



# Steady-state electrical response of homogeneous cation-exchange membrane systems under bi-ionic conditions



A.A. Moya

Universidad de Jaén, Departamento de Física, Edificio A-3, Campus Universitario de Las Lagunillas, 23071 Jaén, Spain.

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## ABSTRACT

This paper aims to numerically study the steady-state electrical response of ion-exchange membrane systems under bi-ionic conditions. The considered particular system is constituted by a membrane with negative fixed charge and two diffusion boundary layers on both sides of the membrane. The system is bathed by two solutions with a common co-ion but different counter-ion. The ionic transport processes of a ternary electrolyte are described by the Nernst-Planck-Poisson equations not only in the membrane but also in the diffusion layers, including the electric double layers at the interfaces. The numerical results are obtained by using the network simulation method. The steady-state voltage-current characteristics are analysed for cation-exchange membrane systems with monovalent ions and systems with a divalent counter-ion. The co-ion concentration polarization phenomena in the electroneutral regions of the diffusion boundary layers of these systems are analysed and discussed in detail. The electroneutral profiles of the counter-ionic concentrations inside the membrane and the counter-ionic fluxes are also analysed for different values of the electric current through the systems.

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## 1. Introduction

Nowadays, studies on electrochemical properties of ion-exchange membranes are receiving considerable attention because of the interesting applications of these systems not only in the field of mass separation technology, such as electrodialysis [1] or capacitive deionization [2], but also in that of renewable energy harvesting [3]. The steady-state, transient and small-signal ac electrical responses of ion-exchange membrane systems are now well-known [4].

Although the most attention has been paid to systems bathed in binary electrolyte solutions, multi-ionic transport in ion-exchange membrane systems has taken special relevance not only in the classical field of chemical analysis but also in separation techniques such as Donnan dialysis [5]. In addition, a growing interest in transport processes of multi-ionic systems has emerged in the fields of electrodialysis for desalination because of necessity of describing the water splitting phenomena at the over-limiting current regime in addition to the salt transport [6], and that of the energy harvesting under salinity gradients because the significant effect of the uphill transport associated to divalent ions which are present in a small concentration [7]. A special case within multi-ionic systems is that where the ion-exchange membrane is under bi-ionic conditions, i.e., the bathing solutions present a common co-ion but different counter-ion at identical concentration. Bi-ionic systems have received special attention in literature and interesting studies dealing with them have been already reported [8–18]. These

studies have focused on the equilibrium state of the systems where a cross flux of counter-ions is established, because the equilibrium membrane potential provides a value for the ratio of the diffusion coefficients of the univalent counter-ions inside the membrane. Moreover, they have not only dealt with univalent ions but also with divalent ones [19–20] and variations in concentration in the bathing solutions [21]. However, theoretical studies on non-equilibrium ionic transport processes through bi-ionic ion-exchange membrane systems are rare in literature, are highly dispersed and usually include a large number of mathematical simplifications.

This manuscript revisits the transport processes through bi-ionic systems and it aims to study in detail the steady-state electrical response of ion-exchange membrane systems under bi-ionic conditions. The particular system under study is constituted by a membrane with negative fixed charge and two diffusion boundary layers (DBLs) on both sides of the membrane. The system is bathed by two solutions with a common co-ion but different counter-ion, the transport of a ternary electrolyte being considered because of the ionic inter-diffusion processes between the two counter-ions due to their concentration gradients. The ionic transport processes are described by the Nernst-Planck-Poisson equations not only in the membrane but also in the DBLs, including the electric double layers at the interfaces. The numerical results are obtained by using the network simulation method [22], which is based on a finite differences scheme. The steady-state voltage-current characteristics are numerically obtained for cation-exchange membrane systems with monovalent ions and systems with a divalent counter-ion. The co-ion concentration polarization phenomena in the electroneutral regions of the DBLs of these systems are analysed

E-mail address: [aamoya@ujaen.es](mailto:aamoya@ujaen.es).

and discussed in detail. The electroneutral profiles of the counter-ionic concentrations inside the membrane and the counter-ionic fluxes are also analysed for different values of the electric current through the systems.

