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Alain Boldini and Maurizio Porfiri

Phys. Rev. Lett. **127**, 156001 — Published 6 October 2021

DOI: [10.1103/PhysRevLett.127.156001](https://doi.org/10.1103/PhysRevLett.127.156001)

Inversion of solvent migration in charged membranes

Alain Boldini

*Department of Mechanical and Aerospace Engineering,
New York University Tandon School of Engineering, Brooklyn, New York 11201, USA*

Maurizio Porfiri*

*Center for Urban Science and Progress, Department of Mechanical and
Aerospace Engineering, and Department of Biomedical Engineering,
New York University Tandon School of Engineering, Brooklyn, New York 11201, USA*

(Dated: August 25, 2021)

We theoretically demonstrate the possibility of inversion of solvent migration in charged membranes, opposing osmosis. Solvent migration inversion is ascribed to the finite volume of ions in the solution permeating the membrane, a quantity that has been neglected in the literature so far. We propose a model of the electrochemistry in the proximity of an electrode, illustrating the range of molar volume of ions that can yield solvent migration inversion. This study poses the basis for novel applications in micro/nanofluidics and electrochemistry, along with new inquiries in biology.

Introduction. – Charged membranes are common across natural processes and technological applications [1–3]. The presence of fixed charges on biological cell membranes has been long hypothesized by pioneering physiology studies [4], before experimental validation [5]. Their fixed charges affect the transport of solute and solvent molecules from and to the cell [6, 7], which occurs via passive diffusion across the membrane and transporter-mediated transfer [8]. On the one hand, water and other small molecules are passively transported through special protein membranes called aquaporins [9]. On the other hand, ions are exchanged through ion channels and pumps, which are at the basis of cell volume regulation [10], neural signaling [11], and muscle contraction [12].

The mechanisms underpinning the function of cell membranes have attracted the attention of physicists and material scientists, who started developing new artificial nano-structures that mimic biological membranes [13–15]. Bio-inspiration is not the sole design approach for charged membranes, whereby considerable effort has been placed over the last seventy years in the study of ionic membranes [2, 3]. In these porous membranes, coions are covalently bonded to the polymeric backbone [2]. A solution composed by counterions and solvent molecules saturates the membrane and neutralizes the fixed charge of the coions [3]. The high permselectivity and conductivity of ionic membranes [16] promoted their widespread use as selectively-permeable membranes in fuel cells [17], electro dialysis and desalination systems [18], and micro/nanofluidics devices [19].

Despite the importance of charged membranes in biological and industrial processes, the coupling between membrane electrochemistry and mechanics is still poorly understood [20]. In cell membranes, the main instance in which this coupling is considered is the study of mechanosensitive ion channels [21], which are activated or deactivated by the mechanical deformation of the membrane. However, most of the literature neglects the

stress induced by transport across the membrane and the effect of mechanical deformations on electrochemistry [22]. In ionic membranes, the coupling between mechanics and electrochemistry is better understood due to the extensive literature on ionic polymer-based actuators driven by ionic transport [23]. Electrochemomechanical treatments of ionic membranes are typically based on homogenized approaches [24–27], adapted from soft biological materials [28] and porous media [29]. The starting point of these theories is the assumption that the volume of the ions in the membrane is negligible compared to the volume of the other constituents (polymeric backbone and solvent) [25, 28, 30, 31], thereby leading to simplified coupling between electrochemistry and mechanics. To date, the validity of this hypothesis has never been challenged.

Here, we demonstrate a counter-intuitive effect in charged membranes due to the bidirectional coupling between mechanics and electrochemistry. Specifically, we predict the possibility of an inversion of the migration of solvent inside charged membranes, from higher to lower ion concentration regions, opposite to osmosis. We attribute such an inversion to the finite volume of ions in the solution permeating the membrane. Starting from a uniform, electroneutral equilibrium condition, the application of an external electric field causes electromigration of the ions, thereby generating a region with a higher ion concentration in the membrane. Accumulation of ions elicits an increase in the hydraulic pressure, which contrasts osmosis and can ultimately reverse the migration of solvent.

