Computational analysis of electric field effects on electrodialysis for enhanced desalination processes

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Abstract   This study elucidates the technologies employed in membrane-based water purification processes. The theoretical underpinnings of semipermeable membrane functionalities are expounded upon through the lens of Onsager's reciprocal relations in non-equilibrium thermodynamics, delineating the fluxes and the driving forces that instigate them. Utilising a simplified Onsager matrix tailored for the ion-exchange membrane electrodialysis process, computational fluid dynamics (CFD) simulations were conducted. The computations presented herein depict the intricacies of both dialysis and electrodialysis in saline water solutions.

Keywords: Membranes; CFD; Electrodialysis; Onsager relations

1   Introduction

Desalination constitutes the technologically-mediated extraction of saline and mineral constituents from marine or brackish water sources, rendering the resultant fluid suitable for potable or industrial applications. A myriad of desalination technologies are extant [1]:

1. Reverse Osmosis (RO): Predominantly, this modality stands as the epitome of energy-efficient desalination, particularly when meticu-

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lously optimised and deployed in locales with constrained freshwater availability.

2. Electrodialysis (ED): This technique excels in the treatment of low-salinity aqueous solutions and may surpass distillation in energy efficiency, albeit falling short in efficiency compared to RO for high-salinity matrices.

3. Heat Pump-Assisted Vacuum Distillation: The incorporation of a heat pump substantially augments the thermodynamic efficiency of the distillation process.

4. Multi-Stage Flash Distillation (MSF).

5. Cryogenic Desalination.

Cutting-edge membrane technologies, distinguished for their energy efficiency, are increasingly prevalent in the domains of fluid filtration and purification [2, 3]. These technologies employ a gamut of physical mechanisms to facilitate the membrane transport of particulates. Inherent and passive transport modalities are governed by osmotic pressure interactions (osmosis) and solute concentration gradients (dialysis). Moreover, externally applied active forces, such as mechanical pressure and electrostatic fields, can also instigate membrane particulate transport.

Osmosis, Reverse Osmosis (RO), Electrodialysis, and Dialysis are distinct membrane-mediated processes, each with unique operational principles and applications, despite their apparent similarities [2]:

- Osmosis is a spontaneous phenomenon where a solvent, predominantly water, traverses a semi-permeable membrane towards a region of higher solute concentration, aiming to achieve osmotic pressure equilibrium. This process is fundamental in various biological systems, including plant water uptake and cellular activities.

- Dialysis facilitates the selective permeation of dissolved substances through a membrane based on molecular size and electrostatic charge. This technique is pivotal in medical applications, notably in renal dialysis, where it substitutes for impaired kidney functions.

- Electrodialysis employs ion-exchange membranes to segregate ions and dissolved substances, leveraging their intrinsic electric charges.

An applied electric current facilitates ion migration across the membrane, making it instrumental in various industrial applications, including water desalination and chemical separation.

- Reverse Osmosis (RO) is an engineered process that employs external pressure to propel a solvent through a semi-permeable membrane, counter to the direction dictated by natural osmotic pressure. RO is extensively utilized in desalination technologies and potable water recovery from lower-salinity sources.

At present, membrane technologies are utilized in thermal energy applications for the preparation of fuels and also in the domain of oxidizer purification and separation [4]. Additionally, membranes are deployed in the purification of combustion by-products and in carbon dioxide capture processes [5].

2   Mathematical model of membrane processes in a thermodynamic framework

Membrane processes are described by mass, momentum, and energy balance equations. Additional relationships, such as Maxwell's equations or chemical reactions, may serve as supplements to the fundamental equations used in describing issues related to transport through membranes. Below are the general equations describing transport through a membrane, which can then be further specified depending on the transport process being modelled. In the dialysis process, the governing equations are those of mass, momentum, and energy balance, as presented below [3,6,7].

