Dear Professor Sapa,

We thank you for the efforts you took to review our paper and provide critical comments. We have carefully addressed the comments, especially in explaining the derivation of the electric field. The references you provided are relevant and helpful, and we have cited them. The domain dimensions of the experiment are included in the abstract, and the jump operator is defined. We hope the revisions meet your standards.

Below we provide the point-by-point responses. All modifications of the manuscript have been highlighted in red.

Sincerely,
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Reviewer's comments

Comment 1 — ... leads to the stationary equation

$$-\nabla \cdot \left(\sum_{i=1}^{N-1} \frac{D_i C_i (z_i F)^2}{RT} \vec{E} - \sum_{i=1}^{N-1} D_i z_i F \nabla C_i \right) = 0 \,. \tag{6}$$

The authors postulate, by the paper due to Tabrizinejadas et al., 2021, that the electric field has the form

$$\vec{E} = \frac{RT \sum_{j=1}^{N-1} D_j z_j \nabla C_j}{F \sum_{k=1}^{N-1} (z_k)^2 D_k C_k} \,. \tag{7}$$

Here is a very big mistake! The formula (7) is true in the 1D case only, if for example $\sum_{i=1}^{N-1} z_i J_i = 0$ on the boundary of a domain. Then (7) is implied by (6) - see the paper:

1. Bernard P. Boudreau, Filip J.R. Meysman, Jack J. Middelburg, *Multicomponent ionic diffusion in porewaters: Coulombic effects revisited*, Earth and Planetary Science Letters 222 (2004), 653–666.

Tabrizinejadas et al., 2021 study the 1D, 2D and 3D models and they refer to the paper 1., so they are right in 1D only. I understand that the authors get some pictures, but mathematics has its laws.

Reply: We appreciate the reviewer pointing out this mistake. We agree that the divergence-free condition, Eq. (6), does not generally imply there are no fluxes, Eq. (7). We rewrite this part in section 2.1.4 to clarify that we employ the null-current condition to achieve strict local electroneutrality at all times. We also cited papers that utilized the null-current condition when modeling multicomponent transport. Please refer to the excerpts below.

2.1.4 Modeling of the electrophoretic flux

We assume the aqueous solution is locally electroneutral,

$$\sum_{i=1}^{N-1} z_i C_i = 0\,, \tag{14}$$

~~and no charge accumulates at the continuum scale of interest,~~

$$\cancel{\frac{\partial \rho_{\mathrm{E}}}{\partial t} = 0}\,.$$

~~The local electroneutrality condition~~ which is an approximation considering the Debye length (typically on the order of nanometers) vanishes at the length scale of the considered system (Dickinson et al., 2011). The electroneutrality assumption eliminates the barycentric flux term in the charge conservation equation. We consider Fickian diffusive flux, Eq. (6), and the electrophoretic flux, Eq. (10), so that the charge conservation is given by

$$\frac{\partial \rho_{\mathrm{E}}}{\partial t} = -\nabla \cdot \left(\sum_{i=1}^{N-1} \frac{D_i C_i (z_i F)^2}{RT} \boldsymbol{E} - \sum_{i=1}^{N-1} D_i z_i F \nabla C_i \right) \cancel{= 0}\,. \tag{15}$$

...

The model that combines mass conservation, Eq. (11), and ~~charge conservation, Eq. (15)~~ Poisson's equation of electrostatics, is known as the Poisson–Nernst–Planck (PNP) model (Pamukcu, 2009).

...

In this work, we enforce the null current condition

$$\sum_{i=1}^{N-1} \frac{D_i C_i (z_i F)^2}{RT} \boldsymbol{E} - \sum_{i=1}^{N-1} D_i z_i F \nabla C_i = 0 \tag{18}$$

to ensure that no charge accumulates at the continuum scale of interest,

$$\frac{\partial \rho_{\mathrm{E}}}{\partial t} = 0\,. \tag{19}$$

This results in a simplification of the PNP model. The null current condition has been utilized in modeling multicomponent ionic transport (Lichtner, 1985; Cappellen and Gaillard, 1996; Giambalvo et al., 2002; Muniruzzaman and Rolle, 2019; Cogorno et al., 2022; López-Vizcaíno et al., 2022). The combined assumptions of local electroneutrality and null current are referred to as strict electroneutrality by Lees et al., 2017. Furthermore, i~~I~~f there are no sources of the electric field (Tabrizinejadas et al., 2021), then the electric field can be represented by

$$\boldsymbol{E} = \frac{RT}{F} \frac{\sum_{j=1}^{N-1} D_j z_j \nabla C_j}{\sum_{k=1}^{N-1} (z_k)^2 D_k C_k}\,, \tag{20}$$

where we use j and k as summation indices.