Model. – We consider a semi-infinite electrode, perpendicular to the x -axis of our reference frame (Fig. 1). The electrode is in contact with a semi-infinite, perfectly permselective [32] charged membrane. Without loss of generality, we consider a uniformly, negatively charged membrane, representing either a cation-exchange membrane or a rough model of the lipid bilayer [1, 2]. For

a semi-infinite membrane, symmetry and translational invariance require variables to vary only along the x direction, normal to the electrode.

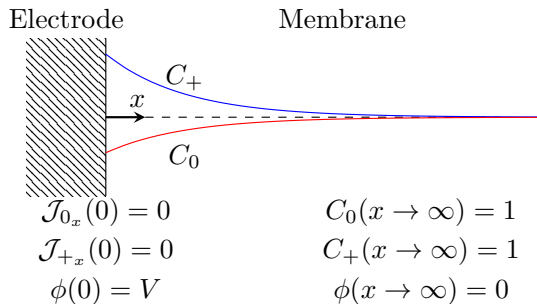


FIG. 1. Schematics of the model problem and boundary conditions, with an example of profiles of concentrations of cations (C_+ , blue) and solvent (C_0 , red) in the case of inversion of solvent migration.

We impose incompressibility of the individual constituents of the mixture (solid polymeric backbone, cations, and solvent molecules). We explicitly consider the finite volume of cations in the incompressibility constraint, which reads

$$1 + \mathcal{V}_0 (C_0 - \bar{C}_0) + \mathcal{V}_+ (C_+ - \bar{C}_+) = J, \quad (1)$$

where \mathcal{V}_0 and \mathcal{V}_+ are the molar volumes of solvent and cations, C_0 and C_+ are the concentrations of solvent and cations, \bar{C}_0 and \bar{C}_+ are the concentrations of solvent and cations in the reference electroneutral configuration, and J is the volumetric deformation of the mixture.

In the literature, the volume of cations is typically neglected ($\mathcal{V}_+=0$) [25, 30, 31], following historical practice in biomechanics and geomechanics [28, 33]. Such an assumption is accurate when considering absorption phenomena, which involve much higher uptake of solvent molecules than cations ($\bar{C}_0 = \bar{C}_+ = 0$, $C_0 \gg C_+$) [34]. By challenging the very foundation of the field, we argue that this is not the case when studying saturated media where pores are completely filled by the solution, since volume changes associated with solvent and ions could be on the same order of magnitude, $|\mathcal{V}_0(C_0 - \bar{C}_0)| \approx |\mathcal{V}_+(C_+ - \bar{C}_+)|$. Neglecting volume changes associated with ions could lead to qualitatively inaccurate predictions, even for commercial ionic membranes that constitute industry standard [35, 36].

We consider a static problem. Under the assumptions of univalent cations and a non-permeable electrode, such that the normal fluxes of solvent \mathcal{J}_{0_x} and cations \mathcal{J}_{+_x} are zero, the (electro)chemical potentials of solvent (μ_0) and cations (μ_+) [37] are constant values independent of the x coordinate ($\underline{\mu}_0$ and $\underline{\mu}_+$, respectively),

$$\mu_0(x) = \mathcal{R}\mathcal{T} \ln \left(\frac{C_0}{C_0 + C_+} \right) + \mathcal{V}_0 \pi \equiv \underline{\mu}_0, \quad (2a)$$

$$\mu_+(x) = \mathcal{R}\mathcal{T} \ln \left(\frac{C_+}{C_0 + C_+} \right) + \mathcal{V}_+ \pi + \mathcal{F} \phi \equiv \underline{\mu}_+. \quad (2b)$$

Here, \mathcal{R} is the universal gas constant, \mathcal{T} is the temperature, \mathcal{F} is the Faraday constant, π is the hydraulic pressure necessary to maintain the incompressibility constraint in Eq. (1), and ϕ is the electric potential. The hydraulic pressure is defined up to an additive constant [38], which we set to zero so that the reference configuration is stress-free.

