevant in the sense that different regions of parameters produce distinct behaviours. We remark that the many different classes of behavior provide the channel, and its designer (evolution) and its enemies (diseases for the most part) with many ways to control the ionic current and thus the function of the channel.

Recently there are several papers on ionic flow with three ion species, two cation species with the same valence and one anion species, and some interesting results are obtained on competition of the two cations [5,61,64]. The mathematical analysis for those work are relatively simpler in the sense that it can be more or less reduced to two ion species cases as in, for example, [35] although the reduction seems not to occur in a straightforward way.

The analysis for two ion species does not work for the present case with three ion species of different valences. Our concrete results are under further assumptions (see Sect. 1.3) including that the permanent charge is small in absolute value and are as specific as possible, and hence, one should expect that statements of results are not so simple and, of course, the analysis would be more involved. Here are two samples of results in this work (see more in Sect. 4).

(i) Under some boundary conditions, a *nonnegative* permanent charge can enhance the flux of a cation (a positively charged ion) species with larger valence more than that of a cation species with smaller valence.
(ii) Under some boundary conditions, a *nonnegative* permanent charge can enhance the flux of a cation species (either of the two cation species) more than that of an anion (a negatively charged ion) species.

As shown in [41], (ii) is impossible for ionic flow with one cation and one anion.

In the rest of this introduction, we recall a quasi-one-dimensional PNP model for ionic flow and the flux ratio for permanent charge effect on individual fluxes, and present the setup of our case study.

1.1 A Quasi-One-Dimensional PNP Model for Ion Flows

For a mixture of n ion species, a quasi-one-dimensional PNP model [43,47] is

$$\begin{aligned} &\frac{1}{A(X)}\frac{\mathrm{d}}{\mathrm{d}X}\left(\varepsilon_r(X)\varepsilon_0 A(X)\frac{\mathrm{d}\Phi}{\mathrm{d}X}\right) = -e_0\left(\sum_{s=1}^n z_s C_s + \mathcal{Q}(X)\right) \\ &\frac{\mathrm{d}\mathcal{J}_k}{\mathrm{d}X} = 0, \quad -\mathcal{J}_k = \frac{1}{k_B T}\mathcal{D}_k(X)A(X)C_k\frac{\mathrm{d}\mu_k}{\mathrm{d}X}, \quad k = 1, 2, \cdots, n, \end{aligned} \tag{1.1}$$

where $X \in [a, b]$ is the coordinate along the longitudinal axis of the channel, $A(X)$ is the area of cross-section of the channel at the location X, $\varepsilon_r(X)$ is the relative dielectric coefficient, ε_0 is the vacuum permittivity, e_0 is the elementary charge, $\mathcal{Q}(X)$ is the permanent charge density, k_B is the Boltzmann constant, T is the absolute temperature; Φ is the electric potential, and, for the k-th ion species, z_k is the valence (the number of charges per particle), C_k is the concentration, $\mathcal{J}_k(X)$ is the flux density through the cross-section over X, $\mathcal{D}_k$ is the diffusion coefficient, and μ_k is the electrochemical potential depending on Φ and C_k.

The electrochemical potential $\mu_k = \mu_k^{id} + \mu_k^{ex}$ for the k-th ion species consists of the ideal component μ_k^{id} given by

$$\mu_k^{id} = z_k e_0 \Phi + k_B T \ln \frac{C_k}{C_0} \tag{1.2}$$

where C_0 is a characteristic concentration, and the excess component μ_k^{ex} that accounts for finite sizes of ions [8,19–21,30,34,37,38,42,49,50,53,56,57]. The *classical* PNP (cPNP) model deals only with the ideal component μ_k^{id}.

Associated to system (1.1), we consider boundary conditions, for $k = 1, 2, \cdots, n$,

$$\Phi(a) = \mathcal{V}, \quad C_k(a) = \mathcal{L}_k > 0; \quad \Phi(b) = 0, \quad C_k(b) = \mathcal{R}_k > 0. \tag{1.3}$$

For boundary conditions, one often imposes the electroneutrality conditions to avoid sharp boundary layers (see, e.g. [62,63])

$$\sum_{s=1}^n z_s\mathcal{L}_s = \sum_{s=1}^n z_s\mathcal{R}_s = 0. \tag{1.4}$$

A major quantity that is measured in labs and used for extracting ion channel properties is *the I-V (current-voltage) relation* defined, in terms of solutions of the boundary value problem (BVP) (1.1) and (1.3), as follows. For fixed $\mathcal{L}_k$'s and $\mathcal{R}_k$'s, a solution $(\Phi, C_k, \mathcal{J}_k)$ of the BVP will depend on the voltage $\mathcal{V}$ only. The stationary current (*the flow rate of charges*), $\mathcal{I}$, is given by

$$\mathcal{I} = \sum_{s=1}^n z_s\mathcal{J}_s(\mathcal{V}). \tag{1.5}$$

1.2 Flux Ratios for Permanent Charge Effects on Ionic Fluxes

We recall the concept of flux ratio for permanent charge effects on ionic fluxes introduced in [41]. *For fixed boundary conditions* $\mathcal{V}$, $\mathcal{L}_k$*'s and* $\mathcal{R}_k$*'s*, let $\mathcal{J}_k(\mathcal{Q})$ be the flux of the k-th ion species associated with the permanent charge $\mathcal{Q} = \mathcal{Q}(X)$, then the *flux ratio for the kth ion species* is

$$\lambda_k(\mathcal{Q}) = \frac{\mathcal{J}_k(\mathcal{Q})}{\mathcal{J}_k(0)}. \tag{1.6}$$

Since the boundary conditions are the same, $\mathcal{J}_k(\mathcal{Q})$ and $\mathcal{J}_k(0)$ have the same sign as that of $\mu_k(a) - \mu_k(b)$ (see [41] and Remark 2.1 therein for cases where $\mu_k(a) = \mu_k(b)$). Thus, $\lambda_k(\mathcal{Q}) \geq 0$. The value of $\lambda_k(\mathcal{Q})$ does depend on the boundary conditions.

Naturally, one says the permanent charge $\mathcal{Q}$ *enhances* the flux of the kth ion species if $\lambda_k(Q) > 1$, it *inhibits* the flux of the kth ion species if $\lambda_k(\mathcal{Q}) < 1$, and it enhances the flux of ith ion species more than that of jth ion species if $\lambda_i(\mathcal{Q}) > \lambda_j(\mathcal{Q})$ (regardless the magnitudes of $\lambda_i(\mathcal{Q})$ and $\lambda_j(\mathcal{Q})$ relative to 1).

For $n = 2$ with $z_1 > 0 > z_2$, it is known [35] that, for $\mathcal{Q} \geq 0$, *depending on also the boundary conditions*, either $\lambda_k(\mathcal{Q}) \geq 1$ or $\lambda_k(\mathcal{Q}) < 1$ may occur for $k = 1, 2$; on the other hand, it is shown in [41] that, if $\mathcal{Q} \geq 0$ (not necessarily a piecewise constant), then $\lambda_1(\mathcal{Q}) < \lambda_2(\mathcal{Q})$, *independent of boundary conditions*.

For $n = 3$ with $z_1 > z_2 > 0 > z_3$, it is not hard to believe that, for $\mathcal{Q} \geq 0$, depending on also the boundary conditions, either $\lambda_k(\mathcal{Q}) \geq 1$ or $\lambda_k(\mathcal{Q}) < 1$ may occur for $k = 1, 2, 3$; we are thus interested in *comparative effects* of $\mathcal{Q}$ among ion species, that is, in signs of $\lambda_i(\mathcal{Q}) - \lambda_j(\mathcal{Q})$. It turns out the situation is much richer than that for $n = 2$ as previously mentioned. In this paper, after a preparation in Sect. 3 for the setup of small $|\mathcal{Q}|$, we will focus on a case study in Sect. 4 with equal-chemical-potential-difference.

1.3 Dimensionless PNP and Setup of Our Case Study

For convenience of mathematical analysis of BVP (1.1) and (1.3), we will work on a dimensionless form. Let C_0 be a characteristic concentration of the problems, for example,

$$C_0 = \max_{1\leq k\leq n} \left\{\mathcal{L}_k, \mathcal{R}_k, \sup_{X\in[0,l]} |\mathcal{Q}(X)|\right\}.$$

Set

$$\mathcal{D}_0 = \max_{1\leq k\leq n} \left\{ \sup_{X\in[0,l]} \mathcal{D}_k(X)\right\} \text{ and } \hat{\varepsilon}_r = \sup_{X\in[0,l]} \varepsilon_r(X).$$

Let

$$\begin{aligned} & x = \frac{X-a}{b-a}, \quad h(x) = \frac{A(X)}{(b-a)^2}, \quad D_k(x) = \frac{\mathcal{D}_k(X)}{\mathcal{D}_0}, \quad Q(x) = \frac{\mathcal{Q}(X)}{C_0}, \\ & \bar{\varepsilon}_r(x) = \frac{\varepsilon_r(X)}{\hat{\varepsilon}_r}, \quad \varepsilon^2 = \frac{\bar{\varepsilon}_r\varepsilon_0 k_B T}{e_0^2(b-a)^2C_0}, \quad \bar{\mu}_k = \frac{1}{k_BT}\mu_k, \\ & \phi(x) = \frac{e_0}{k_BT}\Phi(X), \ c_k(x) = \frac{C_k(X)}{C_0}, \quad \bar{J}_k = \frac{\mathcal{J}_k}{lC_0\mathcal{D}_0}. \end{aligned} \tag{1.7}$$

In terms of the new variables, the BVP (1.1) and (1.3) becomes, for $k = 1, 2, \ldots, n$,

$$\begin{aligned} & \frac{\varepsilon^2}{h(x)}\frac{\mathrm{d}}{\mathrm{d}x}\left(\bar{\varepsilon}_r(x)h(x)\frac{\mathrm{d}\phi}{\mathrm{d}x}\right) = -\sum_{s=1}^{n} z_s c_s - Q(x), \\ & \frac{\mathrm{d}\bar{J}_k}{\mathrm{d}x} = 0, \quad -\bar{J}_k = h(x)D_k(x)c_k\frac{\mathrm{d}\bar{\mu}_k}{\mathrm{d}x}, \end{aligned} \tag{1.8}$$

with the boundary conditions at $x = 0$ and $x = 1$

$$\phi(0) = V = \frac{e_0}{k_BT}\mathcal{V}, \ c_k(0) = l_k = \frac{\mathcal{L}_k}{C_0}; \ \phi(1) = 0, \ c_k(1) = r_k = \frac{\mathcal{R}_k}{C_0}. \tag{1.9}$$

Remark 1.1 Note that, if one swaps the ion channel together with the boundary conditions, that is, if one makes the following change of variables

$$x \to 1 - x; \quad (V, l_k, r_k) \to (-V, r_k, l_k),$$

then one can track the state variables easily. This yields the following symmetry of the boundary value problem:

If $(\phi(x), c_k(x), \bar{J}_k)$ is a solution of the BVP with $(\phi(0), c_k(0); \phi(1), c_k(1)) = (V, l_k; 0, r_k)$, then $(\phi^*(x), c_k^*(x), \bar{J}_k^*) = (\phi(1-x), c_k(1-x), -\bar{J}_k)$ is a solution of the BVP with $(\phi^*(0), c_k^*(0); \phi^*(1), c_k^*(1)) = (-V, r_k; 0, l_k)$.

The main focus of this paper is to examine effects of permanent charges on fluxes for *three* ion species via the simplest model, the cPNP model (1.8) and (1.9) with the ideal electrochemical potential $\bar{\mu}_k = \bar{\mu}_k^{id}$. More precisely, we will assume

(A1) We consider three ion species ($n = 3$) with $z_1 > z_2 > 0 > z_3$;
(A2) We assume that $\bar{\varepsilon}_r(x) = 1$ and $D_k(x) = D_k$ for some positive constants D_k;
(A3) A piecewise constant permanent charge Q with one nonzero region; that is, for a partition $0 = x_0 < x_1 < x_2 < x_3 = 1$ of $[0, 1]$,

$$Q(x) = \begin{cases} Q_1 = Q_3 = 0, & x \in (x_0, x_1) \cup (x_2, x_3), \\ Q_2, & x \in (x_1, x_2), \end{cases} \tag{1.10}$$

where $|Q_2|$ is small relative to l_k's and r_k's;
(A4) For $\bar{\mu}_k$, we only include the ideal component $\bar{\mu}_k^{id} = z_k\phi + \ln c_k$.

We will assume $\varepsilon > 0$ small and treat system (1.8) as a singularly perturbed system and apply the geometric singular perturbation framework from [17,40] for BVP (1.8) and (1.9). To this end, set

$$\Gamma = \mathrm{diag}\{z_1, z_2, \cdots, z_n\}, \quad e_0 = (1, 1, \cdots, 1)^T, \quad H(x) = \int_0^x \frac{\mathrm{d}s}{h(s)}, \quad \alpha_j = \frac{H(x_j)}{H(1)}.$$

The rest of the paper is organized as follows. In Sect. 2, we briefly review *the theory of geometric singular perturbations* (GSP) developed for PNP models in [40,44] and collect relevant results. In Sect. 3, we consider the small permanent charge situation and formulate the quantities and basic results for comparing effects of permanent charges on fluxes of each pair of ion species. Section 4 treats a case with equal chemical potential difference and provides detailed results on comparative effects of permanent charges; in particular, several interesting phenomena are discovered that are not intuitive, some are even counterintuitive to the authors. Several numerical results are provided to illustrate some analytical predictions. Section 5 provides a brief summary of this work. In the Appendix (Sect. 6), we establish two technical results that form the first step for the study in Sect. 3.

2 GSP for the BVP (1.8) and (1.9): A Quick Review

For convenience, we will give a brief and quick account of the GSP framework and relevant results in [40,44] (with slightly different notations) and refer the readers to these papers and references therein for details. We remind the readers that we will work on cPNP with ideal electrochemical potential $\bar{\mu}_k = \bar{\mu}_k^{id} = z_k\phi + \ln c_k$.

2.1 Converting the BVP to a Connecting Orbit Problem

We rewrite system (1.8) into a standard form of singularly perturbed systems and convert the BVP (1.8) and (1.9) to a *connecting orbit problem*.

Denote the derivative with respect to x by overdot and introduce $u = \varepsilon\dot{\phi}$, $w = x$ and $J_k = \bar{J}_k/D_k$. System (1.8) becomes, for $k = 1, 2, \ldots, n$,

$$\begin{aligned} &\varepsilon\dot{\phi} = u, \quad \varepsilon\dot{u} = \sum_{s=1}^{n} z_s c_s - Q(w) - \varepsilon\frac{h_w(w)}{h(w)}u, \\ &\varepsilon\dot{c}_k = -z_k c_k u - \frac{\varepsilon}{h(w)}J_k, \quad \dot{J}_k = 0, \quad \dot{w} = 1. \end{aligned} \tag{2.1}$$

System (2.1) will be treated as a dynamical system with the phase space $\mathbb{R}^{2n+3}$ and the independent variable x is viewed as time for the dynamical system. The boundary condition (1.9) becomes, for $k = 1, 2, \ldots, n$,

$$\phi(0) = V,\ c_k(0) = l_k,\ w(0) = 0; \ \ \phi(1) = 0,\ c_k(1) = r_k,\ w(1) = 1.$$

Following [17,40,44], we convert the boundary value problem to a connecting problem. Let B_L and B_R be the subsets of the phase space $\mathbb{R}^{2n+3}$ defined by

$$\begin{aligned} B_L &= \{(\phi, u, C, J, w) : \ \phi = V,\ C = L,\ w = 0\}, \\ B_R &= \{(\phi, u, C, J, w) : \ \phi = 0,\ C = R,\ w = 1\}, \end{aligned} \tag{2.2}$$

where $C = (c_1, c_2, \ldots, c_n)^T$, $J = (J_1, J_2, \ldots, J_n)^T$, $L = (l_1, l_2, \ldots, l_n)^T$ and $R = (r_1, r_2, \ldots, r_n)^T$. Then, the BVP (1.8) and (1.9) is equivalent to the following *connecting orbit problem: finding an orbit of* (2.1) *from* B_L *to* B_R.

The construction of a connecting orbit consists of two main steps (see, [17,40,44]).

Step 1. The first step is to construct a singular orbit.

Due to the jumps of $Q(x)$ in (1.10) at x_1 and x_2, this construction can be accomplished by constructing a singular orbit over each subinterval. To do so, one preassigns (unknown) values of ϕ and c_k's at each jump point x_j of $Q(x)$ as

$$\phi(x_j) = \phi^{[j]}, \quad c_k(x_j) = c_k^{[j]}, \quad j = 1, 2, \tag{2.3}$$

and, introduces the sets for $j = 0, 1, 2, 3$,

$$B_j = \{(\phi, u, C, J, w) : \ \phi = \phi^{[j]},\ C = C^{[j]},\ w = x_j\}. \tag{2.4}$$

Note that $B_0 = B_L$ and $B_3 = B_R$ (see (2.2)). We then construct singular orbits over each interval $[x_{j-1}, x_j]$ for the connecting problem between B_{j-1} and B_j.