Mass balance equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \tag{1}$$

where: ρ – density, $\mathbf{v}$ – velocity, t – time.

Momentum balance equation:

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla P + \rho g + \nabla \cdot \mathbf{T} + \rho \mathbf{F}_{\text{elmag}}, \tag{2}$$

where: P – pressure, g – gravity vector, $\mathbf{T}$ – shear stress tensor, $\mathbf{F}_{\text{elmag}}$ – electromagnetic force.

Energy balance equation:

$$\rho c \left(\frac{\partial T}{\partial t} + (\mathbf{v} \cdot \nabla) \, \mathbf{T} \right) = -\mathbf{P} \nabla \cdot \mathbf{v} + \nabla \cdot (k \nabla T) + Q_{\text{heat}} + Q_{\text{elmag}} \,, \quad (3)$$

where: T – fluid temperature, c – heat capacity of the fluid, k – thermal conductivity of the fluid, Q_{heat} – heat flux originating from chemical reactions or other processes, Q_{elmag} – heat flux introduced due to electromagnetic field interactions.

To model membrane processes in an electromagnetic field environment, Maxwell's equations are introduced [8].

Gauss's law for electric field:

$$\nabla \cdot E = \frac{\rho_e}{\varepsilon_o} \,, \quad (4)$$

Gauss's law for magnetic field:

$$\nabla \cdot B = 0 \,, \quad (5)$$

Faraday's law of electromagnetic induction:

$$\nabla \times E = -\frac{\partial E}{dt} \,, \quad (6)$$

Ampère's law with conductance:

$$\nabla \times B = \mu_0 J + \mu_0 \varepsilon_o \frac{\partial E}{dt} \,, \quad (7)$$

where: E – electric field, B – magnetic field, ρ_e – electric charge density, J – electric current density, ε_o – electric permittivity in vacuum, μ_0 – magnetic permeability in vacuum, t – time, $\nabla\cdot$ – divergence, $\nabla\times$ – curl.

For the above equations, the general Onsager relations (Fourth Law of Thermodynamics) can be written in matrix form, describing non-equilibrium phenomena occurring in membrane systems interacting with an electromagnetic field [6, 7, 9, 10]:

$$\begin{bmatrix} J_v \\ J_m \\ J_C \\ J_q \\ J_e \\ J_b \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} & L_{13} & L_{14} & L_{15} & L_{16} \\ L_{21} & L_{22} & L_{23} & L_{24} & L_{25} & L_{26} \\ L_{31} & L_{32} & L_{33} & L_{34} & L_{35} & L_{36} \\ L_{41} & L_{42} & L_{43} & L_{44} & L_{45} & L_{46} \\ L_{51} & L_{52} & L_{53} & L_{54} & L_{55} & L_{56} \\ L_{61} & L_{62} & L_{63} & L_{64} & L_{65} & L_{66} \end{bmatrix} \begin{bmatrix} -\nabla P_m \\ -\nabla P_o \\ -\nabla C \\ -\nabla T \\ -\nabla E \\ -\nabla B \end{bmatrix} \,, \quad (8)$$

where: J_v – volumetric flux induced by the mechanical pressure gradient $-\nabla P_m$, J_m – volumetric flux induced by the osmotic pressure gradient $-\nabla P_o$, J_C – volumetric flux induced by the concentration gradient ∇C, J_q – heat flux induced by the temperature gradient ∇T, J_e – electric charge flux induced by the electric field gradient ∇E, J_b – magnetic flux induced by the magnetic field gradient $-\nabla B$.