Neglecting electrodynamic phenomena, the motion of cations in the membrane is dictated by Gauss law [39]. Assuming that the system behaves as a linear dielectric, we find the Poisson equation

$$-\epsilon \phi'' = \mathcal{F} (C_+ - C_-), \quad (3)$$

where ϵ is the dielectric constant, C_- is the concentration of fixed negative charges, assumed equal to the reference concentration of cations \bar{C}_+ , and a prime indicates a derivative with respect to x .

Equations (1), (2), and (3) represent a differential-algebraic second-order system in the variables $C_0(x)$, $C_+(x)$, $\phi(x)$, and $\pi(x)$, for which we need to specify boundary conditions. At the electrode ($x = 0$), we impose a voltage V , along with zero fluxes of solvent and cations. At infinity, we require zero electric potential, along with concentrations of solvent and cations equal to the reference configuration. By taking the limit of Eq. (2) at infinity, we find $\underline{\mu}_0 = \mathcal{R}\mathcal{T} \ln(1/(1 + \gamma))$ and $\underline{\mu}_+ = \mathcal{R}\mathcal{T} \ln(\gamma/(1 + \gamma))$, where $\gamma = \bar{C}_+/\bar{C}_0$ is the ratio of the concentrations of cations and solvent in the reference configuration.

The effect of the volumetric deformation J on electrochemistry is determined by mechanical equilibrium, which in the absence of body forces at steady-state requires the stress tensor to be divergence free [40]. Following common practice in the literature of ionic membranes [26, 31], we assume an additive decomposition of the stress tensor into three contributions: the mechanical stress, the eigenstress associated with hydraulic pressure, and the eigenstress related to Maxwell stress. We hypothesize that the mixture behaves as a linear isotropic material with Lamé parameters μ_{mec} and λ_{mec} [41], and we neglect the deformability of the electrode. Due to symmetry, the only non-zero component of the strain tensor is ε_{xx} . Thus, under the assumption of small deformations, we write $J = 1 + \varepsilon_{xx}$ [40].

Equilibrium requires σ_{xx} to be constant,

$$\sigma_{xx}(x) = (\lambda_{\text{mec}} + 2\mu_{\text{mec}})\varepsilon_{xx} - \pi + \frac{\epsilon}{2}(\phi')^2 \equiv \underline{\sigma}_{xx}. \quad (4)$$

Here, $(\lambda_{\text{mec}} + 2\mu_{\text{mec}})\varepsilon_{xx}$ is the mechanical stress, $-\pi$ is the eigenstress generated by the hydraulic pressure, and $\epsilon(\phi')^2/2$ is the eigenstress related to Maxwell stress. At infinity, the membrane is stress-free, so that $\underline{\sigma}_{xx} = 0$. Thus, from Eq. (4) we can express the strain $\varepsilon_{xx}(x)$ as a

function of $\pi(x)$ and $\phi(x)$, obtaining the incompressibility constraint in Eq. (1) as a function of $C_+(x)$, $C_0(x)$, $\phi(x)$, and $\pi(x)$ only,

$$\mathcal{V}_0 (C_0 - \bar{C}_0) + \mathcal{V}_+ (C_+ - \bar{C}_+) = \frac{1}{\lambda_{\text{mec}} + 2\mu_{\text{mec}}} \left(\pi - \frac{\epsilon}{2} (\phi')^2 \right). \quad (5)$$

The solution of Eqs. (2), (3), and (5) with the appropriate boundary conditions can be reduced to a nonlinear second-order differential equation for the pressure $\pi(x)$, see Supplemental Material [42].

Results. – We focus on the linear regime, where we apply a voltage $V \ll V_{\text{th}}$ to the electrode, with $V_{\text{th}} = \mathcal{RT}/\mathcal{F}$ being the thermal voltage. We linearize the nonlinear second-order differential equation for the pressure around $\pi(x) = 0$, corresponding to the initial equilibrium with $C_0 = \bar{C}_0$, $C_+ = \bar{C}_+$, and $\phi = 0$. We obtain the following ordinary differential equation:

$$\pi'' - \frac{\beta^2}{\lambda_{\text{D}}^2} \pi = 0, \quad (6)$$

where $\lambda_{\text{D}} = \frac{1}{\mathcal{F}} \sqrt{\frac{\epsilon \mathcal{RT}}{C_+}}$ is the Debye screening length [43, 44], and