At the end, we match those singular orbits at x_1 and x_2 to obtain one singular orbit over the whole interval [0,1].

Step 2. It involves a justification of the existence of an orbit for $\varepsilon > 0$ near the singular orbit—the validation of the singular orbit. For $Q(x) = 0$, this is justified in [44], and for small $|Q(x)|$, this is justified by continuity.

For this work, we will be interested in only singular orbits of the problem and focus on consequences about permanent charge effects on fluxes.

2.2 Construction of Singular Orbits Connecting B_{j-1} and B_j

Recall the slow manifold is

$$\mathcal{Z}_j = \Big\{ \sum_{s=1}^{n} z_s c_s + Q_j = 0,\ w \in [x_{j-1}, x_j] \Big\} \subset \mathbb{R}^{2n+3}. \tag{2.5}$$

A typical singular connecting orbit between B_{j-1} and B_j consists of two *fast orbits (singular layers)* $\Gamma^{[j-1,+]}$ at x_{j-1} between B_{j-1} and $\mathcal{Z}_j$ and $\Gamma^{[j,-]}$ at x_j between B_j and $\mathcal{Z}_j$, and one *slow orbit (regular layer)* Ω_j over $[x_{j-1}, x_j]$ on $\mathcal{Z}_j$.

2.2.1 Fast Dynamics for Singular Layers at x_{j-1} and x_j

As in [40], the limiting fast system is

$$\begin{aligned} &\phi' = u, \quad u' = \sum_{s=1}^{n} z_s c_s - Q(w), \\ &c_k' = -z_k c_k u, \quad J_k' = 0, \quad w' = 0. \end{aligned} \tag{2.6}$$

Let $\phi = \phi^{[j-1,+]}$ be the root (it is unique) of

$$\sum_{s=1}^{n} z_s c_s^{[j-1]} e^{z_s(\phi^{[j-1]}-\phi)} + Q_j = 0; \tag{2.7}$$

and let $\phi = \phi^{[j,-]}$ be the unique root of

$$\sum_{s=1}^{n} z_s c_s^{[j]} e^{z_s(\phi^{[j]}-\phi)} + Q_j = 0. \tag{2.8}$$

A characterization of layers $\Gamma^{[j-1,+]}$ and $\Gamma^{[j,-]}$ is provided in Proposition 3.3 in [40]. For this work, we need only the following consequences. Let $N^{[j-1,+]} = M^{[j-1,+]} \cap W^s(\mathcal{Z}_j)$ and let $N^{[j,-]} = M^{[j,-]} \cap W^u(\mathcal{Z}_j)$ where $M^{[j-1,+]}$ is the forward trace of B_{j-1} and $M^{[j,-]}$ is the backward trace of B_j under the flow (2.6).

Proposition 2.1 *(i) At x_{j-1},*

$$u^{[j-1,+]} = \delta_+^{[j-1]} \sqrt{\sum_{s=1}^{n} 2c_s^{[j-1]}\big(1 - e^{z_s(\phi^{[j-1]}-\phi^{[j-1,+]})}\big) - 2Q_j(\phi^{[j-1]} - \phi^{[j-1,+]})}$$

where $\delta_+^{[j-1]} = \mathrm{sgn}(\phi^{[j-1,+]} - \phi^{[j-1]})$; and the ω-limit set of $N^{[j-1,+]}$ is

$$\omega(N^{[j-1,+]}) = \{(\phi^{[j-1,+]}, 0, C^{[j-1,+]}, J, x_{j-1}) : \text{all } J\} \subset \mathcal{Z}_j,$$

with $c_k^{[j-1,+]} = c_k^{[j-1]} e^{z_k(\phi^{[j-1]}-\phi^{[j-1,+]})}$.

(ii) At x_j,

$$u^{[j,-]} = \delta_-^{[j]} \sqrt{\sum_{s=1}^{n} 2c_s^{[j]}\big(1 - e^{z_s(\phi^{[j]}-\phi^{[j,-]})}\big) - 2Q_j(\phi^{[j]} - \phi^{[j,-]})}$$

where $\delta_-^{[j]} = \mathrm{sgn}(\phi^{[j]} - \phi^{[j,-]})$*; and the* α*-limit set of* $N^{[j,-]}$ *is*

$$\alpha(N^{[j,-]}) = \{(\phi^{[j,-]}, 0, C^{[j,-]}, J, x_j) : \ all\ J\} \subset \mathcal{Z}_j,$$

with $c_k^{[j,-]} = c_k^{[j]} e^{z_k(\phi^{[j]} - \phi^{[j,-]})}$.

2.2.2 Slow Dynamics for Regular Layers Over $[x_{j-1}, x_j]$

To obtain a singular orbit connecting B_{j-1} and B_j, which determines J over $[x_{j-1}, x_j]$, we now construct a regular layer Ω_j on $\mathcal{Z}_j$ between $\omega(N^{[j-1,+]})$ and $\alpha(N^{[j,-]})$.

For the slow dynamics, we will follow the treatment in [44] (a refinement of that in [40] for slow dynamics). It turns out the limiting slow system has the same form. The only difference is that the slow manifold or an algebraic constraint is

$$\sum_{s=1}^{n} z_s c_s + Q_j = 0$$

with a nonzero Q_j over the interval $[x_{j-1}, x_j]$.

One rescales some dependent variables by introducing (p, q) as

$$u = \varepsilon p, \quad \sum_{s=1}^{n} z_s c_s + Q_j = -\varepsilon q. \tag{2.9}$$

Replacing (u, c_n) with (p, q), system (2.1) becomes, for $k = 1, 2, \ldots, n-1$,

$$\begin{aligned} &\dot\phi = p, \quad \varepsilon \dot p = q - \varepsilon \frac{h_w(w)}{h(w)} p, \\ &\varepsilon \dot q = \left(\sum_{s=1}^{n-1} (z_s - z_n) z_s c_s - z_n Q_j - \varepsilon z_n q \right) p + h^{-1}(w) I, \\ &\dot c_k = -p z_k c_k - J_k h^{-1}(w), \quad \dot J = 0, \quad \dot w = 1, \end{aligned} \tag{2.10}$$

where $I = \sum_{s=1}^{n} z_s J_s$. The limiting slow system of (2.10) is, for $k = 1, 2, \ldots, n-1$,

$$\begin{aligned} &\dot\phi = p, \ q = 0, \ \left(\sum_{s=1}^{n-1} (z_s - z_n) z_s c_s - z_n Q_j \right) p + h^{-1}(w) I = 0, \\ &\dot c_k = -p z_k c_k - J_k h^{-1}(w), \quad \dot J = 0, \quad \dot w = 1. \end{aligned} \tag{2.11}$$

For this system, the slow manifold is

$$\mathcal{S}_j = \left\{ p = -\frac{h^{-1}(w) I}{\sum_{s=1}^{n-1} (z_s - z_n) z_s c_s - z_n Q_j}, \quad q = 0 \right\}. \tag{2.12}$$

On the slow manifold $\mathcal{S}_j$, system (2.11) reads, for $k = 1, 2, \ldots, n-1$,

$$\begin{aligned} &\dot\phi = -\frac{h^{-1}(w) I}{\sum_{s=1}^{n-1} (z_s - z_n) z_s c_s - z_n Q_j}, \\ &\dot c_k = \frac{h^{-1}(w) I}{\sum_{s=1}^{n-1} (z_s - z_n) z_s c_s - z_n Q_j} z_k c_k - J_k h^{-1}(w), \\ &\dot J = 0, \quad \dot w = 1. \end{aligned} \tag{2.13}$$

Remark 2.2 If $I = 0$, then the solution of (2.13) is given by, for $x \in [x_{j-1}, x_j]$,

$$\phi(x) = \phi^{[j-1,+]} = \phi^{[j,-]}, \quad J = \frac{C^{[j-1,+]} - C^{[j,-]}}{H(x_j) - H(x_{j-1})},$$
$$C(x) = C^{[j-1,+]} - J(H(x) - H(x_{j-1})), \quad w(x) = x.$$

We will then assume $I \neq 0$ in the following.

An observation is that, on the slow manifold $\mathcal{S}_j$ where $\sum_{s=1}^n z_s c_s + Q_j = 0$,

$$\sum_{s=1}^{n-1}(z_s - z_n) z_s c_s - z_n Q_j = \sum_{s=1}^{n} z_s^2 c_s > 0. \tag{2.14}$$

Denote $V_j = \phi^{[j-1,+]} - \phi^{[j,-]}$. Then $V_j I > 0$ from (2.14) and ϕ-equation in (2.13). As in [44], multiply $h(w) V_j I^{-1} \sum_{s=1}^n z_s^2 c_s$ on the right-hand side of (2.13), which keeps the same phase portrait, to get, in term of a new independent variable, say t,

$$\begin{aligned} &\frac{\mathrm{d}\phi}{\mathrm{d}t} = -V_j, \quad \frac{\mathrm{d}C}{\mathrm{d}t} = V_j D C, \quad \sum_{s=1}^n z_s c_s + Q_j = 0, \\ &\frac{\mathrm{d}J}{\mathrm{d}t} = 0, \quad \frac{\mathrm{d}w}{\mathrm{d}t} = h(w) V_j I^{-1} b^T C, \end{aligned} \tag{2.15}$$

where $b = (z_1^2, z_2^2, \dots, z_n^2)^T$ and the matrix D is given by

$$D = \Gamma - I^{-1} J b^T. \tag{2.16}$$

It is easy to check that $\sum_{s=1}^n z_s c_s$ is a *first integral* of system (2.15). So the electroneutrality with permanent charge Q_j defines a level set of the first integral which is a representation of the slow manifold.

System (2.15) is the form treated in [44] with $Q_j = 0$. We now apply the result in [44] to draw conclusions on regular layers and refer the readers to [44] for details. It's known that, corresponding to the electroneutrality condition on the slow manifold, $\sigma = 0$ is one zero of g. Formula (2.17) and Theorem 3.1 in [44] give

Proposition 2.3 *Let $\sigma_1, \dots, \sigma_{p-1}, \sigma_p = 0$ be the distinct eigenvalues of D with algebraic multiplicities $s_1, \dots, s_p$ ($s_1 + s_2 + \dots + s_p = n$). Then $J_k^{[j]} = I^{[j]} f_k^{[j]}$ where*

$$\begin{aligned} I^{[j]} &= \frac{V_j}{H(x_j) - H(x_{j-1})} \int_0^1 b^T e^{V_j D z} C^{[j-1,+]} \,\mathrm{d}z, \\ f_k^{[j]} &= \frac{1}{z_k^2} \frac{\prod_{i=1}^p (z_k - \sigma_i)^{s_i}}{\prod_{1 \le i \le n, i \neq k} (z_k - \sigma_i)} \quad \textit{for } k = 1, 2, \dots, n. \end{aligned} \tag{2.17}$$

For the given $(\phi^{[j-1,+]}, C^{[j-1,+]})$ and $(\phi^{[j,-]}, C^{[j,-]})$, let $g^{[j]} : \mathbb{C} \to \mathbb{C}$ be the meromorphic function defined as

$$g^{[j]}(\sigma) =: \sum_{s=1}^n \frac{z_s^2 c_s^{[j,-]}}{z_s - \sigma} - e^{V_j \sigma} \sum_{s=1}^n \frac{z_s^2 c_s^{[j-1,+]}}{z_s - \sigma}. \tag{2.18}$$

It is shown in [44] that the eigenvalues σ_j's of D satisfy

(a) if $\sigma_j \notin \{z_1, z_2, \cdots, z_n\}$, then σ_j is a root of $g^{[j]}(\sigma) = 0$ with multiplicity s_j;

(b) if $\sigma_j = z_k$ for some k, then $c_k^{[j,-]} = e^{V_j z_k} c_k^{[j-1,+]}$ and $\sigma_j = z_k$ is a root of $g(\sigma) = 0$ with multiplicity $s_j - 1$.
(c) all σ_j's lie in the strip $S = \{x + iy : y \in (-\pi/|V_j|, \pi/|V_j|)\}$.

2.3 Matching for Singular Orbits Over the Whole Interval [0, 1]

Once a singular orbit $\Gamma^{[j-1,+]} \cup \Omega_j \cup \Gamma^{[j,-]}$ over each subinterval $[x_{j-1}, x_j]$ is constructed, we need to match those singular orbits in order to have a singular orbit on the whole interval [0, 1]. As in [40], denote J_k's by $J_k^{[j]}$'s over the interval $[x_{j-1}, x_j]$, the matching conditions are

$$\begin{aligned} u^{[j,-]} &= u^{[j,+]} \ \text{ at each } x_j \text{ for } j = 1, 2, \\ J_k^{[j]} &= J_k^{[j+1]} \ \text{ for } k = 1, \ldots, n;\ \ j = 1, 2, \end{aligned} \tag{2.19}$$

where $u^{[j,-]}$ and $u^{[j,+]}$ are given in Proposition 2.1 and $J_k^{[j]}$'s are in Proposition 2.3.

For $n = 3$, the matching conditions (2.19) lead to the governing system for the preassigned unknowns $(\phi^{[j]}, c_k^{[j]})$ for $j = 1, 2$ and $k = 1, 2, 3$ in (2.3),

$$\begin{aligned} &u^{[1,-]} = u^{[1,+]} \ \text{ at } \ x_1 \iff \sum_{s=1}^{3} c_s^{[1,-]} = \sum_{s=1}^{3} c_s^{[1,+]} + Q_2(\phi^{[1]} - \phi^{[1,+]}), \\ &u^{[2,-]} = u^{[2,+]} \ \text{ at } \ x_2 \iff \sum_{s=1}^{3} c_s^{[2,+]} = \sum_{s=1}^{3} c_s^{[2,-]} + Q_2(\phi^{[2]} - \phi^{[2,-]}), \\ &\quad J_k := J_k^{[1]} = J_k^{[2]} = J_k^{[3]}, \end{aligned} \tag{2.20}$$

where $J_k^{[j]}$'s are provided in Proposition 2.3 and where, in terms of $(\phi^{[j]}, c_k^{[j]})$ variables, $\phi^{[j,+]}$ and $\phi^{[j,-]}$ are determined by

$$\sum_{s=1}^{3} z_s c_s^{[j]} e^{z_s(\phi^{[j]} - \phi^{[j,+]})} + Q_{j+1} = 0, \quad \sum_{s=1}^{3} z_s c_s^{[j]} e^{z_s(\phi^{[j]} - \phi^{[j,-]})} + Q_j = 0,$$

and $c_k^{[j,+]}$ and $c_k^{[j,-]}$ are, in turn, given by

$$c_k^{[j,+]} = c_k^{[j]} e^{z_k(\phi^{[j]} - \phi^{[j,+]})}, \quad c_k^{[j,-]} = c_k^{[j]} e^{z_k(\phi^{[j]} - \phi^{[j,-]})}.$$

3 Flux Ratios for (Small) Permanent Charge for $n = 3$

3.1 Comparative Effects of Permanent Charge Q with Small $|Q_2|$

In this paper, the main focus is to study the effects of small permanent charges on individual flux and only treats the case $I \neq 0$.

For the permanent charge $Q = Q(x)$ in (A3) in the beginning of § 1.3, we will assume now that $|Q_2|$ is small relative to l_k's and r_k's, and expand all unknown quantities in (2.20) in Q_2 as follows, for $j = 1, 2$ and $k = 1, 2, 3$,

$$\begin{aligned}\phi^{[j]} &= \phi_0^{[j]} + \phi_1^{[j]} Q_2 + O(Q_2^2),\\ c_k^{[j]} &= c_{k0}^{[j]} + c_{k1}^{[j]} Q_2 + O(Q_2^2),\\ J_k &= J_{k0} + J_{k1} Q_2 + O(Q_2^2).\end{aligned} \tag{3.1}$$

The coefficients of the zeroth order and first order terms will be examined looking for the dominating effects of the permanent charges on individual fluxes.

For this work, we are mainly interested in properties based on J_k up to $O(Q_2)$. With expansions in (3.1), the flux ratio $\lambda_k(Q)$ of the k-th ion species in (1.6) and the flux ratio difference $\lambda_i(Q) - \lambda_j(Q)$ between the i-th and the j-th ion species are

$$\begin{aligned}\lambda_k(Q) &= \frac{J_k(Q)}{J_k(0)} = 1 + \tau_k Q_2 + o(Q_2),\\ \lambda_i(Q) - \lambda_j(Q) &= \tau_{ij} Q_2 + o(Q_2),\end{aligned} \tag{3.2}$$

where, from (3.1),

$$\tau_k = \frac{J_{k1}}{J_{k0}} \ \text{ and } \ \tau_{ij} = \tau_i - \tau_j. \tag{3.3}$$

Therefore, *comparative effects of* Q on fluxes J_i and J_j are reduced to the study of signs of τ_{ij}, which are determined by boundary conditions and (α_1, α_2).