In the electrodialysis process, it is assumed that only the concentration gradient and the electric field are present, serving as stimuli for ion flow through the membrane system. The general Onsager matrix simplifies to a two-dimensional matrix due to these two stimuli:

$$\begin{bmatrix} J_C \\ J_e \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} -\nabla C \\ -\nabla E \end{bmatrix}. \tag{9}$$

The individual flux equations are represented as:

$$J_C = \frac{dC}{dt} \quad \text{and} \quad J_e = \frac{dq}{dt}, \tag{10}$$

$$\begin{cases} \dfrac{dC}{dt} = -L_{11}\nabla C - L_{12}\nabla E\,, \\[2mm] \dfrac{dq}{dt} = -L_{21}\nabla C - L_{22}\nabla E\,. \end{cases} \tag{11}$$

For each i-th component of the fluid, the equations can be written as:

$$\frac{dC_i}{dt} = D_i \nabla C_i + FC_i z_i u_{m,i} \nabla E, \tag{12}$$

$$\frac{dq}{dt} = I = F \sum_i \left(-FC_i z_i^2 u_{m,i} \right) \nabla E, \tag{13}$$

$$I = -k\nabla E. \tag{14}$$

The Onsager matrix coefficients are (assuming that the cross-effect of concentration on electric current is neglected $L_{21} = 0$)

$$L_{11} = D_i\,, \tag{15}$$

$$L_{12} = FC_i z_i u_{m,i}\,, \tag{16}$$

$$L_{22} = k = F \sum_i \left(-FC_i z_i^2 u_{m,i} \right). \tag{17}$$

3   Computational fluid dynamics calculations of the electrodialysis process for saline water

Computational fluid dynamics (CFD) calculations were performed assuming three computational domains, with the fluids bordering a membrane on which electrodes were placed to induce salt ion transport. The assumptions are as follows [2]:

- For the dialysate and permeate in the steady state, the equation includes convective, diffusive, and migration terms influenced by the electric field:

$$\nabla \cdot \left(-D_i \nabla C_i - F C_i z_i^2 u_{m,i} \nabla E \right) + \mathbf{u} \cdot \nabla C_i = 0. \tag{18}$$

- For the membrane in the steady state, the equation includes diffusive and migration terms influenced by the electric field:

$$\nabla \cdot \left(-D_i \nabla C_i - F C_i z_i^2 u_{m,i} \nabla E \right) = 0. \tag{19}$$

The electric field interacts only within the membrane area due to the placement of electrodes at the membrane boundaries. The equation describing the electric field in the steady state is [2]:

$$\nabla \cdot \left(\varepsilon_0 \varepsilon_r \nabla E \right) = 0. \tag{20}$$

On both boundary conditions for the electric field, it is assumed that $E = V$, which is consistent with the notations in Fig. 1. The following assumptions were made: $D_i = 10^{-9} \ \text{m}^2/\text{s}$ for both the fluid and membrane regions, relative electrical permittivity for water $\varepsilon_r = 80$, moblility $u_{m,i} = 0.000001 \ \text{s mol/kg}$, charge number $z_i = 10 \ \text{l}$, and F is Faraday's constant.

Discontinuities at the phase boundary between the membrane and the fluid are described by the following relations [2]:

- Between the dialysate and the membrane:

$$\left(-D_d \nabla C_1 - F C_1 z_i^2 u_{m,i} \nabla E + C_1 \mathbf{u} \right) \cdot \mathbf{n} = M \left(C_2 - K C_1 \right), \tag{21}$$

$$\left(-D_m \nabla C_2 - F C_2 z_i^2 u_{m,i} \nabla E \right) \cdot \mathbf{n} = M \left(K C_1 - C_2 \right). \tag{22}$$