$$\beta = \sqrt{\frac{\mathcal{RT} \bar{C}_+ + (1 + \gamma)(\lambda_{\text{mec}} + 2\mu_{\text{mec}}) \bar{C}_0^2 \mathcal{V}_0^2}{(\lambda_{\text{mec}} + 2\mu_{\text{mec}})(\bar{C}_0 \mathcal{V}_0 + \bar{C}_+ \mathcal{V}_+)^2}} \quad (7)$$

is a positive nondimensional parameter that scales the size of the double layer. This parameter is on the order of 1 for typical ionic membranes with water solvent. The solution of Eq. (6) is the sum of two exponential functions. By neglecting the diverging exponential at $x \rightarrow \infty$, we find

$$\pi(x) = \mathcal{RT} \bar{C}_+ \Pi e^{-\beta x / \lambda_{\text{D}}}, \quad (8)$$

where $\Pi = -\mathcal{F}V / (\mathcal{RT}(\bar{C}_0 \mathcal{V}_0 + \bar{C}_+ \mathcal{V}_+))$ is a constant whose value is determined by matching the voltage at the electrode surface ($\phi(0) = V$).

The voltage profile is retrieved as

$$\phi(x) = V e^{-\beta x / \lambda_{\text{D}}}, \quad (9)$$

whereas the concentration of cations reads

$$C_+(x) = \bar{C}_+ \left(1 - \beta^2 \frac{\mathcal{F}V}{\mathcal{RT}} e^{-\beta x / \lambda_{\text{D}}} \right). \quad (10)$$

These expressions ensure that $\phi(x)$ and $C_+(x)$ have boundary layers with opposite trend, whereby a positive (negative) voltage applied to the electrode induces a reduction (increase) in the concentration of cations, as one would expect from a classical Poisson-Nernst-Planck system [45–47].

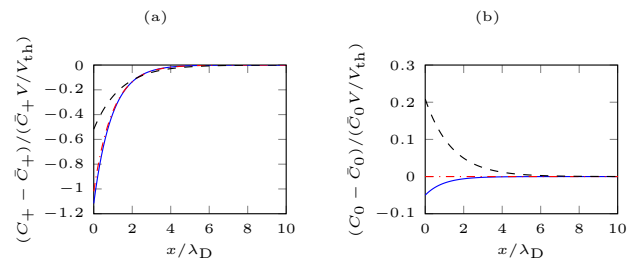


FIG. 2. Profile of differences in concentration of cations (a) and solvent (b) with respect to the reference configuration in the vicinity of the electrode, per unit applied voltage. Concentrations are defined per unit volume of undeformed mixture. The blue solid line, red dash-dotted line, and black dashed line indicate $\mathcal{V}_+ = 0$, $\mathcal{V}_+ = \mathcal{V}_+^{\text{thr}}$, and $\mathcal{V}_+ = 10\mathcal{V}_+^{\text{thr}}$, respectively. Concentrations are nondimensionalized by the corresponding value in the reference configuration, while the distance from the electrodes and the applied voltage are scaled by the Debye screening length and the thermal voltage, respectively. In these plots, $\gamma = 1/15$, $(\lambda_{\text{mec}} + 2\mu_{\text{mec}})/(\mathcal{RT} \bar{C}_+) = 190$, and $\mathcal{V}_0 \bar{C}_0 = 0.32$, which are typical of an ionic membrane with water solvent, see Supplemental Material [42].