Note that, if $Q_2 > 0$ and $z_i > z_j$, one might suspect that the permanent charge Q would enhance the flux J_j more than the flux J_i, that is, $\lambda_i(Q) - \lambda_j(Q) < 0$, or equivalently, $(z_i - z_j)\tau_{ij} \le 0$. Likewise, if $Q_2 < 0$ and $z_i > z_j$, then one might expect that $\lambda_i(Q) - \lambda_j(Q) < 0$, or equivalently, $(z_i - z_j)\tau_{ij} \le 0$. Thus, in either case of $Q_2 > 0$ or $Q_2 < 0$ with $|Q_2|$ small, a question would be:

$$\text{Is } \ (z_i - z_j)\tau_{ij} \le 0\ ? \tag{3.4}$$

This is indeed the case for $n = 2$ [35,41] as mentioned in the introduction. On the other hand, for ionic flows involving three or more ion species, the answer to question (3.4) is not always affirmative as commented in the introduction too. In fact, after some basic preparations in this section, we will show in Sect. 4 that the followings are possible with $z_1 > z_2 > 0 > z_3$: (i) $\tau_{23} > 0$; (ii) $\tau_{12} > 0$ and $\tau_{13} > 0$ simultaneously; (iii) $\tau_{13} + \tau_{23} > 0$.

3.2 Expansions in Q with Small $|Q_2|$

Let σ_1, σ_2, and $\sigma_3 = 0$ be the eigenvalues of D where D is the matrix in (2.16). We will give the detailed treatment for $\sigma_1 \ne \sigma_2$ and the case of $\sigma_1 = \sigma_2$ can be handled by continuity. For $|Q_2| \ll 1$, let

$$\sigma_k(Q) = \sigma_{k0} + \sigma_{k1} Q_2 + O(Q_2^2), \quad D = D_0 + D_1 Q_2 + O(Q_2^2).$$

Note that σ_{k0}'s depend on boundary conditions and σ_{k1}'s depend on boundary conditions as well as (α_1, α_2). For easy of notation, we introduce

$$\begin{aligned}&S_L = l_1 + l_2 + l_3, \quad \Lambda_L = z_1^2 l_1 + z_2^2 l_2 + z_3^2 l_3, \quad L(\sigma) = z_1 z_2 z_3 S_L + \sigma \Lambda_L;\\ &S_R = r_1 + r_2 + r_3, \quad \Lambda_R = z_1^2 r_1 + z_2^2 r_2 + z_3^2 r_3, \quad R(\sigma) = z_1 z_2 z_3 S_R + \sigma \Lambda_R.\end{aligned} \tag{3.5}$$

Under the boundary electroneutrality conditions, we write

$$g(\sigma) = \frac{\sigma\gamma(\sigma)}{(\sigma - z_1)(\sigma - z_2)(\sigma - z_3)} \quad \text{where} \quad \gamma(\sigma) = e^{\sigma V} L(\sigma) - R(\sigma). \tag{3.6}$$

Note that $\gamma(0) = 0$ if and only if $S_L = S_R$.

The next two lemmas are crucial for the study of flux ratios in this paper and they will be established in Appendix (Sect. 6).

Lemma 3.1 *If $\sigma_{10} \neq \sigma_{20}$, then $\gamma'(\sigma_{k0}) \neq 0$ and σ_{k1} is given by*

$$\sigma_{k1} = \frac{1}{\sigma_{k0}\gamma'(\sigma_{k0})} \prod_{s=1}^{3} (\sigma_{k0} - z_s)(e^{\sigma_{k0}\phi_0^{[2]}} - e^{\sigma_{k0}\phi_0^{[1]}}) \ \ if\ \ \sigma_{k0} \neq 0,$$

$$\sigma_{k1} = -\frac{z_1 z_2 z_3}{\gamma'(0)}(\phi_0^{[2]} - \phi_0^{[1]}) = \frac{2}{g''(0)}(\phi_0^{[2]} - \phi_0^{[1]}) \ \ if\ \ \sigma_{k0} = 0,$$

where $\phi_0^{[j]}$ is (uniquely) determined by

$$\begin{aligned} e_0^T e^{(V-\phi_0^{[j]})D_0} L - S_L &= \alpha_j g'(0) \ \ if\ \ \sigma_{10}\sigma_{20} \neq 0, \\ e_0^T \Gamma^{-1} e^{(V-\phi_0^{[j]})D_0} L - \sum_{s=1}^{3} \frac{l_s}{z_s} - (V - \phi_0^{[j]}) S_L &= \frac{1}{2}\alpha_j g''(0) \ \ if\ \ \sigma_{10}\sigma_{20} = 0. \end{aligned} \tag{3.7}$$

We note that $g'(0) = S_R - S_L$ and, if $g'(0) = 0$ (or equivalently, $\sigma_{10}\sigma_{20} = 0$), then

$$g''(0) = 2\sum_{s=1}^{3} \frac{r_s - l_s}{z_s} - 2V S_L.$$

Lemma 3.2 *Assume $\sigma_{10} \neq \sigma_{20}$ and $\sigma_{10}\sigma_{20} \neq 0$. One has*

$$\begin{aligned} \tau_k &= \frac{J_{k1}}{J_{k0}} = \frac{\phi_0^{[1]} - \phi_0^{[2]}}{g'(0)} - \frac{\sigma_{11}}{\sigma_{10}} - \frac{\sigma_{21}}{\sigma_{20}} + \frac{\sigma_{11}}{\sigma_{10} - z_k} + \frac{\sigma_{21}}{\sigma_{20} - z_k}, \\ \tau_{ij} &= \frac{\sigma_{11}}{\sigma_{10} - z_i} + \frac{\sigma_{21}}{\sigma_{20} - z_i} - \frac{\sigma_{11}}{\sigma_{10} - z_j} - \frac{\sigma_{21}}{\sigma_{20} - z_j}. \end{aligned} \tag{3.8}$$

The next result follows directly from Lemmas 3.1 and 3.2 .

Proposition 3.3 *One has*

$$\tau_{ij} = T_{ij}(\phi_0^{[2]}) - T_{ij}(\phi_0^{[1]})$$

where, for a permutation $\{i, j, k\}$ of $\{1, 2, 3\}$ (the convention to be used in the rest),

(a) if $\sigma_{10} \neq \sigma_{20}$, then

$$T_{ij}(\phi) = \frac{(z_i - z_j)(\sigma_{10} - z_k)}{\sigma_{10}\gamma'(\sigma_{10})}(e^{\sigma_{10}\phi} - 1) + \frac{(z_i - z_j)(\sigma_{20} - z_k)}{\sigma_{20}\gamma'(\sigma_{20})}(e^{\sigma_{20}\phi} - 1); \tag{3.9}$$

(If $\sigma_{j0} = 0$, then the above formula is defined by applying L'Hopital rule.)

(b) if $\sigma_{10} = \sigma_{20} = \sigma_0$, then

$$T_{ij}(\phi) = \frac{2(z_i - z_j)(\sigma_0 - z_k)}{\sigma_0\gamma''(\sigma_0)}\Big(\phi e^{\sigma_0\phi} - (e^{\sigma_0\phi} - 1)\big(\frac{\gamma'''(\sigma_0)}{3\gamma''(\sigma_0)} + \frac{1}{\sigma_0} + \frac{1}{z_k - \sigma_0}\big)\Big).$$

(If $\sigma_0 = 0$, then the above formula is defined by applying L'Hopital rule.)

Remark 3.4 If $V=0$, then $\phi_0^{[1]}=\phi_0^{[2]}=0$ (Proposition 2.1 in [18]), and hence, $\tau_{ij}=0$. Thus, up to order $O(Q_2)$, $\lambda_i(Q)=\lambda_j(Q)$. In the sequel, we will assume $V\neq 0$. In addition, we make the following observations.

(a.) For a fixed boundary condition, $\phi_0^{[j]}=\phi_0^{[j]}(\alpha_j)$ depends on α_j through (3.7) so we may treat T_{ij} as a function of α. Also we will use $\tau_{ij}(\alpha_1,\alpha_2)$ whenever needed to emphasize the dependance of τ_{ij} on (α_1,α_2).

(b.) If $V>0$ (resp. $V<0$), then $\phi_0(x)$ is decreasing (resp. increasing) in x, and hence, $\phi_0^{[1]}>\phi_0^{[2]}$ (resp. $\phi_0^{[1]}<\phi_0^{[2]}$) (see, e.g., [44]).

We note a simple relation $\tau_{12}+\tau_{23}=\tau_{13}$, and end this discussion with a result that will be used for Proposition 3.10.

Proposition 3.5 *For $V\neq 0$, the situation $\tau_1=\tau_2=\tau_3$ cannot occur. Each of the following identities is equivalent to the above identities*

$$(i)\ \tau_{12}=\tau_{23}=0,\quad (ii)\ \tau_{12}=\tau_{13}=0,\quad (iii)\ \tau_{13}=\tau_{23}=0.$$

Proof Suppose, on the contrary, that $\tau_{23}=\tau_{12}=0$.

For $\sigma_{10}\neq\sigma_{20}$, Proposition 3.3 implies that, for $k=1$ (associated to $\tau_{23}=0$) and $k=3$ (associated to $\tau_{12}=0$),

$$\frac{e^{\sigma_{10}\phi_0^{[2]}}-e^{\sigma_{10}\phi_0^{[1]}}}{\sigma_{10}\gamma'(\sigma_{10})}(\sigma_{10}-z_k)+\frac{e^{\sigma_{20}\phi_0^{[2]}}-e^{\sigma_{20}\phi_0^{[1]}}}{\sigma_{20}\gamma'(\sigma_{20})}(\sigma_{20}-z_k)=0\ \text{ for }\ k=1,3.$$

Since $z_1\neq z_3$, the two identities immediately give

$$\frac{e^{\sigma_{10}\phi_0^{[2]}}-e^{\sigma_{10}\phi_0^{[1]}}}{\sigma_{10}\gamma'(\sigma_{10})}=\frac{e^{\sigma_{20}\phi_0^{[2]}}-e^{\sigma_{20}\phi_0^{[1]}}}{\sigma_{20}\gamma'(\sigma_{20})}=0,$$

and hence, $\phi_0^{[1]}=\phi_0^{[2]}$, which happens only if $V=0$.

Similarly, for $\sigma_{10}=\sigma_{20}=\sigma_0$, Proposition 3.3 implies that, for $k=1$ and $k=3$,

$$\begin{aligned}\Big(\phi_0^{[2]}e^{\sigma_0\phi_0^{[2]}}-\phi_0^{[1]}e^{\sigma_0\phi_0^{[1]}}-\Big(\frac{\sigma_0\gamma'''(\sigma_0)}{3\gamma''(\sigma_0)}+1\Big)\frac{e^{\sigma_0\phi_0^{[2]}}-e^{\sigma_0\phi_0^{[1]}}}{\sigma_0}\Big)(\sigma_0-z_k)\\ +e^{\sigma_0\phi_0^{[2]}}-e^{\sigma_0\phi_0^{[1]}}=0,\end{aligned}$$

which, for both $\sigma_0\neq 0$ and $\sigma_0=0$, lead again to $\phi_0^{[1]}=\phi_0^{[2]}$. □

3.3 Key Quantities and Preliminary Results

To characterize the monotonicity of $T_{ij}(\phi)$ and present preliminary results, it is convenient to split the discussion into several cases and introduce some quantities. Since the results in this section are prepared to be applied in Sect. 4 for a special case *where σ_{k0}'s are real*, we will consider only this case in this work.

3.3.1 Case I: $\sigma_{10}\neq\sigma_{20}$ and $\sigma_{10},\ \sigma_{20}\in\mathbb{R}$

In this case, the sign of

$$K_{ij}=\frac{(\sigma_{20}-z_k)\gamma'(\sigma_{10})}{(\sigma_{10}-z_k)\gamma'(\sigma_{20})}\tag{3.10}$$

determines monotonicity of $T_{ij}(\phi)$. In fact,

Lemma 3.6 *Assume $V \neq 0$ and $\sigma_{10} \neq \sigma_{20}$.*

(i) If $K_{ij} \geq 0$, then $T_{ij}(\phi)$ is strictly monotone and z_k is between σ_{10} and σ_{20}.
(ii) If $K_{ij} < 0$, then $T_{ij}(\phi)$ has a unique critical point $\phi = V_{ij}$ given by

$$V_{ij} = \frac{1}{\sigma_{10} - \sigma_{20}} \ln(-K_{ij}). \tag{3.11}$$

Proof The quantity K_{ij} is real since σ_{10} and σ_{20} would be conjugate pair if they are complex. A direct calculation gives

$$T'_{ij}(\phi) = \frac{(z_i - z_j)(\sigma_{10} - z_k)e^{\sigma_{10}\phi}}{\gamma'(\sigma_{10})} + \frac{(z_i - z_j)(\sigma_{20} - z_k)e^{\sigma_{20}\phi}}{\gamma'(\sigma_{20})}.$$

If $K_{ij} \geq 0$, then the two terms of $T'_{ij}(\phi)$ have the same sign so $T'_{ij}(\phi)$ has no zeros. For $K_{ij} < 0$, $T'_{ij}(\phi) = 0$ has a unique solution $\phi = V_{ij}$ given in (3.11). □

Now for the case where $K_{ij} < 0$ so that V_{ij} in (3.11) exists, let

$$\theta_{ij} = \begin{cases} \dfrac{1}{g'(0)} e_0^T \left(e^{(V - V_{ij})D_0} L - L \right) & \text{if } \sigma_{10}\sigma_{20} \neq 0, \\ \dfrac{1}{g''(0)} e_0^T \Gamma^{-1} \left(e^{(V - V_{ij})D_0} L - L - (V - V_{ij})\Gamma L \right) & \text{if } \sigma_{10}\sigma_{20} = 0. \end{cases} \tag{3.12}$$

Lemma 3.7 *If $V > 0$, then θ_{ij} is decreasing in V_{ij}; if $V < 0$, then θ_{ij} is increasing in V_{ij}. Furthermore, $\theta_{ij} \in [0, 1]$ if and only if V_{ij} lies between 0 and V.*

Proof We will treat the case $\sigma_{10}\sigma_{20} \neq 0$ only. Set

$$\theta(\phi) = \frac{1}{g'(0)} e_0^T \left(e^{(V-\phi)D_0} L - L \right).$$

Note that $(z_1, z_2, z_3)e^{(V-\phi(x))D_0} L = (z_1, z_2, z_3)C(x) = 0$ and $H(1)F = -g'(0)$. Thus,

$$\begin{aligned} \theta'(\phi) &= -\frac{1}{g'(0)} e_0^T D_0 e^{(V-\phi)D_0} L = -\frac{1}{g'(0)} \left(e_0^T \Gamma - I^{-1} F b^T \right) e^{(V-\phi)D_0} L \\ &= -\frac{1}{g'(0)} \Big((z_1, z_2, z_3) e^{(V-\phi)D_0} L + pg \frac{g'(0)}{H(1)I} b^T e^{(V-\phi)D_0} L \Big) = -\frac{1}{H(1)I} b^T e^{(V-\phi)D_0} L. \end{aligned}$$

The statement on monotonicity of θ_{ij} on V_{ij} then follows from $IV > 0$.

It is clear that if $V_{ij} = V$, then $\theta_{ij} = 0$. If $V_{ij} = 0$, then

$$\theta_{ij} = \frac{1}{g'(0)} e_0^T \left(e^{V D_0} L - L \right) = \frac{1}{S_R - S_L} e_0^T \, (R - L) = 1.$$

This completes the proof. □

Definition 3.8 For $\theta_{ij} \in [0, 1]$, define a function $P_{ij} : [0, \theta_{ij}] \to [\theta_{ij}, \infty)$ as follows: $P_{ij}(\alpha) = \beta$ if $T_{ij}(\beta) = T_{ij}(\alpha)$ (see the left panel of Fig. 1).

Our first main result is for the case where σ_{10} and σ_{20} are real and distinct.

