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A Nernst-Planck analysis on the contributions of the ionic transport in permeable ion-exchange membranes to the open circuit voltage and the membrane resistance in reverse electrodialysis stacks

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ABSTRACT

The contributions of the ionic transport through a cation-exchange membrane, with perfectly stirred bathing solutions, on the open circuit voltage and the membrane ohmic resistance under reverse electrodialysis conditions, have been theoretically investigated. The Nernst-Planck flux equations, together with the Donnan equilibrium relations and the electrical neutrality condition, are numerically solved by using the network simulation method. On the one hand, the voltage-current characteristic, the polarization curves and the contributions of the ion-exchange membrane to the open circuit voltage and the membrane resistance are studied in a single system with NaCl solutions. The results are compared to those analytically obtained by using linear variations of ionic concentrations inside the membrane. On the other hand, a similar study is done for a membrane immersed in solutions constituted by a mixture of NaCl and $MgCl_2$. The uphill transport of the divalent cation against its concentration gradient is considered in the interpretation of the results. The numerical results are compared to those analytically obtained by considering the hypothesis of total co-ion exclusion inside the membrane.

1. Introduction

Nowadays, studies on ionic transport processes through ion-exchange membrane systems are receiving considerable attention because of the interesting applications of these systems in the field of the environmental science and technology, electrodialysis for desalination [1] and renewable energy harvesting [2] being the most representative examples.

Reverse electrodialysis (RED) is one of the emerging membrane-based technologies that can capture the available energy when waters with different salinity mix [3]. RED stacks contain alternating anion and cation exchange membranes that separate solutions with different salt concentration. Selective transport of ions through the membranes creates an electric potential across each one, which drives electric current through an external electric circuit [4–10]. Great efforts have been made in order to identify and minimize power losses in RED stacks [11–16]. Ionic transport through permeable membranes is a significant source of energy loss and the experimental determination of the membrane resistance has been a crucial topic in research [17–20], not only to evaluate the power losses in the systems but also to estimate the value of the load resistance to obtain maximal power from a RED stack. The usual techniques employ direct and alternating current with the membrane immersed in a standard 0.5 M NaCl external solution and a temperature of 25 °C. However, in a RED stack the membranes are placed between two solutions with different concentration and the salt solutions can contain small quantities of other ions. In this way, Dlugolecki et al. [21] have shown that the membrane resistance strongly depends on the concentration of the bathing solutions and the experimental measurements are affected by the resistances of the diffusion boundary layers and the interfacial resistances at the electric double layers. Galama et al. [22] have studied in detail the effect of the salinity gradients on the membrane resistance and they showed that the membrane resistance is mainly determined by the lowest external concentration. Zhang et al. [23] have presented a related study including the effect of the hydrodynamic environment.

From a theoretical viewpoint, the model based on the Nernst-Planck-Donnan equations under electroneutrality is the most widely accepted one when describing the ionic transport processes though ion-exchange membranes [24]. Analytical and numerical solutions of these equations in the Teorell-Meyers-Sievers model are well known in a great number of interesting physical situations. However, detail theoretical studies on the effect of the ionic transport through an ion-exchange membrane on the power loss in

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RED stacks are lacking in literature. In particular, the contribution of an ion-exchange membrane to the open circuit voltage by means of the diffusion potential when ions present different diffusivities and to the internal resistance by means of the ohmic potential drop in a RED stack, to our knowledge, has not been previously examined in detail.

The goal of this paper is to theoretically investigate the contributions of the ionic transport through a cation-exchange membrane, with perfectly stirred bathing solutions, on the open circuit voltage and the membrane ohmic resistance under RED conditions. The Nernst-Planck flux equations, together with the Donnan equilibrium relations and the electrical neutrality condition, are numerically solved by using the network simulation method [25]. Firstly, the voltage-current characteristic, the polarization curves and the contributions of the ion-exchange membrane to the open circuit voltage and the membrane resistance are studied in a single system with NaCl solutions. In this case, the results are compared to those analytically obtained by using linear variations of ionic concentrations inside the membrane. Secondly, a similar study is done for a membrane in a RED stack with ternary electrolyte solutions constituted by a mixture of NaCl and $MgCl_2$. The uphill transport of the divalent cation against its concentration gradient is considered in the interpretation of the results. The numerical results are compared, in a novelty analysis, to those analytically obtained by considering the hypothesis of total co-ion exclusion and that of linear variations of the counter-ionic concentrations inside the membrane.