The profile of solvent concentration shows an interesting dependence on the parameters of the problem. Specifically, we obtain

$$C_0(x) = \bar{C}_0 \left(1 - \delta \frac{\mathcal{F}V}{\mathcal{RT}} e^{-\beta x / \lambda_{\text{D}}} \right), \quad (11)$$

where

$$\delta = \frac{\mathcal{RT} \bar{C}_+ - (1 + \gamma)(\lambda_{\text{mec}} + 2\mu_{\text{mec}}) \bar{C}_0 \bar{C}_+ \mathcal{V}_0 \mathcal{V}_+}{(\lambda_{\text{mec}} + 2\mu_{\text{mec}})(\bar{C}_0 \mathcal{V}_0 + \bar{C}_+ \mathcal{V}_+)^2} \quad (12)$$

is a nondimensional parameter that modulates the redistribution of solvent near the electrode. For $\delta > 0$, solvent migration is concurrent to that of cations, whereby the concentration of solvent decreases for positive applied voltages and increases for negative applied voltages. This phenomenon is associated with osmotic effects within the membrane and is well-documented in the literature [24, 48]. However, if $\delta < 0$, solvent concentration follows the opposite trend of the concentration of cations. This inversion determines migration of solvent from higher to lower cation concentration regions, opposite to osmosis.

We attribute the inversion of solvent migration to finite volume effects of cations in the solution permeating the ionic membrane. In fact, imposing $\mathcal{V}_+ = 0$ yields $\delta > 0$ for any combination of parameters, thus making solvent migration inversion impossible. On the contrary, by increasing \mathcal{V}_+ , we register a progressive decrease in the motion of solvent concurrent with cations (Fig. 2), due to the more significant effect of the hydraulic pressure in the cation pile-up region.

Solvent migration is completely inhibited ($\delta = 0$, see

Fig. 2) for

$$\mathcal{V}_+^{\text{thr}} = \frac{RT}{(\bar{C}_0 + \bar{C}_+)(\lambda_{\text{mec}} + 2\mu_{\text{mec}})\mathcal{V}_0}. \quad (13)$$

For values of \mathcal{V}_+ over this threshold, we record $\delta < 0$, corresponding to the solvent migration inversion regime (Fig. 2). Interestingly, for typical parameters of an ionic membrane with water as a solvent [49], this threshold is $\mathcal{V}_+^{\text{thr}} \approx 1.3 \times 10^{-5} \text{ m}^3/\text{mol}$, which is slightly above the molar volume of potassium ions [50]. Thus, when an ionic membrane is neutralized by a solution of ions with a molar volume lower than this threshold, such as sodium, water migrates as one would expect from osmosis. For neutralizing solutions of ions larger than potassium, such as cesium, we expect an inversion in the direction of solvent migration. An indirect evidence of this behavior could be drawn from actuators based on ionic membranes [23]. For the same applied voltage, actuators neutralized by small ions show steady-state curvatures of opposite sign compared to actuators neutralized by large ions [51]. In the Supplemental Material [42], we demonstrate that an extension of our model to actuators based on ionic membranes can predict the change in steady-state curvature observed in experiments.

Equation (13) highlights the material and electrochemical characteristics that favor the inversion of solvent migration. We find that membranes with higher charge and solvent densities and higher stiffness facilitate the inversion of migration of solvent molecules, which could occur with cations with a smaller molar volume. Interestingly, we observe that Eq. (12) depends symmetrically on the molar volume of solvent and of cations. Thus, solvent migration inversion will be more significant for solvents with higher molar volume, for which the threshold in Eq. (13) decreases.

Solvent migration inversion is accompanied by a modest reduction of the modulus of the eigenstress due to the pressure π [52]. In fact, the presence of non-zero volume of cations causes a decrease of the constant Π in Eq. (8). Figure 3(a) shows a parametric analysis of the pressure at the electrode for varying \mathcal{V}_0 and \mathcal{V}_+ . For a positive applied voltage, we always record a negative pressure, which decreases for higher values of either \mathcal{V}_0 or \mathcal{V}_+ . In this case, a negative pressure indicates a pressure smaller than the one at infinity. The pressure has a singularity at $\mathcal{V}_0 = \mathcal{V}_+ = 0$, corresponding to infinitesimal solution volume.