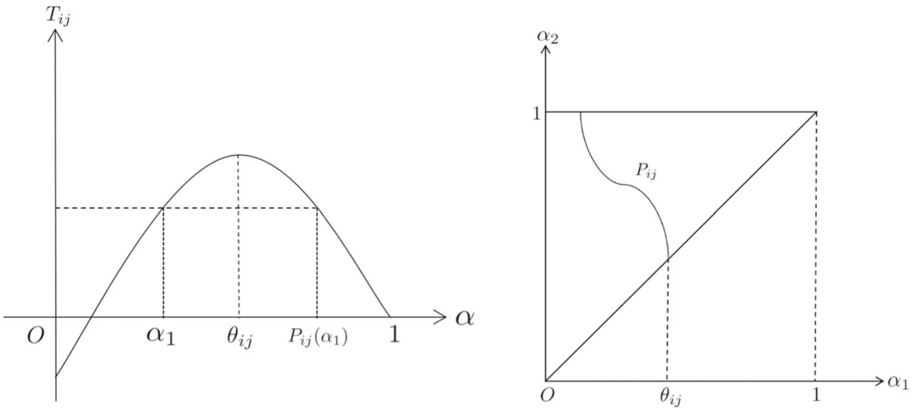


Fig. 1 Function T_{ij} on α and P_{ij} for case (ii) **a** in Proposition 3.9

Proposition 3.9 *Assume $\sigma_{10} > \sigma_{20}$. For $V \neq 0$, one has*

(i) if $K_{ij} \geq 0$, then $(z_i - z_j)\tau_{ij}(\alpha_1, \alpha_2) < 0$ for any $0 \leq \alpha_1 \leq \alpha_2 \leq 1$;
(ii) if $K_{ij} < 0$, then exactly one of the followings occurs

(a) when $(z_i - z_j)\frac{(\sigma_{10}-z_k)}{\gamma'(\sigma_{10})} > 0$,

$$\tau_{ij}(\alpha_1, \alpha_2) = \begin{cases} < 0 \ \ for\ \alpha_1 < \theta_{ij}\ and\ \alpha_2 < P_{ij}(\alpha_1) \\ > 0 \ \ for\ \alpha_1 > \theta_{ij}\ or\ \alpha_2 > P_{ij}(\alpha_1); \end{cases}$$

(b) when $(z_i - z_j)\frac{(\sigma_{10}-z_k)}{\gamma'(\sigma_{10})} < 0$,

$$\tau_{ij}(\alpha_1, \alpha_2) = \begin{cases} > 0 \ \ for\ \alpha_1 < \theta_{ij}\ and\ \alpha_2 < P_{ij}(\alpha_1) \\ < 0 \ \ for\ \alpha_1 > \theta_{ij}\ or\ \alpha_2 > P_{ij}(\alpha_1). \end{cases}$$

Proof For $V \neq 0$, it can be shown that $\tau_{ij}(\alpha, \alpha) = 0$ for any $\alpha \in [0, 1]$ and

$$\partial_{\alpha_1}\tau_{ij}(\alpha_1, \alpha_2) = -\frac{\mathrm{d}\phi_0^{[1]}}{\mathrm{d}\alpha_1}T'_{ij}(\phi_0^{[1]}), \quad \partial_{\alpha_2}\tau_{ij}(\alpha_1, \alpha_2) = \frac{\mathrm{d}\phi_0^{[2]}}{\mathrm{d}\alpha_2}T'_{ij}(\phi_0^{[2]}). \tag{3.13}$$

Note that for $V > 0$, $\frac{\mathrm{d}\phi_0^{[1]}}{\mathrm{d}\alpha_1}, \frac{\mathrm{d}\phi_0^{[2]}}{\mathrm{d}\alpha_2} < 0$; for $V < 0$, $\frac{\mathrm{d}\phi_0^{[1]}}{\mathrm{d}\alpha_1}, \frac{\mathrm{d}\phi_0^{[2]}}{\mathrm{d}\alpha_2} > 0$. For $\sigma_{10} > \sigma_{20} \in \mathbb{R}$, it follows from Lemma 6.1 that for $V > 0$, $\gamma'(\sigma_{10}) > 0 > \gamma'(\sigma_{20})$; for $V < 0$, $\gamma'(\sigma_{10}) < 0 < \gamma'(\sigma_{20})$.

(i) If $K_{ij} \geq 0$, then, for $V > 0$ and $\sigma_{10} > \sigma_{20}$, one has, from Lemma 3.6,

$$\frac{\sigma_{10} - z_k}{\gamma'(\sigma_{10})} > 0, \quad \frac{\sigma_{20} - z_k}{\gamma'(\sigma_{20})} \geq 0,$$

which leads to $(z_i - z_j)T'_{ij}(\phi) > 0$, and hence, $(z_i - z_j)\tau_{ij}(\alpha_1, \alpha_2) < 0$ since $\phi_0^{[1]} > \phi_0^{[2]}$.
Similarly, for $V < 0$, $(z_i - z_j)T'_{ij}(\phi) < 0$, and hence, $(z_i - z_j)\tau_{ij}(\alpha_1, \alpha_2) < 0$ since $\phi_0^{[1]} < \phi_0^{[2]}$.

(ii) If $K_{ij} < 0$, then $T'_{ij}(V_{ij}) = 0$ and a direct calculation gives

$$\partial_{\alpha_1\alpha_1}\tau_{ij}(\theta_{ij},\theta_{ij}) = -\left(\frac{d\phi_0^{[1]}}{d\alpha_1}\right)^2 T''_{ij}(V_{ij}), \quad \partial_{\alpha_2\alpha_2}\tau_{ij}(\theta_{ij},\theta_{ij}) = \left(\frac{d\phi_0^{[2]}}{d\alpha_2}\right)^2 T''_{ij}(V_{ij}),$$

where

$$T''_{ij}(V_{ij}) = (z_i - z_j)\frac{(\sigma_{10} - z_k)(\sigma_{10} - \sigma_{20})e^{\sigma_{10}V_{ij}}}{\gamma'(\sigma_{10})}.$$

It follows from

$$\partial_{\alpha_1\alpha_1}\tau_{ij}(\theta_{ij},\theta_{ij})\partial_{\alpha_2\alpha_2}\tau_{ij}(\theta_{ij},\theta_{ij}) < 0, \quad \partial_{\alpha_1\alpha_2}\tau_{ij}(\alpha_1,\alpha_2) = \partial_{\alpha_2\alpha_1}\tau_{ij}(\alpha_1,\alpha_2) = 0$$

that $(\alpha_1,\alpha_2) = (\theta_{ij},\theta_{ij})$ is the unique saddle point. Let $\alpha_1 < \alpha_2 \le \theta_{ij} \le \beta_1 < \beta_2$.

(a) For $T''_{ij}(V_{ij}) > 0$, that is $(z_i - z_j)\frac{(\sigma_{10}-z_k)}{\gamma'(\sigma_{10})} > 0$, we have

$$\partial_{\alpha_1\alpha_1}\tau_{ij}(\theta_{ij},\theta_{ij}) < 0 < \partial_{\alpha_2\alpha_2}\tau_{ij}(\theta_{ij},\theta_{ij}),$$

which leads to $\partial_{\alpha_1}\tau_{ij}(\alpha_1,\alpha_2) > 0$ and $\partial_{\alpha_2}\tau_{ij}(\beta_1,\beta_2) > 0$. Thus, $\tau_{ij}(\alpha_1,\alpha_2) < 0 < \tau_{ij}(\beta_1,\beta_2)$.

(b) For $T''_{ij}(V_{ij}) < 0$, that is $(z_i - z_j)\frac{(\sigma_{10}-z_k)}{\gamma'(\sigma_{10})} < 0$, we have

$$\partial_{\alpha_1\alpha_1}\tau_{ij}(\theta_{ij},\theta_{ij}) > 0 > \partial_{\alpha_2\alpha_2}\tau_{ij}(\theta_{ij},\theta_{ij}),$$

which leads to $\partial_{\alpha_1}\tau_{ij}(\alpha_1,\alpha_2) < 0$ and $\partial_{\alpha_2}\tau_{ij}(\beta_1,\beta_2) < 0$. Thus, $\tau_{ij}(\alpha_1,\alpha_2) > 0 > \tau_{ij}(\beta_1,\beta_2)$.

Moreover, it follows from the implicit function theorem that $\tau_{ij}(\alpha_1,\alpha_2) = 0$ has a solution $\alpha_2 = P_{ij}(\alpha_1) \ge \theta_{ij}$ for $\alpha_1 \in [0,\theta_{ij}]$ satisfying $\theta_{ij} = P_{ij}(\theta_{ij})$ (see Fig. 1). The proof is completed. □

Proposition 3.10 *Graphs of P_{12}, P_{23} and P_{13} in Δ do not intersect with each other.*

Proof Suppose, at least two of the graphs, say of P_{23} and P_{12} would intersect at a point $(\alpha_1,\alpha_2) \in \Delta$. One would have $\tau_{23}(\alpha_1,\alpha_2) = \tau_{12}(\alpha_1,\alpha_2) = 0$, which contradicts to the statement in Proposition 3.5. □

3.3.2 Case II: $\sigma_{10} = \sigma_{20} := \sigma_0 \in \mathbb{R}$

In this case, one has

Lemma 3.11 *Assume $\sigma_{10} = \sigma_{20} := \sigma_0 \in \mathbb{R}$. For $V \ne 0$, one has*

(i) If $\sigma_0 = z_k$, then $T_{ij}(\phi)$ is strictly monotone.
(ii) If $\sigma_0 \ne z_k$, then $T_{ij}(\phi)$ has a unique critical point $\phi = V_{ij}$ given by

$$V_{ij} = \frac{V(VL(\sigma_0) + 3\Lambda_L)}{3(VL(\sigma_0) + 2\Lambda_L)} + \frac{1}{z_k - \sigma_0}. \tag{3.14}$$

Proof It follows from part (b) of Proposition 3.3 that

$$T'_{ij}(\phi) = \frac{2(z_i - z_j)(\sigma_0 - z_k)}{\gamma''(\sigma_0)}\left(\phi - \frac{\gamma'''(\sigma_0)}{3\gamma''(\sigma_0)}\right) + \frac{2(z_i - z_j)}{\gamma''(\sigma_0)}.$$

Thus, if $\sigma_0 = z_k$, then T_{ij} is strictly monotone. If $\sigma_0 \neq z_k$, then T_{ij} has a unique critical point

$$V_{ij} = \frac{\gamma'''(\sigma_0)}{3\gamma''(\sigma_0)} + \frac{1}{z_k - \sigma_0},$$

which, together with (3.6), gives (3.14). □

For $\sigma_0 \neq z_k$ where V_{ij} in (3.14) exists, let

$$\theta_{ij} = \begin{cases} \dfrac{1}{g'(0)} e_0^T \left(e^{(V-V_{ij})D_0} L - L \right), & \sigma_0 \neq 0, \\ \dfrac{1}{g''(0)} e_0^T \Gamma^{-2} \left(e^{(V-V_{ij})D_0} L - \displaystyle\sum_{s=0}^{2} \frac{1}{s!} (V - V_{ij})^s \Gamma^s L \right), & \sigma_0 = 0. \end{cases} \tag{3.15}$$

Lemma 3.12 *One has that θ_{ij} is monotone in V_{ij} and $\theta_{ij} \in [0, 1]$ if and only if V_{ij} lies between 0 and V.*

Proof It can be proved in the similar way as that of Lemma 3.7. □

If $\theta_{ij} \in [0, 1]$, we will define a function $P_{ij} : [0, \theta_{ij}] \to [\theta_{ij}, \infty)$ in the same way as in Definition 3.8.

Proposition 3.13 *Assume $\sigma_{10} = \sigma_{20} := \sigma_0 \neq 0$. For $V \neq 0$, one has*

(i) if $\sigma_0 = z_k$, then $(z_i - z_j)\tau_{ij}(\alpha_1, \alpha_2) < 0$ for any $0 \leq \alpha_1 \leq \alpha_2 \leq 1$;
(ii) if $\sigma_0 \neq z_k$, then exactly one of the followings occurs

(a) when $(z_i - z_j)\frac{(\sigma_0 - z_k)}{\gamma''(\sigma_0)} > 0$,

$$\tau_{ij}(\alpha_1, \alpha_2) = \begin{cases} < 0 & \text{for } \alpha_1 < \theta_{ij} \text{ and } \alpha_2 < P_{ij}(\alpha_1) \\ > 0 & \text{for } \alpha_1 > \theta_{ij} \text{ or } \alpha_2 > P_{ij}(\alpha_1); \end{cases}$$

(b) when $(z_i - z_j)\frac{(\sigma_0 - z_k)}{\gamma''(\sigma_0)} < 0$,

$$\tau_{ij}(\alpha_1, \alpha_2) = \begin{cases} > 0 & \text{for } \alpha_1 < \theta_{ij} \text{ and } \alpha_2 < P_{ij}(\alpha_1) \\ < 0 & \text{for } \alpha_1 > \theta_{ij} \text{ or } \alpha_2 > P_{ij}(\alpha_1). \end{cases}$$

Proof Note that for $V > 0$, $\gamma''(\sigma_0) > 0$; for $V < 0$, $\gamma''(\sigma_0) < 0$.

(i) If $\sigma_0 = z_k$, then

$$T'_{ij}(\phi) = \frac{2(z_i - z_j)e^{\sigma_0 \phi}}{\gamma''(\sigma_0)},$$

which leads to $V(z_i - z_j)T'_{ij}(\phi) > 0$ so $T_{ij}(\phi)$ is monotone and $(z_i - z_j)\tau_{ij}(\alpha_1, \alpha_2) < 0$.

(ii) If $\sigma_0 \neq z_k$, then $T'_{ij}(V_{ij}) = 0$ and

$$T''_{ij}(V_{ij}) = \frac{2(z_i - z_j)(\sigma_0 - z_k)e^{\sigma_0 \phi}}{\gamma''(\sigma_0)}.$$

The same proof for (ii) of Proposition 3.9 can be applied to completes the proof. □

3.4 Limiting Behavior as $z_1 \to z_2$

To motivate possible features of τ_{ij}, we look at the "limiting" behavior as $z_1 \to z_2$ of two ion species.

Proposition 3.14 *For fixed boundary conditions (more precisely, for fixed V and (l_1, l_2, r_1, r_2) with (l_3, r_3) from electroneutrality), if $z_1 \to z_2$, then $\tau_{13} < 0$ and $\tau_{23} < 0$.*

Proof Recall that

$$\gamma(\zeta) = e^{\sigma V} L(\sigma) - R(\sigma), \quad \gamma'(\sigma) = V e^{\sigma V} L(\sigma) + e^{\sigma V} \Lambda_L - \Lambda_R,$$

where $L(\sigma) = \Lambda_L(\sigma - \eta_l)$ and $R(\sigma) = \Lambda_R(\sigma - \eta_r)$ with

$$\eta_l = -z_1 z_2 z_3 \frac{S_L}{\Lambda_L} \in (z_2, z_1), \quad \eta_r = -z_1 z_2 z_3 \frac{S_R}{\Lambda_R} \in (z_2, z_1).$$

Thus, $\lim_{z_1 \to z_2} \gamma(\sigma) = 0$ has two roots $\sigma_{10} = -\frac{1}{V} \ln \frac{l_1 + l_2}{r_1 + r_2}$ and $\sigma_{20} = z_2$. If $\sigma_{10} \neq \sigma_{20}$, then

$$\gamma'(\sigma_{10}) = V R(\sigma_{10}) = V \Lambda_R(\sigma_{10} - z_2) \neq 0 \ \text{ and } \gamma'(\sigma_{20}) = e^{\sigma_{20} V} \Lambda_L - \Lambda_R \neq 0.$$

It follows from (i) in Proposition 3.9 that $K_{13} = K_{23} = 0$, and hence $\tau_{13} < 0$ and $\tau_{23} < 0$. Similarly, if $\sigma_{10} = \sigma_{20} = z_2$, then by (i) in Proposition 3.13, we know $\tau_{13} < 0$ and $\tau_{23} < 0$. □

Remark 3.15 In Proposition 3.14, the assumption of "Fixed boundary conditions" indicates that the formal limiting process as $z_1 \to z_2$ that leads to $\tau_{13} < 0$ and $\tau_{23} < 0$ is not uniform in boundary conditions; in fact, as long as $z_1 \neq z_2$, there are boundary conditions so that $\tau_{13} > 0$ or $\tau_{23} > 0$.

In Sect. 4, we will show that, it is possible that, $\tau_{13} > 0$, or $\tau_{23} > 0$, or even, $\tau_{13} + \tau_{23} > 0$. On the other hand, we believe that $\tau_{13} > 0$ and $\tau_{23} > 0$ cannot occur simultaneously.

4 Equi-Chemical-Potential-Difference: $\rho = \frac{l_1}{r_1} = \frac{l_2}{r_2} = \frac{l_3}{r_3}$

In this section, we will conduct a detailed study for the case of equi-chemical-potential-difference: $\rho = \frac{l_1}{r_1} = \frac{l_2}{r_2} = \frac{l_3}{r_3}$. As mentioned in the introduction and at the end of Sect. 3, even for this simple setup, there are a number of new and unintuitive phenomena. Due to the symmetry in Remark 1.1, we will consider $\rho \leq 1$ only.

In this case of equi-chemical-potential-difference, the function γ in (3.6) becomes

$$\gamma(\sigma) = \Big(e^{\sigma V} - \frac{1}{\rho}\Big)\Big(z_1 z_2 z_3 S_L + \sigma \Lambda_L\Big),$$

where S_L, S_R, Λ_L and Λ_R are defined in (3.5). Hence, its two roots are

$$\sigma_{10} = -\frac{\ln \rho}{V}, \quad \sigma_{20} = -z_1 z_2 z_3 \frac{S_L}{\Lambda_L} = -z_1 z_2 z_3 \frac{S_R}{\Lambda_R} \in (z_2, z_1). \tag{4.1}$$

One also has

$$\gamma'(\sigma_{10}) = \frac{V}{\rho}\Big(z_1 z_2 z_3 S_L - \frac{\Lambda_L \ln \rho}{V}\Big) = -\frac{V \Lambda_L}{\rho}\Big(\sigma_{20} - \sigma_{10}\Big),$$

$$\gamma'(\sigma_{20}) = \Lambda_L\Big(e^{\sigma_{20} V} - \frac{1}{\rho}\Big) = \frac{\Lambda_L}{\rho}\Big(e^{(\sigma_{20} - \sigma_{10})V} - 1\Big).$$

Remark 4.1 Note that for $V > 0$, $z_k > \sigma_{10}$ iff $\mu_k(0) - \mu_k(1) > 0$ iff $J_k > 0$; for $V < 0$, $z_k > \sigma_{10}$ iff $\mu_k(0) - \mu_k(1) < 0$ iff $J_k < 0$.