2. Theoretical basis

2.1. Ionic transport in ion-exchange membrane systems

Let us consider an ion-exchange membrane, which is assumed to have a negative fixed-charge, bathed by two well-stirred bulk solutions of a multi-ionic electrolyte. Fig. 1a shows a sketch of the system. Ionic transport is supposed to be one-dimensional and perpendicular to the membrane-solution interfaces, with x the direction of transport. If we denote by X the fixed-charge concentration inside the cation-exchange membrane, the equations determining the steady-state behaviour of the membrane, lying from $x = 0$ to $x = d$, are the laws of mass conservation or continuity equations:

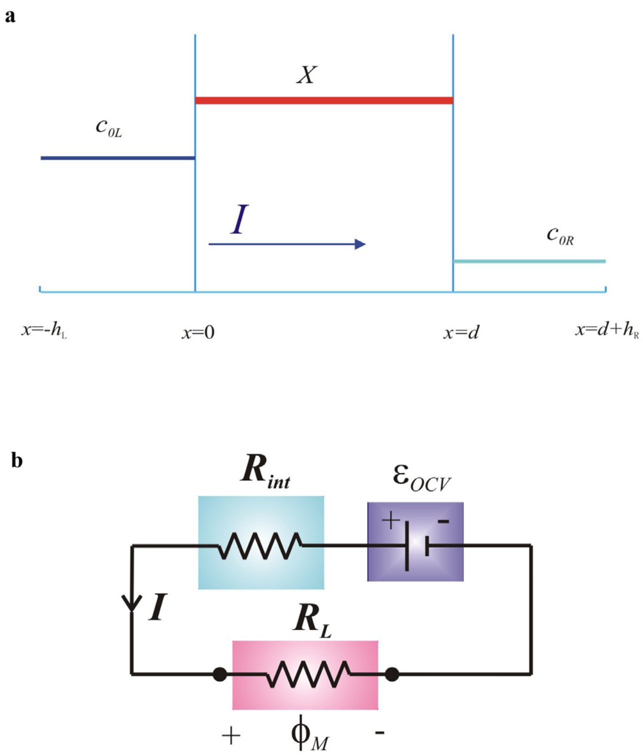

Fig. 1. a) Sketch of the ion-exchange membrane system under study; b) Equivalent electric circuit of a RED stack.

$$\frac{dJ_i}{dx} = 0 \tag{1}$$

the Nernst-Planck flux equations written for dilute solutions:

$$J_i = -D_i\left[\frac{dc_i(x)}{dx} - \frac{F}{RT}z_i c_i(x)E(x)\right] \tag{2}$$

and the electrical neutrality condition:

$$\sum_i z_i c_i(x) = X \tag{3}$$

Here J_i, D_i, $c_i(x)$ and z_i denote the flux, the diffusion coefficient, the molar concentration and the charge number of ion i, respectively, while the electric field is represented by $E(x)$. Now, the electric potential $\phi(x)$ is given by the following relation:

$$E(x) = -\frac{d\phi(x)}{dx} \tag{4}$$

while the faradaic electric current, I, is:

$$I = F\sum_i z_i J_i \tag{5}$$

and it is not a function of x, such as the ionic flux J_i, according to Eq. (1). It must be noted that, for the sake of simplicity, topics such as apparent permselectivity and activity coefficient [26] have been ignored.

Now, we consider that c_{0L} and c_{0R} respectively are the constant salt concentrations in the left and right bathing solutions of the system. If we suppose that $c_{0L} > c_{0R}$, an electric current I flow through the system from the left bathing solution to the right one. If we consider two electrodes placed at $x = -h_L$ and $x = d + h_R$, the uncompensated resistances of the left and right bathing solutions are given by:

$$R_{SL} = \frac{RTh_L}{F^2\sum_i z_i^2 D_{iS} c_{iSL}} \tag{6a}$$

$$R_{SR} = \frac{RTh_R}{F^2\sum_i z_i^2 D_{iS} c_{iSR}} \tag{6b}$$

where D_{iS} is the diffusion coefficient of ion i in the solution phase, and c_{iSL} and c_{iSR} respectively are the concentrations of ion i in the left and right bathing solutions. If we define the reference level for the electric potential at the right bathing solution at $x = d + h_R$, the Donnan potential difference at the interfaces can be written as:

$$\phi_D = \frac{RT}{z_1 F}\ln\left[\frac{c_{1L}}{c_{1R}}\right] + \frac{RT}{z_1 F}\ln\left[\frac{c_{0R}}{c_{0L}}\right] \tag{7}$$

where $\overline{c_{iK}}$ is the concentration of ion i in the boundary K of the membrane ($K = L$ for the left and $K = R$ for the right). Therefore, according to the Teorell-Meyer-Sievers model, the electric potential of the whole system, $\phi(-h_L) = \phi_M$, is:

$$\phi_M = \phi_{mb} + \phi_D + (R_{SL} + R_{SR})I \tag{8a}$$