Our results are not an artifact from the definition of concentrations per unit reference volume of mixture, in place of the concentrations of solvent \mathcal{C}_0 and cations \mathcal{C}_+ per unit volume of solution permeating the membrane that are typically used in the electrochemistry literature [28] [53]. These quantities are found from their counterparts C_0 and C_+ by dividing by the referential volume fraction of solution $\mathcal{V}_0 C_0 + \mathcal{V}_+ C_+$. We define the variations $\Delta\mathcal{C}_0$ and $\Delta\mathcal{C}_+$ of the concentrations of solvent and

cations per unit volume of solution with respect to their values in the reference configuration, $\bar{C}_0/(\mathcal{V}_0 C_0 + \mathcal{V}_+ C_+)$ and $\bar{C}_+/(\mathcal{V}_0 C_0 + \mathcal{V}_+ C_+)$, respectively. In addition, we consider the solution volume fractions of solvent and cations, which are defined as $\chi_0 = \mathcal{V}_0 C_0$ and $\chi_+ = \mathcal{V}_+ C_+$, along with their variations $\Delta\chi_0$ and $\Delta\chi_+$ from their values in the reference configuration, $\mathcal{V}_0 \bar{C}_0/(\mathcal{V}_0 \bar{C}_0 + \mathcal{V}_+ \bar{C}_+)$ and $\mathcal{V}_+ \bar{C}_+/(\mathcal{V}_0 \bar{C}_0 + \mathcal{V}_+ \bar{C}_+)$, respectively.

In the linear regime, we find

$$\Delta\mathcal{C}_0 = \frac{\bar{C}_0 \bar{C}_+ \mathcal{V}_0 \mathcal{V}_+}{(\mathcal{V}_0 \bar{C}_0 + \mathcal{V}_+ \bar{C}_+)^3} (\bar{C}_0 + \bar{C}_+) \frac{\mathcal{FV}}{\mathcal{RT}} e^{-\beta x/\lambda_D}, \quad (14a)$$

$$\Delta\mathcal{C}_+ = -\frac{\bar{C}_0 \bar{C}_+ \mathcal{V}_0^2}{(\mathcal{V}_0 \bar{C}_0 + \mathcal{V}_+ \bar{C}_+)^3} (\bar{C}_0 + \bar{C}_+) \frac{\mathcal{FV}}{\mathcal{RT}} e^{-\beta x/\lambda_D}, \quad (14b)$$

and

$$\Delta\chi_0 = -\Delta\chi_+ = \frac{\bar{C}_0 \bar{C}_+ \mathcal{V}_0^2 \mathcal{V}_+}{(\mathcal{V}_0 \bar{C}_0 + \mathcal{V}_+ \bar{C}_+)^3} (\bar{C}_0 + \bar{C}_+) \frac{\mathcal{FV}}{\mathcal{RT}} e^{-\beta x/\lambda_D}. \quad (15)$$

In Fig. 3(b), we show a parametric analysis of $\Delta\chi_0$ at the electrode, as a function of \mathcal{V}_0 and \mathcal{V}_+ . $\Delta\mathcal{C}_0$ and $\Delta\chi_0$ only differ by a factor \mathcal{V}_0 , and in particular they have the same sign. Since $\Delta\chi_0 \geq 0$, the concentration of solvent and its volumetric fraction per unit volume of solution both increase for a positive voltage. While $\Delta\mathcal{C}_0$ is dominated by a singularity for $\mathcal{V}_0 = \mathcal{V}_+ = 0$, similar to the pressure in Fig. 3(a), the variation in the volumetric fraction of solvent is free of singularity. In this case, the symmetry in the contributions of the molar volumes breaks down, as evidenced by Eq. (15) and Fig. 3(b). Independent on the definition of concentrations, let them be per unit reference volume of mixture or per unit volume of solution, we register the possibility of migration of solvent in the direction opposite to that expected from osmosis.

Our formulation encompasses excluded volume effects necessary to contain the packing of solute and solvent molecules, especially for large solute molecules [54–56]. From their definition, \mathcal{C}_0 and \mathcal{C}_+ are bound by $1/\mathcal{V}_0$ and $1/\mathcal{V}_+$, corresponding to the number of moles per unit volume of solvent and cations, respectively. Interestingly, the boundedness of these quantities does not prevent the concentrations of solvent \mathcal{C}_0 and cations \mathcal{C}_+ per unit volume of mixture to grow unbounded, as the volume of the mixture increases according to Eq. (1). In the Supplemental Material [42], we prove that, for a rigid membrane, our formulation reduces to a modified Poisson-Boltzmann equation that accounts for the finite volume of cations [57].