In the following, we will examine as systematically as possible behaviors of τ_{ij}'s. The reason is, as commented in the introduction, that not much specifics about permanent charge effects on fluxes are known. We hope to reveal some significant characteristics from our study for this specific cases. It turns out, even for this special cases, extremely rich behaviors are already present. The advantage that more or less explicit dependence of relative quantities in terms of system parameters is quite useful for the study as a first step.

4.1 Case $\sigma_{10} = \sigma_{20} = \sigma_0$

Note that $\sigma_0 \in (z_2, z_1)$. It follows from (4.1) that $\sigma_{10} = \sigma_{20}$ if and only if

$$V = V^* := \frac{\Lambda_L \ln \rho}{z_1 z_2 z_3 S_L}.$$

Since we consider, WLOG, $\rho \le 1$ and $V \neq 0$, one has $\rho < 1$, and hence, $V = V^* > 0$.

It follows from from $z_3 < z_2 < \sigma_{10} = \sigma_0 < z_1$ and Remark 4.1 that

$$J_1 > 0, \quad J_2 < 0, \quad J_3 < 0. \tag{4.2}$$

We first determine conditions for $V_{ij} \in [0, V]$ where V_{ij}'s are in (3.14).

Lemma 4.2 *Assume $V = V^*$ and $\rho < 1$. One has $V_{13} < V_{12} < V/2 < V_{23}$. Moreover,*

(i) $0 < V_{23} < V$ if and only if

$$\ln \rho < \frac{2z_2 z_3 S_L}{z_2 z_3 S_L + \Lambda_L} = \frac{2z_2 z_3 S_L}{(z_1 - z_2)(z_1 - z_3) l_1} < 0; \tag{4.3}$$

(ii) $0 < V_{13} < V$ if and only if

$$\ln \rho < -\frac{2z_1 z_3 S_L}{z_1 z_3 S_L + \Lambda_L} = \frac{2z_1 z_3 S_L}{(z_1 - z_2)(z_2 - z_3) l_2} < 0; \tag{4.4}$$

(iii) $0 < V_{12} < V$ if and only if

$$\ln \rho < -\frac{2z_1 z_2 S_L}{z_1 z_2 S_L + \Lambda_L} = -\frac{2z_1 z_2 S_L}{(z_1 - z_3)(z_2 - z_3) l_3} < 0. \tag{4.5}$$

Proof Since $L(\sigma_0) = \rho R(\sigma_0) = 0$, it follows from (3.14) that

$$V_{ij} = \frac{V(VL(\sigma_0) + 3\Lambda_L)}{3(VL(\sigma_0) + 2\Lambda_L)} + \frac{1}{z_k - \sigma_0} = \frac{1}{2}V + \frac{1}{z_k - \sigma_0}.$$

Thus, $V_{13} < V_{12} < V/2 < V_{23}$. Moreover, $0 < V_{ij} < V$ if and only if

$$-\frac{1}{2}V < \frac{1}{z_k - \sigma_0} < \frac{1}{2}V.$$

For (i), we have $V_{23} > 0$ and for $V_{23} < V$,

$$\frac{1}{2}V > \frac{1}{z_1 - \sigma_0},$$

which leads to (4.3). The other cases can be obtained similarly. $\square$

Recall, from Lemma 3.12, that $V_{ij} \in (0, V)$ implies $\theta_{ij} \in (0, 1)$.

Theorem 4.3 *Assume $V = V^*$ and $\rho < 1$. Suppose the conditions for $V_{ij} \in (0, V)$ in Lemma 4.2. One has,*

(i) $\tau_{23} > 0$ for $\alpha_1 < \theta_{23}$ and $\alpha_2 < P_{23}(\alpha_1)$; $\tau_{23} < 0$ for $\alpha_1 > \theta_{23}$ or $\alpha_2 > P_{23}(\alpha_1)$;
(ii) $\tau_{13} < 0$ for $\alpha_1 < \theta_{13}$ and $\alpha_2 < P_{13}(\alpha_1)$; $\tau_{13} > 0$ for $\alpha_1 > \theta_{13}$ or $\alpha_2 > P_{13}(\alpha_1)$;
(iii) $\tau_{12} < 0$ for $\alpha_1 < \theta_{12}$ and $\alpha_2 < P_{12}(\alpha_1)$; $\tau_{12} > 0$ for $\alpha_1 > \theta_{12}$ or $\alpha_2 > P_{12}(\alpha_1)$.

Proof Note that,

$$\frac{\sigma_0 - z_k}{\gamma''(\sigma_0)} = -\frac{\mu_k^\delta}{2V^2\Lambda_L e^{\sigma_0 V}},$$

where $\mu_k^\delta = \mu_k(0) - \mu_k(1)$ is the *transmembrane* electrochemical potential of the kth ion species. For the case under consideration, one has $\mu_3^\delta < \mu_2^\delta < 0 < \mu_1^\delta$, and hence,

$$(z_2 - z_3)\frac{\sigma_0 - z_1}{\gamma''(\sigma_0)} < 0, \quad (z_1 - z_3)\frac{\sigma_0 - z_2}{\gamma''(\sigma_0)} > 0, \quad (z_1 - z_2)\frac{\sigma_0 - z_3}{\gamma''(\sigma_0)} > 0.$$

The conclusion then follows from Proposition 3.13. □

As a consequence of Proposition 3.10, Lemma 4.2 and Theorem 4.3, one has

Corollary 4.4 *Assume $V = V^*$ and $\rho < 1$. The situation that $\tau_{13} > 0$ and $\tau_{23} > 0$ cannot occur simultaneously. Hence, the situation that $\tau_{12} > 0$ and $\tau_{23} > 0$ cannot occur simultaneously since $\tau_{13} = \tau_{12} + \tau_{23}$. Furthermore, if either $\tau_{12} > 0$ or $\tau_{13} > 0$, then $\tau_{23} < 0$, and hence, in either case, $\tau_{12} = \tau_{13} - \tau_{23} > \tau_{13}$.*

Recall that $(\alpha_1, \alpha_2) \in \Delta := \{0 \le \alpha_1 \le \alpha_2 \le 1\}$. It is obvious that τ_{ij} is continuous on Δ and the sign of τ_{ij} changes at $(\alpha_1, P_{ij}(\alpha_1))$. Assume $V = V^*$ and the conditions for $0 < V_{ij} < V$ in Lemma 4.2. Since $0 < V_{13} < V_{12} < V_{23} < V$, one has $0 < \theta_{23} < \theta_{12} < \theta_{13} < 1$ and graphs of P_{12}, P_{13} and P_{23} on Δ are illustrated in Fig. 2. Note that by Proposition 3.10, graphs of P_{ij}'s do not intersect.

Corollary 4.5 *Note that $\tau_{12} = \tau_{13} - \tau_{23}$, the sign of τ_{12} depends on the order of τ_{13} and τ_{23}. It follows from Theorem 4.3 and Fig. 2 that*

(i) $\tau_{23} > 0 > \tau_{13}$ for $\alpha_1 < \theta_{23}$ and $\alpha_2 < P_{23}(\alpha_1)$;
(ii) $0 > \tau_{23} > \tau_{13}$ for $P_{23}(\alpha_1) < \alpha_2 < P_{12}(\alpha_1)$ or $\theta_{23} < \alpha_1 < \alpha_2 < P_{12}(\alpha_1)$;
(iii) $0 > \tau_{13} > \tau_{23}$ for $P_{12}(\alpha_1) < \alpha_2 < P_{13}(\alpha_1)$ or $\theta_{12} < \alpha_1 < \alpha_2 < P_{13}(\alpha_1)$;
(iv) $\tau_{12} + \tau_{23} = \tau_{13} > 0 > \tau_{23}$ for $\alpha_1 > \theta_{13}$ or $\alpha_2 > P_{13}(\alpha_1)$.

Figure 3 contains numerical simulation profiles of concentrations, electrical potential, and electrochemical potential for one set of parameter values under this case.

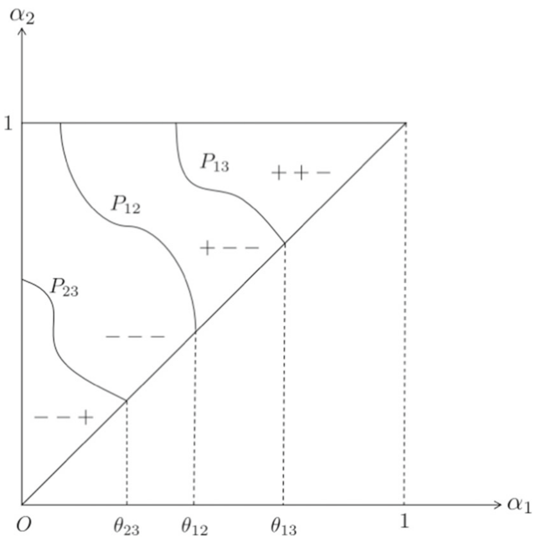
Figure 4 includes numerical simulations for $\lambda_j(Q_2)$ for $Q_2 = 2Q_0$ near 0. The figure on the right hand side has two implications: (a) in general, $\tau_j(0^\pm) \neq 0$ and (b) $\tau_{12} = \tau_1 - \tau_2 > 0$ is realized for the choice of L and R indicated.

Numerical results presented in Figs. 3 and 4 here as well as in Fig. 7 in next subsection have been obtained using MMPDElab, A MATLAB package for adaptive mesh movement and finite element computation in 1D, 2D, and 3D, developed by Huang [28].

In Corollary 4.5, for (ii) and (iii), $\tau_{13} + \tau_{23} < 0$; for (i) and (iv), the sign of $\tau_{13} + \tau_{23}$ is not clear. We now show that $\tau_{13} + \tau_{23}$ may be positive, which justifies the last assertion made in Remark 3.15. Set

$$\tau_3^c = \frac{\tau_{13} + \tau_{23}}{2}. \tag{4.6}$$

Fig. 2 Graphs of functions P_{12}, P_{13} and P_{23} in domain Δ when $V = V^*$ and the conditions for $0 < V_{ij} < V$ in Lemma 4.2 hold. The sign patterns are for the signs of components of $(\tau_{12}, \tau_{13}, \tau_{23})$. For example, in the left bottom corner region where $\alpha_1 < \theta_{23}$ and $\alpha_2 < P_{23}(\alpha_1)$, the patten "$- - +$" means $\tau_{12} < 0$, $\tau_{13} < 0$ and $\tau_{23} > 0$



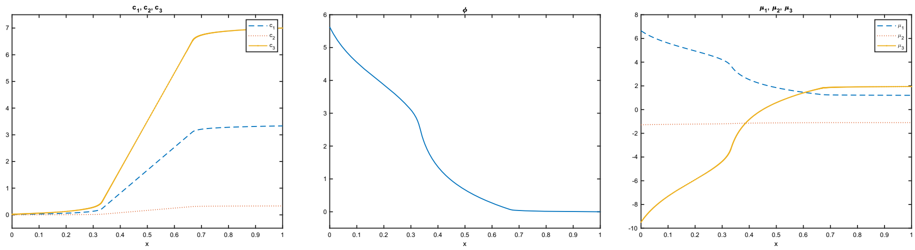


Fig. 3 Profiles of concentrations (*left*), electric potential (*middle*) and electrochemical potentials (*right*) with $Q_0 = -.0008$, $L = (.01, .001, .021)$, $R = (10/3, 1/3, 7)$, and $V = V^* \approx 5.6276$

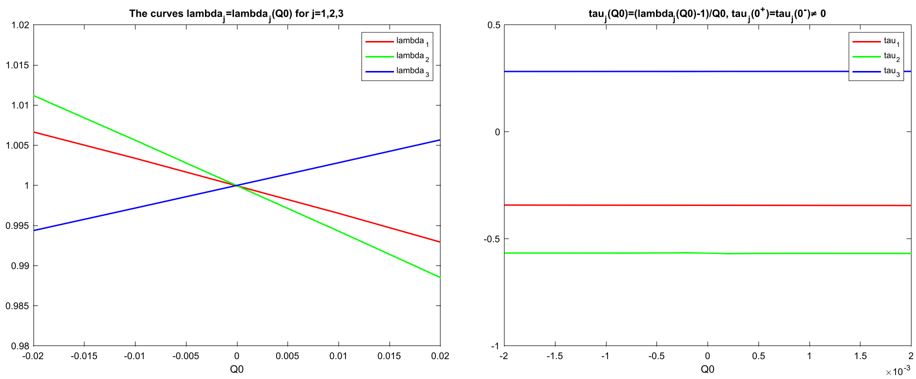


Fig. 4 $L = (.01, .001, .021)$, $R = (10/3, 1/3, 7)$, $V = V^* \approx 5.6276$: $\lambda_j(2Q_0)$ where $\lambda_1(2Q_0) > \lambda_2(2Q_0)$ for $Q_0 > 0$ and $\lambda_1(2Q_0) < \lambda_2(2Q_0)$ for $Q_0 < 0$ (left); $\tau_j(0^{\pm}) \neq 0$ and $\tau_{12} = \tau_1 - \tau_2 > 0$ (case (iii) in Corollary 4.5) (right)

If we formally take $z_2 \to z_1$ (or $z_1 \to z_2$), then $\tau_3^c < 0$ from Proposition 3.14.

Let

$$z_3^c = \frac{z_1(z_2 - z_3) + z_2(z_1 - z_3)}{z_1 + z_2 - 2z_3} \in (z_2, z_1),$$

and, for $\sigma_0 \neq z_3^c$, let

$$V_3^c = \frac{1}{2}V + \frac{1}{z_3^c - \sigma_0} \quad \text{and} \quad \theta_3^c = \frac{S_L}{S_R - S_L}\left(e^{\sigma_0(V - V_3^c)} - 1\right).$$

Lemma 4.6 *Assume $V = V^*$ and $\rho < 1$.*

(i) If $z_1 l_1 > z_2 l_2$, then $V_3^c < V$ if and only if

$$\ln \rho < \frac{2\sigma_0}{\sigma_0 - z_3^c} = -\frac{2z_1 z_2 z_3 S_L(z_1 + z_2 - 2z_3)}{(z_1 - z_2)(z_1 - z_3)(z_2 - z_3)(z_2 l_2 - z_1 l_1)} < 0. \tag{4.7}$$

(ii) If $z_1 l_1 < z_2 l_2$, then $0 < V_3^c$ if and only if

$$\ln \rho < -\frac{2\sigma_0}{\sigma_0 - z_3^c} = \frac{2z_1 z_2 z_3 S_L(z_1 + z_2 - 2z_3)}{(z_1 - z_2)(z_1 - z_3)(z_2 - z_3)(z_2 l_2 - z_1 l_1)} < 0. \tag{4.8}$$

Proof Recall that, for $V = V^*$, one has $\sigma_{10} = \sigma_{20} = \sigma_0$ and

$$T_{ij}(\phi) = \frac{2(z_i - z_j)(\sigma_0 - z_k)}{\sigma_0 \gamma''(\sigma_0)}\left(\phi e^{\sigma_0\phi} - (e^{\sigma_0\phi} - 1)\left(\frac{\gamma'''(\sigma_0)}{3\gamma''(\sigma_0)} + \frac{1}{\sigma_0} + \frac{1}{z_k - \sigma_0}\right)\right).$$

Therefore,

$$\begin{aligned} T_3^c(\phi) &:= \frac{T_{13}(\phi) + T_{23}(\phi)}{2} \\ &= \frac{(z_1 + z_2 - 2z_3)(\sigma_0 - z_3^c)}{\sigma_0 \gamma''(\sigma_0)}\left(\phi e^{\sigma_0\phi} - (e^{\sigma_0\phi} - 1)\left(\frac{\gamma'''(\sigma_0)}{3\gamma''(\sigma_0)} + \frac{1}{\sigma_0} + \frac{1}{z_3^c - \sigma_0}\right)\right). \end{aligned}$$

Since

$$\frac{\mathrm{d}T_3^c}{\mathrm{d}\phi}(\phi) = \frac{(z_1 + z_2 - 2z_3)(\sigma_0 - z_3^c)e^{\sigma_0\phi}}{\gamma''(\sigma_0)}\left(\phi - \frac{\gamma'''(\sigma_0)}{3\gamma''(\sigma_0)} - \frac{1}{z_3^c - \sigma_0}\right),$$

we have

$$\frac{\mathrm{d}T_3^c}{\mathrm{d}\phi}(V_3^c) = 0 \quad \text{where} \quad V_3^c = \frac{1}{2}V + \frac{1}{z_3^c - \sigma_0}.$$

A direct calculation gives

$$\sigma_0 - z_3^c = \frac{(z_1 - z_2)(z_1 - z_3)(z_2 - z_3)(z_2 l_2 - z_1 l_1)}{(z_1 + z_2 - 2z_3)\Lambda_L}.$$

If $z_1 l_1 > z_2 l_2$, then $\sigma_0 < z_3^c < z_1$; if $z_1 l_1 < z_2 l_2$, then $z_2 < z_3^c < \sigma_0$; Applying the same procedure of the proof in Lemma 4.2, the statements then follow. □

The next result is a direct consequence of the above.

