Limiting current density in the electrodialysis of multi-ionic solutions

Vítor Geraldes*, Maria Diná Afonso

Technical University of Lisbon, Instituto Superior Técnico, Department of Chemical and Biological Engineering/ICEMS, Av. Rovisco Pais, 1, 1049-001 Lisbon, Portugal

ABSTRACT

The aim of this work was the development of an explicit model to estimate the limiting current density in the electrodialysis of dilute multi-ionic solutions. The model assumes that the ionic transport occurs in a film layer adjacent to an ion exchange membrane and it is quantified by a linearized form of the Nernst–Planck (NP) equations together with the electroneutrality requirement at the solution/ion exchange membrane interface. An explicit expression for the limiting current density of a dilute multi-ionic solution was derived, involving a mass-transfer coefficient based on an effective diffusivity of the multi-ionic solution. The model further assumes that the steric exclusion of the ions by the membrane is negligible, and thereby the limiting current density is attained when the concentration of each and every ion is null at the solution/membrane interface.

The model predictions for the limiting current density were compared with experimental data of single salt solutions ($MgCl_2$) and multi-ionic solutions ($MgSO_4 + MgCl_2$) in a bench-scale electrodialysis unit (EUR2C-7P18, Eurodia, France) for various Reynolds numbers and salts concentrations. The average relative deviations between the model predictions and the experimental data were lower than 13% for $MgCl_2$ solutions (10, 20 equiv./m^3) and solutions of $MgSO_4 + MgCl_2$ (5 + 5, 10 + 10 equiv./m^3). The dimensionless limiting current density and the counterions transport numbers predicted by the linearized and non-linear Nernst–Planck equations were also compared for a broad range of dimensionless operating parameters and a fair to good agreement was observed between the two approaches.

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1. Introduction

The flow pattern inside the channels of an ED stack exhibits a three-dimensional structure and a periodic nature due to the mesh-type spacers that are commonly used to keep the membranes apart and to enhance the mass-transfer, as well. In such a case, the concentration boundary layers adjacent to the ion exchange membranes, which develop under applied electrical current, are confined to a narrow region in the membranes vicinity. The thickness of these concentration boundary layers do not increase along the channel due to the periodic mixing promoted by the spacers filaments. Thus, in the design of ED equipment it is common practise to apply the film theory to estimate the concentration polarization and the limiting current density, assuming that the steady one-dimensional ionic transport occurs in stagnant film layers adjacent to the ion exchange membranes. For the transport of single salt solutions through the diluate/ion exchange membranes interfaces in the Ohmic regime (linear variation of the electrical current density versus potential difference), the integration of the Nernst–Planck (NP) equations within a stagnant film layer adjacent to an ion exchange membrane has been widely used to predict the limiting current density (e.g., [1–3]). The film thickness is estimated from the salt mass-transfer coefficient, k_c, which in turn is usually determined based on the salt diffusivity, D_S, and a suitable mass-transfer correlation. For an unstirred cell comprising two-compartments split by a cation exchange membrane, an expression for the limiting current density of single salt solutions of valence-symmetric and valence-asymmetric salts was deduced from the Nernst–Planck equations. The match between the predictions and the experimental data of monovalent (Na^+, K^+, Li^+), divalent (Ca^{2+}, Mg^{2+}) and trivalent (Al^{3+}) cations was excellent, except for H^+ [4].

The prediction of the limiting current density may also be accomplished based on the first principles by solving the continuity, momentum, and NP equations in a small computation domain of the feed channel inside which the velocity and concentration distributions are cyclic. For instance, computational fluid dynamics was applied to predict the concentration distributions of a single salt solution in laminar flow within a diluate channel with transverse rectangular spacers [5]. Although this method is extremely accurate, it is cumbersome and very time-consuming for the expedite prediction of the limiting current density in ED stacks containing multi-ionic solutions, complex spacers geometries and membranes of non-negligible roughness.

* Corresponding author. Tel.: +351 218417511; fax: +351 218499242.
E-mail address: vitor.geraldes@ist.utl.pt (V. Geraldes).

The prediction of the ionic transport across ion-selective membranes has also relied on the integration of the NP equations within stagnant film layers adjacent to ion exchange membranes [6–8]. For the ED of multi-ionic solutions, Nikonenko et al. [6] assumed an arbitrary film layer thickness instead of estimating it because no effective diffusivity was ever deduced for a multi-ionic solution. Moreover, since the ionic transport numbers in the membranes are unknown a priori, these authors calculated them by an intricate mass-transport model inside the membranes. Fíla and Bouzek [7,8] have also computed the ionic fluxes across ion-selective membranes by a similar model, assuming that the concentration polarization is controlled by a diffusion layer adjacent to the membrane. These authors estimated the film thickness based on a mass-transfer correlation for laminar flow in an open narrow rectangular channel. This mass-transfer correlation requires an effective diffusivity, but the authors did not specify how it was calculated. In sum, an expedite method is not available yet to estimate the limiting current density and the ionic fluxes in the ED of multi-ionic solutions.