- Between the membrane and the permeate:

$$\left(-D_m \nabla C_2 - F C_2 z_i^2 u_{m,i} \nabla E \right) \cdot \mathbf{n} = M \left(K C_3 - C_2 \right), \tag{23}$$

$$\left(-D_p \nabla C_3 - F C_3 z_i^2 u_{m,i} \nabla E + C_3 \mathbf{u} \right) \cdot \mathbf{n} = M \left(C_2 - K C_3 \right), \tag{24}$$
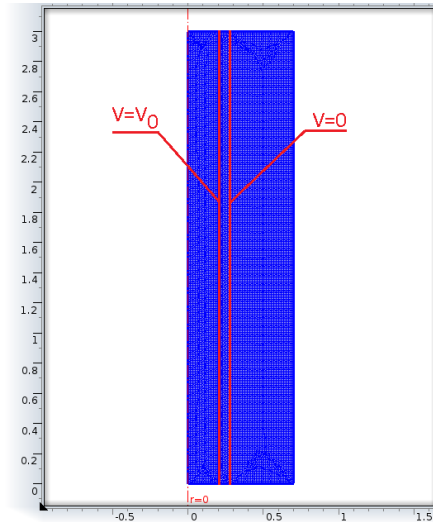
where $K = 0.7$ and $M = 1e^4 \ \text{m/s}$.

Figure 1: Geometry of the membrane system and boundary conditions for the electric field.

The meshing parameters (Fig. 1) for this process include several key settings. Firstly, the "Maximum Element Growth Rate" is set to 1.3, limiting the allowed increase in mesh element size from one region to another. A higher value would permit more significant size variation. Secondly, the "Resolution of Curvature" is established at 0.3, indicating a finer mesh resolution around curved features for improved accuracy. In contrast, the "Resolution of Narrow Regions" is set to 2, specifying a moderate level of refinement for tight geometry areas. Additionally, a "Minimum Element Size" of 0.0009 is enforced to prevent excessively small elements. Finally, the chosen mesh generation method is the "Free Triangular Delaunay", which employs Delaunay triangulation to create high-quality triangular elements without predefined shapes, ensuring flexibility in mesh generation. These parameters collectively govern the mesh quality and adaptability to meet specific modelling and simulation requirements.

The solver employed for solving the electrostatic equations is MUMPS (Multifrontal Massively Parallel Sparse direct Solver) [11], which is known for its efficiency in handling sparse linear systems in parallel computing environments. In contrast, the PARDISO [11] solver is utilized for solving equations related to diluted species, providing a specialized approach for this type of problem.

Figures 3 and 4 present the modelling results of the electrodialysis process when the electric field is activated (Fig. 4). Electrodes generating the
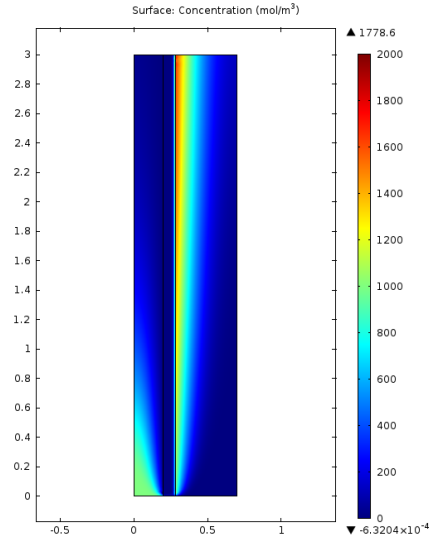

Figure 3: Calculations of transport intensification through the membrane due to the applied electric field.
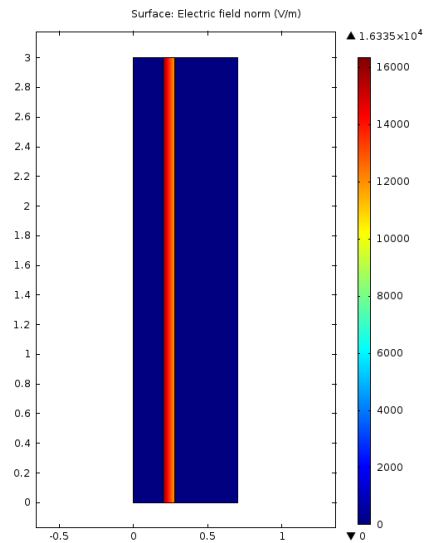

Figure 4: Electric field resulting from the interaction of electrodes placed at the membrane boundaries.

electric field are placed at the membrane boundaries, intensifying the salt
ion transport into the permeate space (Fig. 3).