Theorem 4.7 *Assume $V = V^*$ and $\rho < 1$. There is a function $P_3^c : [0, \theta_3^c] \to [\theta_3^c, +\infty)$ so that,*

(i) if $z_1 l_1 > z_2 l_2$ and (4.7) holds, then $\tau_3^c > 0$ (with $\tau_{23} > 0 > \tau_{13}$) for $\alpha_1 < \theta_3^c$ and $\alpha_2 < P_3^c(\alpha_1)$; $\tau_3^c < 0$ for $\alpha_1 > \theta_3^c$ or $\alpha_2 > P_3^c(\alpha_1)$;

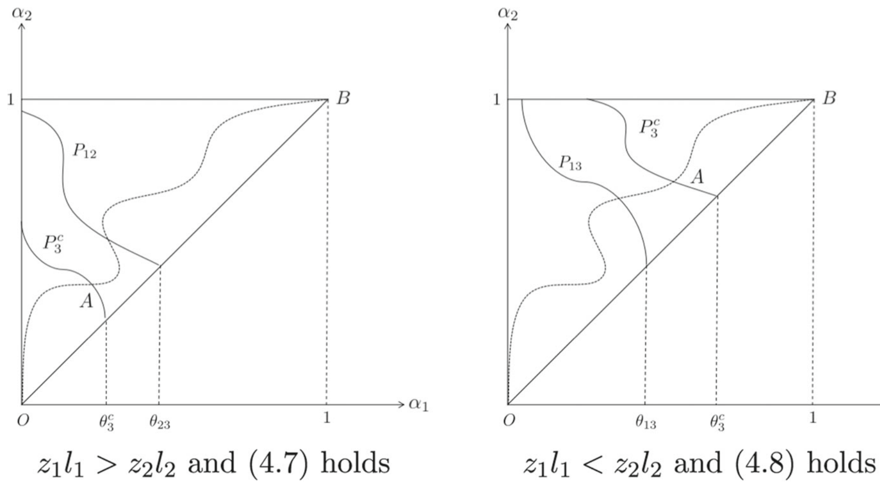


Fig. 5 Graphs of function P_3^c in domain Δ when $V = V^*$. Let OB be any curve in Δ intersecting P_3^c at A. From O to A to B, if $z_1l_1 > z_2l_2$ and (4.7) holds, then τ_3^c changes form positive to zero to negative; if $z_1l_1 < z_2l_2$ and (4.8) holds, then τ_3^c changes form negative to zero to positive

(ii) *if* $z_1l_1 = z_2l_2$, *then* $\tau_3^c < 0$ *for any* $(\alpha_1, \alpha_2) \in \Delta$;
(iii) *if* $z_1l_1 < z_2l_2$ *and (4.8) holds, then* $\tau_3^c < 0$ *for* $\alpha_1 < \theta_3^c$ *and* $\alpha_2 < P_3^c(\alpha_1)$; $\tau_3^c > 0$ *(with* $\tau_{13} > 0 > \tau_{23}$*) for* $\alpha_1 > \theta_3^c$ *or* $\alpha_2 > P_3^c(\alpha_1)$.

Proof Note that if $z_1l_1 > z_2l_2$, then $V_3^c < V$ implies $0 < V_{23} < V_3^c < V$, and hence, $0 < \theta_3^c < \theta_{23} < 1$. Similarly, if $z_1l_1 < z_2l_2$, then $V_3^c > 0$ implies $0 < V_3^c < V_{13} < V$, and hence, $0 < \theta_{13} < \theta_3^c < 1$. The conclusion follows from Proposition 3.13 directly. □

Note that $J_1 > 0 > J_2$ from (4.2). In some sense, one of the cation species is preparing to "sacrifice" for the other: Under one set of conditions, the first cation species sacrifices so that $\tau_{23} > 0$ and under some other set of conditions, the second cation species sacrifices so that $\tau_{13} > 0$. Also, $\tau_3^c > 0$ could be interpreted as that the total "gain" is more than the sacrifice that one of the cation made so that $\tau_3^c = (\tau_{13} + \tau_{23})/2 > 0$. One asks naturally: Can J_1 and J_2 have the same sign yet $\tau_3^c > 0$? The answer is affirmative and is justified in next part (see Remark 4.16).

4.2 $\sigma_{10} \neq \sigma_{20}$

Note that $\sigma_{10} \neq \sigma_{20}$ if and only if $V \neq V^*$. If $V \neq V^*$, then, from (3.10),

$$K_{ij} = \frac{(\sigma_{20} - z_k)\gamma'(\sigma_{10})}{(\sigma_{10} - z_k)\gamma'(\sigma_{20})} = -\frac{\sigma_{20} - z_k}{\sigma_{10} - z_k} \cdot \frac{(\sigma_{20} - \sigma_{10})V}{e^{(\sigma_{20} - \sigma_{10})V} - 1}. \tag{4.9}$$

In particular,

Lemma 4.8 *Assume* $V \neq V^*$ *and* $\rho \leq 1$.

(i) *For* $V < 0$, *one has* $K_{13} > 0 > K_{23}$, *and*

$$V < V_{23} < 0 \text{ if and only if } T_{23}'(V) < 0 < T_{23}'(0);$$

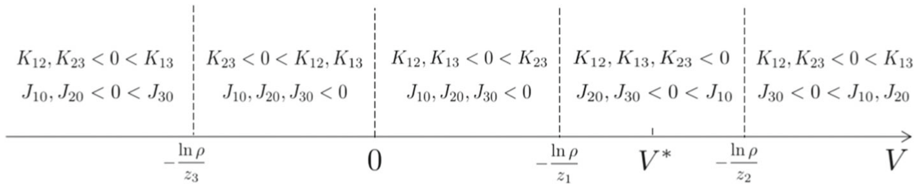


Fig. 6 Signs of K_{ij} and J_{k0} for $V \neq V^*$ and $\rho < 1$. Also, as $V \to V^*$ one always has $K_{ij} < 0$ in limit, and hence, V_{ij} exists as in the case $\sigma_{10} = \sigma_{20}$

Furthermore, $K_{12} < 0$ *if and only if* $V < -\frac{\ln\rho}{z_3} < 0$, *and hence,*

$$V < V_{12} < 0 \ \text{ if and only if } \ T'_{12}(V) > 0 > T'_{12}(0).$$

(ii) For $V > 0$,

(a) if $0 < V \leq V^*$ *(necessarily,* $\rho < 1$*), then* $K_{12}, K_{13} < 0$, *and*

$$V > V_{12}, V_{13} > 0 \ \text{ if and only if } \ T'_{12}(V), T'_{13}(V) > 0 > T'_{12}(0), T'_{13}(0);$$

Furthermore, $K_{23} < 0$ *if and only if* $-\frac{\ln\rho}{z_1} < V < V^*$, *and hence,*

$$V > V_{23} > 0 \ \text{ if and only if } \ T'_{23}(V) < 0 < T'_{23}(0);$$

(b) if $0 \leq V^* < V$, *then* $K_{12}, K_{23} < 0$, *and*

$$V > V_{12}, V_{23} > 0 \ \text{ if and only if } T'_{12}(0), T'_{23}(V) < 0 < T'_{12}(V), T'_{23}(0);$$

Furthermore, $K_{13} < 0$ *if and only if* $V^* < V < -\frac{\ln\rho}{z_2}$, *and hence,*

$$V > V_{13} > 0 \ \text{ if and only if } \ T'_{13}(V) > 0 > T'_{13}(0).$$

Proof It is easy to see that

$$\frac{(\sigma_{20} - \sigma_{10})V}{e^{(\sigma_{20}-\sigma_{10})V} - 1} > 0.$$

The statements on sign of K_{ij} follow from (4.9) and detailed statements in (i) and (ii) follow directly from (4.1) and (4.9).

For $V < 0$, we have $\sigma_{10} < \sigma_{20}$ and $\frac{\sigma_{20}-z_1}{\gamma'(\sigma_{20})} > 0$, which leads to that $T'_{23}(\phi)$ is increasing. Since $T'_{23}(V_{23}) = 0$, it follows form Lemma 3.6 that $V < V_{23} < 0$ if and only if $T'_{23}(V) < 0 < T'_{23}(0)$. The other cases can be obtained similarly. □

From above result, we know the order of θ_{ij}, 0 and 1 depends on signs of $T'_{ij}(V)$ and $T'_{ij}(0)$. Note that by Proposition 3.3, $T'_{ij}(V)$ and $T'_{ij}(0)$ can be rewritten as

$$T'_{ij}(V) = \frac{(z_i - z_j)\Lambda_L L_{ij}(V)}{V\gamma'(\sigma_{10})\gamma'(\sigma_{20})} e^{(\sigma_{10}+\sigma_{20})V}, \quad T'_{ij}(0) = \frac{(z_i - z_j)\Lambda_R R_{ij}(V)}{V\gamma'(\sigma_{10})\gamma'(\sigma_{20})},$$

with

$$L_{ij}(\phi) = (z_k\phi + \ln\rho)(\frac{1}{\rho}e^{-\sigma_{20}\phi} - 1) + \phi(\sigma_{20}\phi + \ln\rho)(z_k - \sigma_{20}),$$
$$R_{ij}(\phi) = (z_k\phi + \ln\rho)(1 - \rho e^{\sigma_{20}\phi}) + \phi(\sigma_{20}\phi + \ln\rho)(z_k - \sigma_{20}).$$

For signs of τ_{23}, we can establish the following result.

Theorem 4.9 *Assume $V \neq V^*$ and $\rho \leq 1$. Then, for $V < 0$, $R_{23}(V) = 0$ has a unique root V_{23}^R; for $V > 0$, $L_{23}(V) = 0$ has a unique root $V_{23}^L \in (-\frac{\ln\rho}{z_1}, +\infty)$, and $V_{23}^L < V^*$ if and only if (4.3) holds. Furthermore,*

(i) if $V < V_{23}^R$, then $\tau_{23} < 0$ for $\alpha_1 < \theta_{23}$ and $\alpha_2 < P_{23}(\alpha_1)$; $\tau_{23} > 0$ for $\alpha_1 > \theta_{23}$ or $\alpha_2 > P_{23}(\alpha_1)$;
(ii) if $V_{23}^R < V < V_{23}^L$, then $\tau_{23} < 0$ for any $(\alpha_1, \alpha_2) \in \Delta$;
(iii) if $V_{23}^L < V$, then $\tau_{23} > 0$ for $\alpha_1 < \theta_{23}$ and $\alpha_2 < P_{23}(\alpha_1)$; $\tau_{23} < 0$ for $\alpha_1 > \theta_{23}$ or $\alpha_2 > P_{23}(\alpha_1)$.

In order to prove Theorem 4.9, we need to determine signs of $T_{23}'(V)$ and $T_{23}'(0)$ to check if $\theta_{23} \in (0, 1)$.

Lemma 4.10 *Assume $V \neq V^*$ and $\rho \leq 1$. One has*

(i) If $V < 0$, then $T_{23}'(V) < 0$ and $R_{23}(V) = 0$ has a unique root V_{23}^R such that for $V \leq V_{23}^R$, $T_{23}'(0) \geq 0$ and $0 < \theta_{23} < 1$; for $V_{23}^R < V < 0$, $T_{23}'(0) < 0$ and $1 < \theta_{23}$.
(ii) If $V > 0$, then $T_{23}'(0) > 0$ and $L_{23}(V) = 0$ has unique root V_{23}^L such that for $0 < V < -\frac{\ln\rho}{z_1}$, $T_{23}'(V) > 0$; for $-\frac{\ln\rho}{z_1} < V \leq V_{23}^L$, $T_{23}'(V) \geq 0$ and $\theta_{23} < 0$; for $V_{23}^L < V$, $T_{23}'(V) < 0$ and $0 < \theta_{23} < 1$.

In particular, if (4.3) holds, then $V_{23}^L < V^*$.

Proof Note that $R_{23}'''(\phi) = 0$ only has one root and

$$R_{23}'''(-\infty) = 0^+, \quad R_{23}'''(+\infty) < 0, \quad R_{23}''(-\infty) > 0 > R_{23}''(V^*), R_{23}''(+\infty).$$

It is direct to obtain $R_{23}''(\phi) = 0$ has a unique root $\phi_{23}^{R''} \in (-\infty, V^*)$. Since

$$R_{23}'(-\infty), R_{23}'(+\infty) < 0 = R_{23}'(V^*),$$

we know that $R_{23}'(\phi) = 0$ has two different roots $\phi_{23}^{R'} < V^*$. It follows from

$$R_{23}(-\infty) > 0 = R_{23}(V^*) > R_{23}(0), R_{23}(+\infty),$$

that $R_{23}(\phi) = 0$ has two different roots $V_{23}^R < 0 < V^*$ such that for $\phi \in (-\infty, V_{23}^R)$, $R_{23}(\phi) > 0$, for $\phi \in (V_{23}^R, V^*) \cup (V^*, +\infty)$, $R_{23}(\phi) < 0$. Since $\lim_{V \to V^*} T_{23}'(0) > 0$, we have for $V < V_{23}^R$, $T_{23}'(0) > 0$ and $V_{23} < 0$; for $V_{23}^R < V < 0$, $T_{23}'(0) < 0$ and $0 < V_{23}$; for $0 < V$, $T_{23}'(0) > 0$ and $V_{23} < 0$ (if V_{23} exists).

Note that $L_{23}'''(\phi) = 0$ only has one root and

$$L_{23}'''(-\infty) > 0, \quad L_{23}'''(+\infty) = 0^-, \quad L_{23}''(-\infty) < 0 < L_{23}''(+\infty).$$

Then $L_{23}''(\phi) = 0$ has a unique root $\phi_{23}^{L''}$ satisfying that if (4.3) holds, that is $L_{23}''(V^*) > 0$, then $\phi_{23}^{L''} < V^*$, if $L_{23}''(V^*) < 0$, then $\phi_{23}^{L''} > V^*$. Now we only consider (4.3) holds. Since

$$L_{23}'(-\infty), L_{23}'(+\infty) > 0 = L_{23}'(V^*),$$

we know that $L_{23}'(\phi) = 0$ has two different roots $\phi_{23}^{L'} < V^*$. It follows from

$$L_{23}(-\infty), L_{23}(0), L_{23}(-\frac{\ln\rho}{z_1}) < 0 = L_{23}(V^*) < L_{23}(+\infty),$$

that $L_{23}(\phi) = 0$ has two different roots $V_{23}^L < V^* \in (-\frac{\ln\rho}{z_1}, +\infty)$ such that for $\phi \in (-\infty, V_{23}^L)$, $L_{23}(\phi) < 0$, for $\phi \in (V_{23}^L, V^*) \cup (V^*, +\infty)$, $L_{23}(\phi) > 0$. Since $\lim_{V \to V^*} T_{23}'(V) <$

0, we have for $V < 0$, $T_{23}'(V) < 0$ and $V_{23} < V$; for $0 < V < V_{23}^L$, $T_{23}'(V) > 0$ and $V_{23} > V$ (if V_{23} exists); for $V_{23}^L < V$, $T_{23}'(V) < 0$ and $V_{23} < V$.

An application of Lemma 4.8 completes the proof. □

Theorem 4.9 can be established easily from Proposition 3.9 and Lemma 4.10. Similarly, results on signs of τ_{13} and τ_{12} are as follows.

Theorem 4.11 *Assume $V \neq V^*$, $\rho \leq 1$ and (4.4) holds. Then $R_{13}(V) = 0$ has two different roots $V_{13}^{R1} \in (0, V^*)$ and $V_{13}^{R2} \in (V^*, -\frac{\ln\rho}{z_2})$. Furthermore,*

(i) if $V < V_{13}^{R1}$, then $\tau_{13} < 0$ for any $(\alpha_1, \alpha_2) \in \Delta$;
(ii) if $V_{13}^{R1} < V < V_{13}^{R2}$, then $\tau_{13} < 0$ for $\alpha_1 < \theta_{13}$ and $\alpha_2 < P_{13}(\alpha_1)$; $\tau_{13} > 0$ for $\alpha_1 > \theta_{13}$ or $\alpha_2 > P_{13}(\alpha_1)$;
(iii) if $V_{13}^{R2} < V$, then $\tau_{13} < 0$ for any $(\alpha_1, \alpha_2) \in \Delta$.