Comment 2 — In 2D and 3D we can for example assume that $\vec{E}$ is an irrotational vector field, $\nabla \times \vec{E} = 0$, and then $\vec{E}$ is a potential field

$$\vec{E} = -\nabla\varphi. \tag{8}$$

This equation together with (6) imply the Poisson equation on φ of the form

$$\nabla \cdot \left(\sum_{i=1}^{N-1} \frac{D_i C_i (z_i F)^2}{RT} \nabla\varphi + \sum_{i=1}^{N-1} D_i z_i F \nabla C_i \right) = 0. \tag{9}$$

...(see Comment 3) The paper has an engineering and numerical nature, and is interesting. But the error I mentioned above must be reliably described and explained, even if the authors are currently unable to do calculations in 2D and 3D with the equation (9). I suggest to start with experiments and calculations in 1D.

Reply: Thank you for considering our paper interesting! In this work, we do not consider solving the electric potential, φ, because we utilized the null current assumption, and there is no imposed electric potential in the experiments we compared. We have explained and edited the derivations by utilizing the null current assumption, see the excerpts in Comment 1. Numerical benchmarks of multicomponent diffusion using the null current assumption in 1D and 2D are performed by Rasouli et al., 2015.

Although not explicitly stated in the paper, we did numerical tests of multicomponent diffusion of two species in 1D. The tests are named 'dg0_charge_balance_test.py' and 'dg0_exp_charge_balance_test.py', and they are located in the 'tests' folder.

Comment 3 — I refer the authors to the papers in which a similar situation appears, but with the drift u instead of the electric field $\vec{E}$:

2. B. Bożek, L. Sapa, K. Tkacz-Śmiech, M. Zajusz, M. Danielewski, *Compendium about multicomponent interdiffusion in two dimensions*, Metallurgical and Materials Transactions A 52A (2021), 3221–3231.

3. L. Sapa, B. Bożek, K. Tkacz-Śmiech, M. Zajusz, M. Danielewski, *Interdiffusion in many dimensions: mathematical models, numerical simulations and experiment*, Mathematics and Mechanics of Solids 25 (2020), 2178–2198.

4. B. Bożek, L. Sapa, M. Danielewski, *Difference methods to one and multidimensional interdiffusion models with Vegard rule*, Mathematical Modelling and Analysis 24 (2019), 276–296.

Reply: We have read the suggested work; they are helpful in addressing Comment 1. We consider the models of multicomponent interdiffusion between solids relevant to our work and have cited them in the paragraph where we discuss the mathematical properties of the PNP model.

2.1.4 Modeling of the electrophoretic flux

The PNP model aims at resolving both the electric potential and the molar concentrations, subject to the boundary conditions of the electric potential. ... Models similar to the PNP model also arise in modeling multicomponent interdiffusion of solids (Bożek et al., 2019), where the experimental comparison and the development of numerical methods are studied by Sapa et al., 2020 and Bożek et al., 2021.

Comment 4 — Moreover, the jump operator $[\bullet]$ should be defined.

Reply: We apologize for being unclear. We have made the following modifications to clarify the meaning of the jump operator. Furthermore, we specified the software packages we used to define the variational formulations.

2.2.2 Transport of fluid components

where Γ_{int} denotes the interior ~~boundaries~~ cell interfaces, $[\bullet]$ is the jump operator that evaluates the difference of a function across a common interface of two cells, and h is the distance between the cell centers. ... UFL (Alnæs, 2012) is utilized for defining the variational forms in our code implementation.

Comment 5 — It would be better to write c_i instead of C_i.

Reply: We have employed consistent definitions of our variables to make sure everything is clear. No change is made.

Comment 6 — Domain dimension in experiments and calculations should be written in Abstract.

Reply: Thank you for the comment! We think it is helpful to state the dimensions of the experiments in the abstract. Please refer to the modifications below.

Abstract

... To demonstrate the advantages of the Nernst–Planck model, we compare the simulation results of transport under reaction-driven flow conditions using the Nernst–Planck model with those of the commonly used single-diffusivity model. All simulations are also compared to well-defined experiments on the scale of centimeters. ...

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