In the present work, an explicit though approximate model is proposed to predict the limiting current density in the ED of dilute multi-ionic solutions. Our method relies on a pioneering derivation of the effective diffusivity of a multi-ionic solution and on the linearization of the NP equations within stagnant film layers adjacent to ion exchange membranes in the presence of an electric field. Under limiting current conditions, both the limiting current density and the counterions transport numbers in the membrane are expeditely predicted by our method (the coions transport numbers are assumed to be null), without resorting to complex models to assess the counterions transport numbers in the membrane.

The limiting current density and the counterions transport numbers predicted by the linearized and non-linear NP equations were compared for a broad range of operating parameters. Furthermore, the model predictions of the limiting current density were compared with experimental data of dilute solutions of $MgCl_2$ and $MgSO_4 + MgCl_2$ in a bench-scale ED unit. The mass-transfer correlation for this ED stack was determined from experimental limiting current densities of NaCl solutions at various Reynolds numbers.

2. Model

Let's consider that the diluate solution contains n ions, $C_{j,b}$ being the bulk concentration of the ion j (mol/m^3), and z_j its ionic charge (or charge number). The first n_c ions refer to the cations and the remaining n_a ions to the anions. It is assumed that the ionic transport occurs in a film layer of thickness δ_{eff} that may be estimated by the film theory:

$$\delta_{eff} = \frac{D_{eff}}{k_{c,eff}} \tag{1}$$

where D_{eff} is the effective diffusivity of the multi-ionic solution and $k_{c,eff}$ is the mass-transfer coefficient determined by an adequate mass-transfer correlation using D_{eff}. The application of the film theory is reasonable provided that the electric current density is below the limiting current density and thereby no electro-convection occurs within the stagnant film layer [9,10]. The method to determine the effective diffusivity is described in Appendix A, where an analogy was made with the classical determination of a single salt diffusivity based on the cation and anion diffusivities. As more than two ions were considered, we assumed that the ratio between the concentrations of distinct ions within the film layer is invariant. Under limiting current conditions, for which all ionic concentrations are null in the solution/membrane interface, this condition is plausible if the ionic concentrations distributions are approximately linear.

Within the diluate film layer adjacent to an ion exchange membrane, the total flux of the ion j, N_j ($mol\,m^{-2}\,s^{-1}$) is given by the Nernst–Planck equation:

$$N_j = -D_j \frac{dC_j}{dx} - z_j C_j D_j \frac{F}{RT} \frac{d\psi}{dx} \tag{2}$$

where x is the distance from the film layer edge (in contact with the bulk diluate) towards the membrane, D_j is the diffusivity of the ion j, F is the Faraday constant, R is the molar gas constant, T is the absolute temperature and ψ is the electrical potential. Eq. (2) does not take into account the friction between distinct ions, thus it just holds for dilute multi-ionic solutions, i.e., only the solute–solvent interactions are considered by the individual ionic diffusivities.

In electrodialysis, it is common practise to assume that the counterion concentration inside an ion exchange membrane is nearly constant, thereby the ionic diffusion within the membrane is negligible and the ionic transport therein occurs only by electro-migration. Thus, the total molar flux of the ion j in the membrane, N_j^m, may be related to the electrical current density, i, as:

$$N_j^m = \frac{t_j^m i}{z_j F} \tag{3}$$

where t_j^m is the transport number of the ion j in the membrane. In the steady-state, N_j^m and N_j (Eq. (2)) are equal, i.e.:

$$\frac{t_j^m i}{z_j F} = -D_j \frac{dC_j}{dx} - z_j C_j D_j \frac{F}{RT} \frac{d\psi}{dx} \tag{4}$$

For electrical current densities below the limiting current density, i_{lim}, the electroneutrality requirement holds within the film layer:

$$\sum_{j=1}^{n} z_j C_j = 0 \tag{5}$$

The integration of the system of explicit differential equations (Eq. (4) for each ion and Eq. (5)) enables the computation of the ionic concentrations and electrical potential distributions within the film layer. For a given set of t_j^m, the current density at which the concentration of the ion j vanishes in the diluate/membrane interface may be determined iteratively by the manipulation of the electrical current density, i.

For negligible steric exclusion, it is expectable that as long as there are counterions at the diluate/membrane interface to transport the electrical current, the latter may be further increased and the limiting current density will be attained when the concentration of each and every counterion is null at the interface (likewise for the coions due to the electroneutrality condition). As the limiting current density is approached, the ionic transport numbers inside the membrane evolve such that the limiting current density is only attained when the concentrations of each and every counterion and coion vanish simultaneously at the diluate/membrane interface.

An analysis of the degrees of freedom reveals that all ionic concentrations are null at the diluate/membrane interface for unique values of the electrical current density and counterions transport numbers in the membrane. Seeking for this set of limiting transport numbers is quite complex because the differential equations resolution requires an iterative method by which both the electrical current density and the counterions transport numbers must be manipulated until the limiting current density is attained. Thus, the computation of the limiting current density by the Nernst–Planck equations is time-consuming and its complexity increases with the number of distinct ions in the multi-ionic solution. Fortunately, by assuming negligible steric exclusion no mass-transport model in the membrane is required to estimate the counterions transport