The role of steric effects becomes prominent in the non-linear regime. For positive applied voltages, we observe depletion of cations near the electrode, with inversion of solvent migration for values of \mathcal{V}_+ higher than in the linear case. For negative applied voltages, we register remarkable pile-up of cations, with a significant depletion

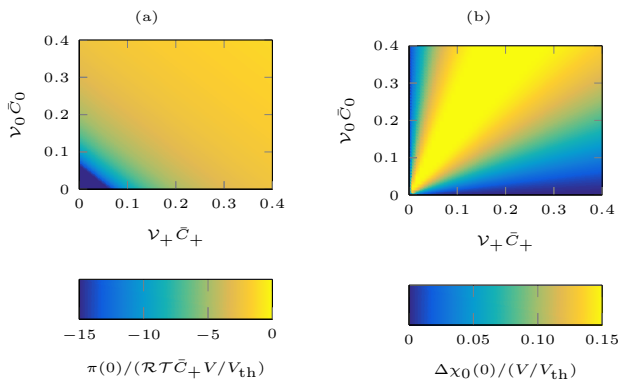


FIG. 3. Contour plots of (a) the pressure at the electrode and (b) the difference in volume fraction of solvent with respect to the reference configuration at the electrode, as a function of the molar volumes of cations and solvent, per unit applied voltage. Volume fractions are defined per unit volume of solution. Pressures are nondimensionalized with respect to $\mathcal{RT}\bar{C}_+$, while the applied voltage is scaled by the thermal voltage. Note that in (a) the maximum absolute value of $\pi(0)$ (which diverges for $\mathcal{V}_0 = \mathcal{V}_+ = 0$) has been limited for illustration purposes. In these plots, $\gamma = 1/15$, which is typical of an ionic membrane with water solvent, see Supplemental Material [42].

of solvent. Predictably, the concentration of cations is at most $1/\mathcal{V}_+$. More details on the nonlinear solution are in the Supplemental Material [42].

Conclusions.— The inclusion of the molar volume of ions in the incompressibility constraint in Eq. (1), systematically neglected in the literature [25, 30, 31], can significantly affect transport within charged membranes. In this Letter, we demonstrate the existence of a threshold for the molar volume of ions above which we record an inversion of solvent migration, in the direction opposite to that expected from osmosis. While this phenomenon shares similarities with reverse osmosis and analogous separation processes [58], it is fundamentally different as it occurs within the membrane and not across. Solvent migration inversion is linear in nature, whereby it occurs even for infinitesimal variations in solute concentration.

The results of our study have direct implications in the field of separation processes and electrochemistry. We envision new filtration and particle concentration processes in microfluidics and nanofluidics [59], due to the possibility of localizing the inversion of solvent migration [60]. These fields constitute the ideal test-bed for an experimental validation of our results, building upon previous studies that experimentally demonstrated the emergence of solvent migration from high to low concentrations of solute in nanochannels [61].

Although our model is only a rough approximation of the lipid bilayer, our results pave the way for new inquiries on biological membranes, toward the inclusion of bidirectional coupling between membrane mechanics and

electrochemistry. Similar investigations are needed to verify the effect of membrane deformations on the transport of ions, macromolecules, and water across the membrane through extended continuum or molecular dynamics simulations [22]. We anticipate that solvent migration inversion could interact with cell volume regulation mechanisms [10]. To study such interaction, one could modify the classical Goldman-Hodgkin-Katz system [1] to account for mechanical deformations of the membrane during ionic transport.

While making analytical solution feasible, the simplicity of our model warrants future efforts to extend the validity of our results. Non-idealities in the behavior of solutions in porous media [62], which were not considered herein, could potentially affect the motion of solvent and solute. For ions, polar molecules, and macromolecules, solvation could play a significant role by affecting solvent co-transport [50, 63]. Finally, further studies are required to assess the consequences of solvent migration inversion on multiphase flows [64].

The authors acknowledge financial support from the National Science Foundation under grant No. OISE-1545857.

* mporfiri@nyu.edu

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