The results presented in Figs. 3 and 4 illustrate the impact of the electric
field on the process of salt ion transport through the membrane. The in-
fluence of the electric field operating within the membrane region enhances
mass exchange. Reduced salt solution concentrations in water are observed
at the dialysate-membrane phase boundary. Additionally, an increase in
concentration is evident in the solid-liquid phase boundary region at the
membrane-permeate interface. Comparing the calculation results (Fig. 5),
it is clear that the effluent (purified) liquid exhibits significantly lower salt
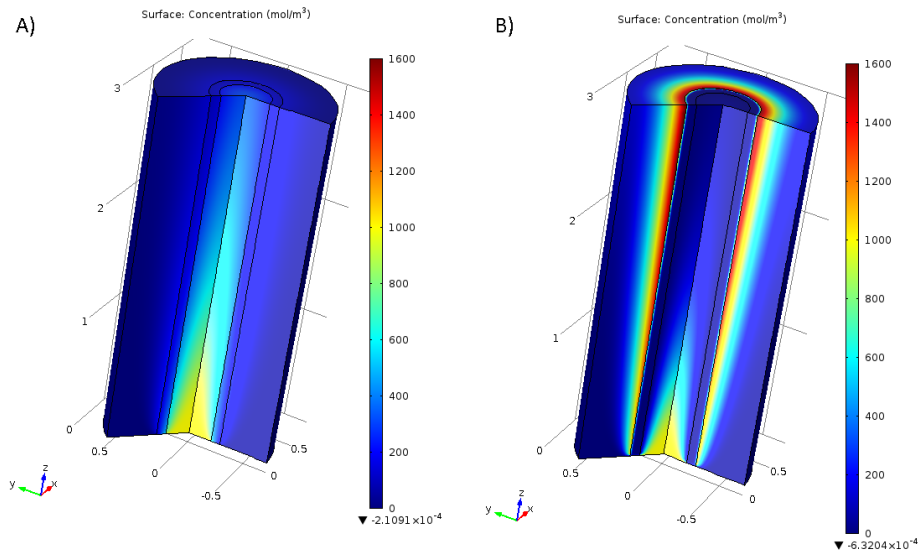concentrations in the presence of an electric field.

Figure 5: Calculation results in 3D geometry for the dialysis (A) and electrodialysis (B)
membrane system.

4   Summary

This study focuses on modelling the impact of an electric field in the elec-
trodialysis process, aiming to intensify desalination procedures. The paper
presents:

1. Description of membrane technologies: Various desalination technolo-
gies such as reverse osmosis, electrodialysis, vacuum distillation with

a heat pump, multi-stage distillation, and cryogenic desalination are discussed. It is pointed out that membrane technologies are currently the most energy-efficient in the field of fluid filtration and purification.

2. Theoretical foundations of membrane operations: Differences between osmosis, dialysis, electrodialysis, and reverse osmosis are presented. Attention is drawn to particle transport mechanisms through the membrane, such as osmotic pressure, concentration differences, and active interactions.

3. Mathematical model of membrane processes: Membrane processes are described in the context of mass, momentum, and energy balance equations. Maxwell's equations, which describe electromagnetic interactions in membrane systems, are introduced. Onsager's relations, describing non-equilibrium issues in membrane systems under the influence of an electromagnetic field, are also presented.

4. CFD calculations of electrodialysis in saline water: Modeling results of electrodialysis in the absence and presence of an electric field are presented. The results show that the electric field intensifies the transport of salt ions through the membrane, leading to more efficient desalination.

The study proves that the electric field can significantly impact the efficiency of the electrodialysis process, which is crucial for the industry of water purification and seawater desalination.

Received 5 October 2023

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