Theorem 4.12 *Assume $V \neq V^*$ and $\rho \leq 1$. Then for $V < 0$, $L_{12}(V) = 0$ has a unique root $V_{12}^L \in (-\infty, -\frac{\ln\rho}{z_3})$, for $V > 0$, $R_{12}(V) = 0$ has a unique root V_{12}^R, and $V_{12}^R < V^*$ if and only if (4.5) holds. Furthermore,*

(i) if $V < V_{12}^L$, then $\tau_{12} > 0$ for $\alpha_1 < \theta_{12}$ and $\alpha_2 < P_{12}(\alpha_1)$; $\tau_{12} < 0$ for $\alpha_1 > \theta_{12}$ or $\alpha_2 > P_{12}(\alpha_1)$;
(ii) if $V_{12}^L < V < V_{12}^R$, then $\tau_{12} < 0$ for any $(\alpha_1, \alpha_2) \in \Delta$;
(iii) if $V_{12}^R < V$, then $\tau_{12} < 0$ for $\alpha_1 < \theta_{12}$ and $\alpha_2 < P_{12}(\alpha_1)$; $\tau_{12} > 0$ for $\alpha_1 > \theta_{12}$ or $\alpha_2 > P_{12}(\alpha_1)$.

Remark 4.13 (i) When (4.4) holds, (4.5) holds automatically and $V_{13}^{R1} > V_{12}^R$.
(ii) Note that without (4.4), it is possible that either $R_{13}(V) \leq 0$ or $R_{13}(V) = 0$ has two roots in $(0, -\frac{\ln\rho}{z_2})$, which are vary complex to write the conditions clearly and concisely. However, no matter whether (4.4) holds or not, it can be shown that $\tau_{13} > 0$ and $\tau_{23} > 0$ can never occur simultaneously.

In particular,

Corollary 4.14 *Assume $\rho \leq 1$ and (4.4), (4.3) hold. Suppose*

$$\max\{V_{13}^{R1}, V_{23}^L\} < V < V_{13}^{R2}.$$

Then statements (i)-(iv) in Corollary 4.5 hold true for this case of $\sigma_{10} \neq \sigma_{20}$.

In the previous part, we have shown that $\tau_3^c > 0$ while $J_{10} > 0 > J_{20}$. Here we will show that $\tau_3^c > 0$ while $J_{10}J_{20} > 0$ under some boundary conditions and for some choices of (α_1, α_2). Let

$$L_3^c(\phi) = (z_3^c\phi + \ln\rho)(\frac{1}{\rho}e^{-\sigma_{20}\phi} - 1) + \phi(\sigma_{20}\phi + \ln\rho)(z_3^c - \sigma_{20}),$$

$$R_3^c(\phi) = (z_3^c\phi + \ln\rho)(1 - \rho e^{\sigma_{20}\phi}) + \phi(\sigma_{20}\phi + \ln\rho)(z_3^c - \sigma_{20}),$$

$$K_3^c = \frac{(\sigma_{20} - z_3^c)\gamma'(\sigma_{10})}{(\sigma_{10} - z_3^c)\gamma'(\sigma_{20})}, \quad V_3^c = \frac{1}{\sigma_{10} - \sigma_{20}}\ln(-K_3^c), \quad \theta_3^c = \frac{S_L}{g'(0)}\left(e^{\sigma_0(V - V_3^c)} - 1\right).$$

Theorem 4.15 *Assume $V \neq V^*$, $\rho \leq 1$ and $z_1 l_1 > z_2 l_2$. Then for $V < 0$, $R_3^c(V) = 0$ has a unique root V_3^{cR}, for $V > 0$, $L_3^c(V) = 0$ has a unique root $V_3^{cL} \in (-\frac{\ln\rho}{z_3^c}, +\infty)$, and $V_3^{cL} < V^*$ if and only if (4.7) holds. Furthermore,*

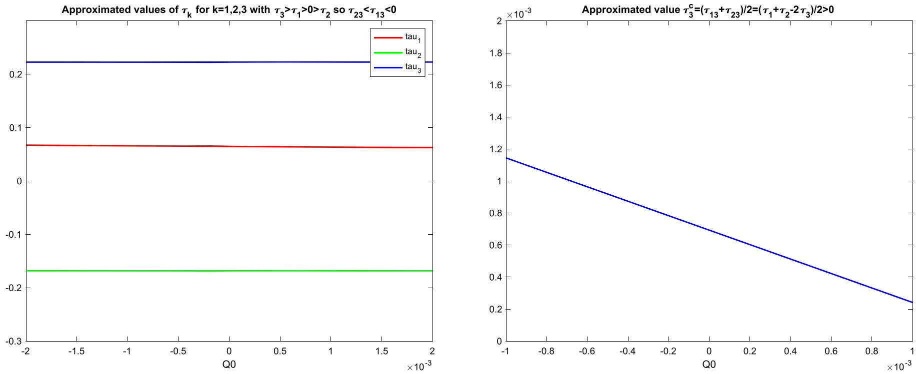


Fig. 7 Numerical examples with $L = (0.0001, 0.01, 0.0102)$, $R = (0.1, 10, 10.2)$, and $V = 3.4$. Left: $\tau_3^c < 0$ with $\tau_3 > \tau_1 > 0 > \tau_2$, particularly, $\tau_{23} < \tau_{13} < 0$ for $\alpha_1 < \theta_3^c$ and $\alpha_2 < P_3^c(\alpha_1)$; Right: $\tau_3^c > 0$ for $\alpha_1 > \theta_3^c$ or $\alpha_2 > P_3^c(\alpha_1)$

(i) *if* $V < V_3^{cR}$, *then* $\tau_3^c < 0$ *for* $\alpha_1 < \theta_3^c$ *and* $\alpha_2 < P_3^c(\alpha_1)$; $\tau_3^c > 0$*(with* $\tau_{23} > 0 > \tau_{13} > \tau_{12}$*) for* $\alpha_1 > \theta_3^c$ *or* $\alpha_2 > P_3^c(\alpha_1)$;

(ii) *if* $V_3^{cR} < V < V_3^{cL}$, *then* $\tau_3^c < 0$ *for any* $(\alpha_1, \alpha_2) \in \Delta$;

(iii) *if* $V_3^{cL} < V$, *then* $\tau_3^c > 0$ *(with* $\tau_{23} > 0 > \tau_{13} > \tau_{12}$*) for* $\alpha_1 < \theta_3^c$ *and* $\alpha_2 < P_3^c(\alpha_1)$; $\tau_3^c < 0$ *for* $\alpha_1 > \theta_3^c$ *or* $\alpha_2 > P_3^c(\alpha_1)$.

Proof Denote

$$T_3^c(\phi) := \frac{T_{13}(\phi) + T_{23}(\phi)}{2}.$$

For $V \neq V^*$, one has $\sigma_{10} \neq \sigma_{20}$ and

$$\frac{\mathrm{d}T_3^c}{\mathrm{d}\phi}(V) = \frac{(z_1 + z_2 - 2z_3)\Lambda_L L_3^c(V)}{V\gamma'(\sigma_{10})\gamma'(\sigma_{20})} e^{(\sigma_{10}+\sigma_{20})V}, \quad \frac{\mathrm{d}T_3^c}{\mathrm{d}\phi}(0) = \frac{(z_1 + z_2 - 2z_3)\Lambda_R R_3^c(V)}{V\gamma'(\sigma_{10})\gamma'(\sigma_{20})}.$$

Note that for $z_1 l_1 > z_2 l_2$, $\sigma_0 < z_3^c < z_1$. Adopting the same procedure of the proof in Theorem 4.9, signs of τ_3^c can be completed directly.

Note that if V_{13}, V_{23} and V_3^c exist, then $V_{13} < V_{23} < V_3^c$ and hence for $V < 0$, $\theta_{23} < \theta_3^c$, for $V > 0$, $\theta_3^c < \theta_{23} < \theta_{13}$. It can be shown that for $V < V_3^{cR} < 0$, then $\tau_{13} < 0 < \tau_{23}$ for $\alpha_1 > \theta_3^c$ or $\alpha_2 > P_3^c(\alpha_1)$; for $0 < V_3^{cL} < V$, then $\tau_{13} < 0 < \tau_{23}$ for $\alpha_1 < \theta_3^c$ and $\alpha_2 < P_3^c(\alpha_1)$. □

In Fig. 7, for the set of boundary conditions L, R and V, $\theta_3^c \in (0, 1)$ exists. But, for a choice of (α_1, α_2) with $\alpha_1 < \theta_3^c$ and $\alpha_2 < P_3^c(\alpha_1)$, one has $\tau_3^c < 0$ with $\tau_3 > \tau_1 > 0 > \tau_2$ as in the left panel. On the other hand, for a choice of (α_1, α_2) with $\alpha_1 > \theta_3^c$ or $\alpha_2 > P_3^c(\alpha_1)$, one has $\tau_3^c > 0$ as shown in the right panel.

Remark 4.16 (i) Note that for $\max\{V_3^{cL}, -\frac{\ln\rho}{z_2}\} < V < +\infty$, $J_{10} > 0$ and $J_{20} > 0$; for $V < V_3^{cR} < 0$, $J_{10} < 0$ and $J_{20} < 0$. Therefore, it is indeed possible that $\tau_3^c > 0$ while $J_{10}J_{20} > 0$ (see the claim at the end of Sect. 4.1).

(ii) As for $V \neq V^*$, $\rho \leq 1$ and $z_1 l_1 < z_2 l_2$, if $R_3^c(-\frac{\ln\rho}{z_1}) > 0$, then $R_3^c(V) = 0$ has two different roots $V_3^{cR1} \in (0, -\frac{\ln\rho}{z_1})$ and $V_3^{cR2} \in (-\frac{\ln\rho}{z_1}, -\frac{\ln\rho}{z_3^c})$. In particular, if $V_3^{cR1} < V < -\frac{\ln\rho}{z_1}$, then $\tau_3^c > 0$(with $\tau_{12} > \tau_{13} > 0 > \tau_{23}$) for $\alpha_1 > \theta_3^c$ or $\alpha_2 > P_3^c(\alpha_1)$, and $J_{10}, J_{20} < 0$.

Table 1 Signs in each row occur simultaneously for same set of boundary conditions. "+ or −" means either sign is possible while the other signs in the row are fixed

τ_{12}	τ_{23}	τ_{13}	$\tau_{12} - \tau_{23}$	$\tau_{12} + \tau_{13}$	$\tau_{13} + \tau_{23}$
–	+	–	–	–	+ or –
–	–	–	+ or –	–	–
+	–	–	+	+ or –	–
+	–	+	+	+	+ or –

(iii) By Theorems 4.7 and 4.15 and (ii) above, it can be shown that $\tau_3^c > 0$ can hold for either $J_{10}J_{20} < 0$ or $J_{10}J_{20} > 0$. In particular, if $\tau_3^c > 0$ holds, then for $z_1l_1 > z_2l_2$, $\tau_{23} > 0 > \tau_{13} > \tau_{12}$; for $z_1l_1 < z_2l_2$, $\tau_{12} > \tau_{13} > 0 > \tau_{23}$.

5 A Short Summary

We give a summary of some results from this study and provide discussions on possible further directions with a couple of questions.

In this work we focus on the relative effects of permanent charges on individual fluxes for the case with three ion species. The characteristic used for this measure is in terms of the flux ratio λ_k's; more precisely, we consider, for small Q_2, the quantities τ_{ij}'s (state definition and implications of signs of τ_{ij}).

Recall the relation $\tau_{12} + \tau_{23} = \tau_{13}$. Each of the situation about signs in Table 1 can be realized.

It is natural to ask

Question 1. Can $\tau_{13} > 0$ and $\tau_{23} > 0$ occur simultaneously?

We believe it cannot. If it is the case, then the above table includes all possible situations for signs of τ_{ij}'s.

It follows from $\tau_{12} + \tau_{23} = \tau_{13}$ that, if $\tau_{12} > 0$ and $\tau_{23} > 0$, then $\tau_{13} > 0$. Therefore, it is more "difficult" to have $\tau_{12} > 0$ and $\tau_{23} > 0$ than to have $\tau_{13} > 0$ and $\tau_{23} > 0$. Thus, one may ask

Question 2. Can $\tau_{12} > 0$ and $\tau_{23} > 0$ occur simultaneously?

Note that an affirmative answer to Question 2 implies an affirmative answer to Question 1. One may indeed have $\tau_{12} > 0$ and $\tau_{13} > 0$ as claimed in the table.

Recall in [41] that, for $n = 2$ with $z_1 > 0 > z_2$, if $Q(x) > 0$ (not necessarily piecewise constant and not necessarily small), then $\lambda_1(Q) < \lambda_2(Q)$. Accordingly, Questions 1 and 2 can be asked for general case of permanent charges $Q(x)$ with one fixed sign. It would be more interesting to know what happens to $\lambda_i(Q) - \lambda_j(Q)$ for sign changing permanent charges $Q(x)$, even for $n = 2$.

6 Appendix: Proofs of Lemmas 3.1 and 3.2

In view of *limiting slow system* (2.15), one has

$$C^{[j,-]} = e^{(\phi^{[j-1,+]} - \phi^{[j,-]})D} C^{[j-1,+]}. \tag{6.1}$$

Recall that $J_k = If_k$. It follows from Proposition 3.13 and Corollary 3.14 in [44] that

$$I = \frac{z_1 z_2 z_3}{\sigma_1 \sigma_2} F \quad \text{and} \quad F = \frac{-\frac{\mathrm{d}}{\mathrm{d}\sigma} g^{[j]}(0)}{H(x_j) - H(x_{j-1})} \quad \text{if} \quad \sigma_1 \sigma_2 \neq 0, \tag{6.2}$$

and

$$I = -\frac{z_1 z_2 z_3}{\sigma_1} \sum_{s=1}^{n} \frac{J_s}{z_s} \quad \text{and} \quad \sum_{s=1}^{n} \frac{J_s}{z_s} = -\frac{1}{2} \frac{\frac{\mathrm{d}^2}{\mathrm{d}\sigma^2} g^{[j]}(0)}{H(x_j) - H(x_{j-1})} \quad \text{if for } \sigma_2 = 0,$$

where $g^{[j]}(\sigma)$ is defined in (2.18).

Here we should note that once σ_1 and σ_2 are determined, then the other unknown quantities in (2.20) can be obtained directly. Therefore, we will firstly determine the zeroth order and first order terms of σ_1 and σ_2.

6.1 Expansion of σ_1 and σ_2

Denote

$$\gamma^{[j]}(\sigma) = g^{[j]}(\sigma) \frac{1}{\sigma} \prod_{s=1}^{3} (\sigma - z_s).$$

It can be shown that all the zeros and removable poles of $g^{[j]}(\sigma)$ are the zeros of $\gamma^{[j]}(\sigma)$. Therefore, σ_1 and σ_2 are uniquely determined by $\gamma^{[j]}(\sigma) = 0$. The advantages are that $\gamma^{[j]}(\sigma)$ is sufficiently smooth and we need not discuss whether σ is zeros or removable poles of $g^{[j]}(\sigma)$.

6.1.1 Zeroth Order of σ_1 and σ_2.

Recall, from (3.6), that for $Q_2 = 0$,

$$g(\sigma) = \sum_{s=1}^{3} \frac{z_s^2 r_s}{z_s - \sigma} - e^{V\sigma} \sum_{s=1}^{3} \frac{z_s^2 l_s}{z_s - \sigma}, \quad \gamma(\sigma) = \frac{g(\sigma)}{\sigma} \prod_{s=1}^{3} (\sigma - z_s) = e^{\sigma V} L(\sigma) - R(\sigma).$$

One has that σ_{10} and σ_{20} are the unique solution of $\gamma(\sigma) = 0$ in the strip

$$S = \{z = x + iy : y \in (-\pi/|V|, \pi/|V|)\}.$$

Lemma 6.1 *Assume $\sigma_{10} > \sigma_{20}$. If $V > 0$, then $\gamma'(\sigma_{10}) > 0 > \gamma'(\sigma_{20})$. If $V < 0$, then $\gamma'(\sigma_{10}) < 0 < \gamma'(\sigma_{20})$.*

Proof Note that

$$\gamma'(\sigma) = e^{\sigma V} (V L(\sigma) + \Lambda_L) - \Lambda_R, \quad \gamma''(\sigma) = V e^{\sigma V} (V L(\sigma) + 2\Lambda_L).$$

It follows from $\gamma''(\sigma) = 0$ that $\gamma'(\sigma) < 0$. For $V > 0$,

$$\lim_{\sigma \to -\infty} \gamma'(\sigma) = -\Lambda_R, \quad \lim_{\sigma \to +\infty} \gamma'(\sigma) = +\infty, \quad \lim_{\sigma \to \pm\infty} \gamma(\sigma) = +\infty,$$

then $\gamma'(\sigma_{10}) > 0 > \gamma'(\sigma_{20})$. For $V < 0$,

$$\lim_{\sigma \to -\infty} \gamma'(\sigma) = +\infty, \quad \lim_{\sigma \to +\infty} \gamma'(\sigma) = -\Lambda_R, \quad \lim_{\sigma \to \pm\infty} \gamma(\sigma) = -\infty,$$

then $\gamma'(\sigma_{10}) < 0 < \gamma'(\sigma_{20})$. The proof is completed. □

6.1.2 First Order of σ_1 and σ_2.

In this part, we will give the conditions of determining the first order σ_{11} and σ_{21} for $\sigma_{10} \neq \sigma_{20}$, and the explicit formulas will be given in Sect. 6.3.

Note that $\gamma(\sigma) := \gamma(\sigma, y^{[j]})$ depends on $y^{[j]} = (\phi^{[j-1,+]}, C^{[j-1,+]}, \phi^{[j,-]}, C^{[j,-]})^T$, which can be expanded as $y^{[j]} = y_0^{[j]} + y_1^{[j]} Q_2 + O(Q_2^2)$ with

$$y_0^{[j]} = (\phi_0^{[j-1,+]}, C_0^{[j-1,+]}, \phi_0^{[j,-]}, C_0^{[j,-]})^T, \quad y_1^{[j]} = (\phi_1^{[j-1,+]}, C_1^{[j-1,+]}, \phi_1^{[j,-]}, C_1^{[j,-]})^T.$$

Set $\gamma_\sigma(\sigma, y^{[j]}) = \frac{\partial}{\partial\sigma}\gamma(\sigma, y^{[j]})$ and $\gamma_y(\sigma, y^{[j]}) = \nabla_{y^{[j]}}\gamma(\sigma, y^{[j]})$.

Proposition 6.2 *For $\sigma_{10} \neq \sigma_{20} \in \mathbb{C}$, σ_{k1} is uniquely determined by*

$$\sigma_{k1} = -\frac{\gamma_y(\sigma_{k0}, y_0^{[1]})y_1^{[1]}}{\gamma_\sigma(\sigma_{k0}, y_0^{[1]})} = -\frac{\gamma_y(\sigma_{k0}, y_0^{[2]})y_1^{[2]}}{\gamma_\sigma(\sigma_{k0}, y_0^{[2]})} = -\frac{\gamma_y(\sigma_{k0}, y_0^{[3]})y_1^{[3]}}{\gamma_\sigma(\sigma_{k0}, y_0^{[3]})}. \tag{6.3}$$

Proof For $\sigma_{10} \neq \sigma_{20} \in \mathbb{C}$, we expand $\gamma(\sigma_k, y^{[j]})$ as

$$\gamma(\sigma_k, y^{[j]}) = \gamma(\sigma_{k0}, y_0^{[j]}) + \left(\gamma_\sigma(\sigma_{k0}, y_0^{[j]})\sigma_1 + \gamma_y(\sigma_{k0}, y_0^{[j]})y_1^{[j]}\right) Q_2 + O(Q_2^2).$$

Since $\gamma(\sigma_k, y^{[j]}) = \gamma(\sigma_{k0}, y_0^{[j]}) = 0$, $\gamma_\sigma(\sigma_{k0}, y_0^{[1]}) \neq 0$, $\gamma_\sigma(\sigma_{k0}, y_0^{[2]}) \neq 0$, and $\gamma_\sigma(\sigma_{k0}, y_0^{[3]}) \neq 0$, one has that σ_{k1} is uniquely determined by the linear system

$$\gamma_1(\sigma_{k1}, y^{[1]}) = \gamma_1(\sigma_{k1}, y^{[2]}) = \gamma_1(\sigma_{k1}, y^{[3]}) = 0, \tag{6.4}$$

which is equivalent to (6.3). □

Next, we will determine the zeroth order and first order terms of $\phi^{[j]}$, $c_k^{[j]}$ and J_k.

6.2 Zeroth Order Solution of (2.20)

For the zeroth order terms, we will first use the results of *limiting fast system* in Theorem 2.1 and the first two equations in (2.20) to express the intermediate intermediate such as $\phi_0^{[1,-]}$, $c_{k0}^{[1,-]}$, etc., in terms of $\phi_0^{[1]}$, $c_{k0}^{[1]}$, etc. Then, we can obtain the zeroth order solution of (2.20) by the results of *limiting slow system*.

Proposition 6.3 *Suppose $V \neq 0$. The zeroth order solution of (2.20) satisfies*

$$c_{k0}^{[j,-]} = c_{k0}^{[j,+]} = c_{k0}^{[j]}, \quad \phi_0^{[j,-]} = \phi_0^{[j,+]} = \phi_0^{[j]}, \quad u_0^{[j,-]} = u_0^{[j,+]} = 0. \tag{6.5}$$

Furthermore, (i) if $\sigma_{10}\sigma_{20} \neq 0$, then $\phi_0^{[j]}$ is uniquely determined by

$$e_0^T e^{(V-\phi_0^{[j]})D_0} L - S_L = \alpha_j g'(0),$$

and

$$C_0^{[j]} = e^{(V-\phi_0^{[j]})D_0} L, \quad J_{k0} = I_0 f_{k0}, \quad I_0 = \frac{z_1 z_2 z_3}{\sigma_{10}\sigma_{20}} F_0, \quad F_0 = -\frac{g'(0)}{H(1)}. \tag{6.6}$$

(ii) If $\sigma_{10} \neq 0$ and $\sigma_{20} = 0$, then $\phi_0^{[j]}$ is uniquely determined by

$$e_0^T \Gamma^{-1} e^{(V-\phi_0^{[j]})D_0} - \sum_{s=1}^{3} \frac{l_s}{z_s} - (V - \phi_0^{[j]})S_L = \alpha_j g''(0),$$

and

$$C_0^{[j]} = e^{(V-\phi_0^{[j]})D_0}L,\ J_{k0} = I_0 f_{k0},\ I_0 = -\frac{z_1z_2z_3}{\sigma_{10}}\sum_{s=1}^{3}\frac{J_{s0}}{z_s},\quad \sum_{s=1}^{3}\frac{J_{s0}}{z_s} = -\frac{g''(0)}{2H(1)},$$

Proof It follows from Theorem 2.1 that the zeroth order in Q_2 are as follows

$$c_{k0}^{[j,-]} = c_{k0}^{[j]}e^{-z_k(\phi_0^{[j,-]}-\phi_0^{[j]})},\quad u_0^{[j,-]} = \operatorname{sgn}(\phi_0^{[j]}-\phi_0^{[j,-]})\sqrt{\sum_{s=1}^{3}2c_{s0}^{[j]}(1-e^{z_s(\phi_0^{[j]}-\phi_0^{[j,-]})}},$$

$$c_{k0}^{[j,+]} = c_{k0}^{[j]}e^{-z_k(\phi_0^{[j,+]}-\phi_0^{[j]})},\quad u_0^{[j,+]} = \operatorname{sgn}(\phi_0^{[j,+]}-\phi_0^{[j]})\sqrt{\sum_{s=1}^{3}2c_{s0}^{[j]}(1-e_0^{z_s(\phi_0^{[j]}-\phi^{[j,+]})}}.$$

Then (6.5) can be proved directly by the matching condition $u_0^{[j,-]} = u_0^{[j,+]}$.

Next, we only prove the case $\sigma_{10}\sigma_{20}\neq 0$, the other case can be obtained similarly. By (6.1) and (6.2), we have

$$C_0^{[j]} = e^{(V-\phi_0^{[j]})D_0}L,\ J_{k0} = I_0 f_{k0},\ I_0 = \frac{z_1z_2z_3}{\sigma_{10}\sigma_{20}}F_0,$$
$$F_0 = \frac{S_L - e_0^TC_0^{[1]}}{H(x_1)} = \frac{e_0^TC_0^{[1]} - e_0^TC_0^{[2]}}{H(x_2)-H(x_1)} = \frac{e_0^TC_0^{[2]} - S_R}{H(1)-H(x_2)},$$

which leads to

$$F_0 = \frac{S_L - S_R}{H(1)} = -\frac{g'(0)}{H(1)},\quad \alpha_j g'(0) = e_0^TC_0^{[j]} - S_L.$$

The proof is completed. □

6.3 First Order Solution of (2.20)

For the first order terms, we will first express the intermediate variables such as $\phi_1^{[1,-]}$, $c_{k1}^{[1,-]}$, etc., in terms of zeroth order terms and $\phi_1^{[1]}$, $c_{k1}^{[1]}$, etc.

Lemma 6.4 *One has, for $k = 1, 2, 3$ and $j = 1, 2$,*

$$\phi_1^{[j,-]} = \phi_1^{[j]} - \frac{1}{2\sum_{s=1}^{3}z_s^2c_{s0}^{[j]}},\quad c_{k1}^{[j,-]} = c_{k1}^{[j]} + \frac{z_kc_{k0}^{[j]}}{2\sum_{s=1}^{3}z_s^2c_{s0}^{[j]}},\quad u_1^{[j,-]} = \frac{1}{2\sqrt{\sum_{s=1}^{3}z_s^2c_{s0}^{[j]}}},$$
$$\phi_1^{[j,+]} = \phi_1^{[j]} + \frac{1}{2\sum_{s=1}^{3}z_s^2c_{s0}^{[j]}},\quad c_{k1}^{[j,+]} = c_{k1}^{[j]} - \frac{z_kc_{k0}^{[j]}}{2\sum_{s=1}^{3}z_s^2c_{s0}^{[j]}},\quad u_1^{[j,+]} = \frac{1}{2\sqrt{\sum_{s=1}^{3}z_s^2c_{s0}^{[j]}}}.$$

Proof Here we only prove the case $j = 1$, the proof of $j = 2$ is similar. Recall that system (2.6) has four nontrivial first integrals given by, for $k = 1, 2, 3$,

$$H_k = c_ke^{z_k\phi},\quad H_4 = \frac{1}{2}u^2 - \sum_{s=1}^{3}c_s + Q_j\phi. \tag{6.7}$$

Substituting (3.1) into (6.7) and expanding in Q_2 to obtain, it follows from Lemma 6.3 that for the first order in Q_2,

$$c_{k1}^{[1,-]} = c_{k1}^{[1]} - z_k c_{k0}^{[1]}(\phi_1^{[1,-]} - \phi_1^{[1]}),\;\; u_0^{[1,-]}u_1^{[1,-]} = \sum_{s=1}^{3}(c_{s1}^{[1]} - c_{s1}^{[1,-]}) = 0,$$

$$c_{k1}^{[1,+]} = c_{k1}^{[1]} - z_k c_{k0}^{[1]}(\phi_1^{[1,+]} - \phi_1^{[1]}),\;\; u_0^{[1,+]}u_1^{[1,+]} = \sum_{s=1}^{3}(c_{s1}^{[1]} - c_{s1}^{[1,+]}) + \phi_0^{[1,+]} - \phi_0^{[1]} = 0,$$

which leads to

$$\phi_1^{[1,-]} = \phi_1^{[1]} + \frac{\sum_{s=1}^{3} z_s c_{s1}^{[1]}}{\sum_{s=1}^{3} z_s^2 c_{s0}^{[1]}},\;\; \phi_1^{[1,+]} = \phi_1^{[1]} + \frac{1 + \sum_{s=1}^{3} z_s c_{s1}^{[1]}}{\sum_{s=1}^{3} z_s^2 c_{s0}^{[1]}},$$

provided by $\sum_{s=1}^{3} z_s c_{s1}^{[1,-]} = \sum_{s=1}^{3} z_s c_{s1}^{[1,+]} + 1 = 0$. Then we have

$$c_{k1}^{[1,-]} = c_{k1}^{[1]} - z_k c_{k0}^{[1]} \frac{\sum_{s=1}^{3} z_s c_{s1}^{[1]}}{\sum_{s=1}^{3} z_s^2 c_{s0}^{[1]}},\;\; c_{k1}^{[1,+]} = c_{k1}^{[1]} - z_k c_{k0}^{[1]} \frac{1 + \sum_{s=1}^{3} z_s c_{s1}^{[1]}}{\sum_{s=1}^{3} z_s^2 c_{s0}^{[1]}}.$$

In order to determine $u_1^{[1,-]}$ and $u_1^{[1,+]}$, we expand (6.7) up to Q_2^2 terms to get

$$\begin{aligned}
c_{k2}^{[1,-]} &= c_{k2}^{[1]} - z_k\big(c_{k1}^{[1,-]}\phi_1^{[1,-]} - c_{k1}^{[1]}\phi_1^{[1]}\big) - \frac{1}{2}z_k^2 c_{k0}^{[1]}\big((\phi_1^{[1,-]})^2 - (\phi_1^{[1]})^2\big)\\
&\quad - z_k c_{k0}^{[1]}\big(\phi_2^{[1,-]} - \phi_2^{[1]}\big),\\
c_{k2}^{[1,+]} &= c_{k2}^{[1]} - z_k\big(c_{k1}^{[1,+]}\phi_1^{[1,+]} - c_{k1}^{[1]}\phi_1^{[1]}\big) - \frac{1}{2}z_k^2 c_{k0}^{[1]}\big((\phi_1^{[1,+]})^2 - (\phi_1^{[1]})^2\big)\\
&\quad - z_k c_{k0}^{[1]}\big(\phi_2^{[1,+]} - \phi_2^{[1]}\big),\\
\frac{1}{2}(u_1^{[1,-]})^2 + u_0^{[1,-]}u_2^{[1,-]} &= \sum_{s=1}^{3}(c_{s2}^{[1]} - c_{s2}^{[1,-]}),\\
\frac{1}{2}(u_1^{[1,+]})^2 + u_0^{[1,+]}u_2^{[1,+]} &= \sum_{s=1}^{3}(c_{s2}^{[1]} - c_{s2}^{[1,+]}) + (\phi_1^{[1,+]} - \phi_1^{[1]}),
\end{aligned}$$

which arrives at

$$u_1^{[1,-]} = \mathrm{sgn}(\phi_1^{[1]} - \phi_1^{[1,-]})\frac{\sqrt{(\sum_{s=1}^{3} z_s c_{s1}^{[1]})^2}}{\sqrt{\sum_{s=1}^{3} z_s^2 c_{s0}^{[1]}}},\;\; u_1^{[1,+]} = \mathrm{sgn}(\phi_1^{[1,+]} - \phi_1^{[1]})\frac{\sqrt{(1 + \sum_{s=1}^{3} z_s c_{s1}^{[1]})^2}}{\sqrt{\sum_{s=1}^{3} z_s^2 c_{s0}^{[1]}}}.$$

According to the matching condition $u_1^{[1,-]} = u_1^{[1,+]}$ we have $\sum_{s=1}^{3} z_s c_{s1}^{[1]} = -\frac{1}{2}$. The proof is completed. □

Proof of Lemma 3.1. Set $\phi_0^{[3]} = 0$. It follows from Proposition 6.3 and Lemma 6.4 that

$$\sum_{j=1}^{3} e^{\sigma_{k0}\phi_0^{[j]}}\gamma_y(\sigma_{k0}, y_0^{[j]})y_1^{[j]} = \frac{1}{\sigma_{k0}}\prod_{s=1}^{3}(\sigma_{k0} - z_s)(e^{\sigma_{k0}\phi_0^{[1]}} - e^{\sigma_{k0}\phi_0^{[2]}}).$$

Since

$$\gamma(\sigma_{k0}) = \sum_{j=1}^{3} e^{\sigma_{k0}\phi_0^{[j]}}\gamma(\sigma_{k0}, y_0^{[j]}),$$

it follows from $\gamma(\sigma_{k0}, y_0^{[j]}) = 0$ that

$$\sum_{j=1}^{3} e^{\sigma_{k0}\phi_0^{[j]}} \gamma_\sigma(\sigma_{k0}, y_0^{[j]}) = \gamma'(\sigma_{k0}).$$

The expression for σ_{k1} in Lemma 3.1 follows directly from (6.3). □

Proof of Lemma 3.2. Since $\sum_{s=1}^{3} c_{s1}^{[j,-]} = \sum_{s=1}^{3} c_{s1}^{[j,+]} = \sum_{s=1}^{3} c_{s1}^{[j]}$, it follows from (6.2) that

$$F_1 = -\frac{\sum_{s=1}^{3} c_{s1}^{[1]}}{H(x_1)} = -\frac{\sum_{s=1}^{3} c_{s1}^{[2]} - \sum_{s=1}^{3} c_{s1}^{[1]} + (\phi_0^{[1]} - \phi_0^{[2]})}{H(x_2) - H(x_1)} = \frac{\sum_{s=1}^{3} c_{s1}^{[2]}}{H(1) - H(x_2)},$$

which leads to $F_1 = -\frac{\phi_0^{[1]} - \phi_0^{[2]}}{H(x_3)}$. For $\sigma_{10} \neq \sigma_{20}$, a direct calculation gives

$$\tau_k = \frac{J_{k1}}{J_{k0}} = \frac{I_1}{I_0} + \frac{f_{k1}}{f_{k0}}, \quad \frac{I_1}{I_0} = \frac{F_1}{F_0} - \frac{\sigma_{11}}{\sigma_{10}} - \frac{\sigma_{21}}{\sigma_{20}}.$$

The proof is completed. □

Acknowledgements The authors thank the reviewer for the many comments and suggestions that improve the work. Ning Sun was partially supported by the Joint Ph.D. Training Program sponsored by the China Scholarship Council and a Graduate Innovation Fund of Jilin University. He thanks the Department of Mathematics at University of Kansas for its hospitality during his visit from October 2019 - June 2021 when this research is conducted. Weishi Liu was partially supported by Simons Foundation Mathematics and Physical Sciences-Collaboration Grants for Mathematicians 581822.

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