## 2. Steady-state ionic transport in ion-exchange membrane systems

Let us consider an ion-exchange membrane that extends from  $x = 0$  to  $x = d$ , and two DBLs adjacent to the membrane lying from  $x = -\delta_L$  to  $x = 0$  and from  $x = d$  to  $x = d + \delta_R$ , such as shown in the sketch of Fig. 1. The membrane is bathed by two different bulk solutions each consisting in a binary electrolyte with common anion. The membrane will be assumed to have a negative fixed-charge. Ionic transport process is supposed to be one-dimensional and perpendicular to the membrane-solution interface, with  $x$  the direction of transport. The dimensionless equations (see Appendix A) determining the steady-state behaviour of the system are the laws of mass conservation or continuity equations [23]:

$$\frac{dJ_i}{dx} = 0, \quad i = 1, 2, 3 \quad (1)$$

the Nernst-Planck flux equations written for dilute solutions:

$$J_i = -D_{ip} \left[ \frac{dc_i(x)}{dx} + z_i c_i(x) \frac{d\phi(x)}{dx} \right] \quad (2)$$

and the Poisson equation:

$$\frac{dD(x)}{dx} = \left[ \sum_{i=1}^3 z_i c_i(x) \right] - \theta(x) \quad (3)$$

where

$$D(x) = \varepsilon E(x) = -\varepsilon \frac{d\phi(x)}{dx} \quad (4)$$

Here  $J_i$ ,  $D_{ip}$ ,  $c_i(x)$  and  $z_i$  denote the ionic flux, the diffusion coefficient, the molar concentration and the charge number of ion  $i$ , respectively. We consider the ions  $i = 1$  and  $i = 2$  as the cations while  $i = 3$  is the anion. In this work, the ionic diffusion coefficients are different in the DBLs and in the ion-exchange membrane, and  $D_{iS}$  and  $D_{iM}$  stand for the diffusion coefficients of ion  $i$  in the solution ( $p = S$ ) and membrane ( $p = M$ ) phases, respectively. The electric potential is represented by  $\phi(x)$ , the electric permittivity by  $\varepsilon$ , the electric displacement by  $D(x)$ , and the electric field by  $E(x)$ .  $\theta(x)$  is the fixed-charge concentration,

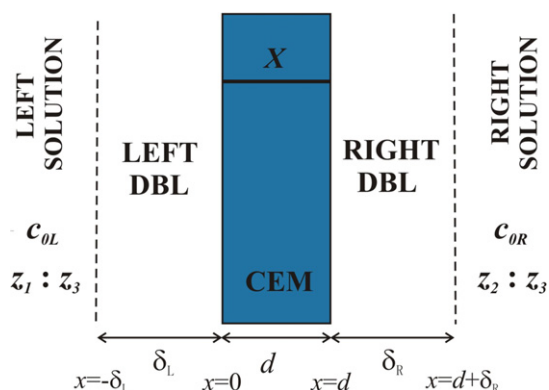


Fig. 1. Sketch of the ion-exchange membrane system under study.

which is known and expressed in a general way as a function of position,  $x$ . It is given by:

$$\theta(x) = \begin{cases} 0, & -\delta_L \leq x < 0 \\ X, & 0 \leq x \leq d \\ 0, & d < x \leq d + \delta_R \end{cases} \quad (5)$$

where the membrane fixed-charge concentration,  $X$ , is assumed to be homogeneously distributed inside the membrane.

On the other hand, the faradaic electric current density,  $I$ , is:

$$I = \sum_{i=1}^3 z_i J_i \quad (6)$$

and the boundary conditions for the ionic concentrations can be expressed as:

$$c_1(-\delta_L) = -\frac{z_3}{z_1} c_{0L} \quad (7a)$$

$$c_1(d + \delta_R) = 0 \quad (7b)$$

$$c_2(-\delta_L) = 0 \quad (8a)$$

$$c_2(d + \delta_R) = -\frac{z_3}{z_2} c_{0R} \quad (8b)$$

$$c_3(-\delta_L) = c_{0L} \quad (9a)$$

$$c_3(d + \delta_R) = c_{0R} \quad (9b)$$

where  $c_{0L}$  and  $c_{0R}$  respectively are the total concentrations of the common co-ion into the left and right bathing solutions. In this way, Eqs. (7a)–(9b) indicate that the system is electrically neutral at the outer boundaries of the DBLs. The reader must note that the above formulation includes the electrical double layers at the interfaces and the equations modelling ionic partitioning, i.e., the relationships between the concentrations of each ion inside and outside the membrane, are not necessary.

## 3. Results and discussion

In this paper, the numerical results are obtained by using the network simulation method, which has been briefly described elsewhere [22], and they are presented for cation-exchange membranes with  $X = 50$  and  $d = 10^5$  placed between two solutions with identical DBL thickness  $\delta_L = \delta_R = 10^5$ , and identical salt concentration  $c_{0L} = c_{0R} = 1$ . We have considered a fixed salt in the right bathing solution with  $z_2 = 1, z_3 = 1, D_{2S} = 1 \cdot 10^4$ , and  $D_{3S} = 2 \cdot 10^4$ , which could correspond to a LiCl solution. In the left bathing solutions two different systems have been considered with  $z_1 = 1$  and  $D_{1S} = 1.3 \cdot 10^4$ , and  $z_1 = 2$  and  $D_{1S} = 0.8 \cdot 10^4$ , which respectively could correspond to NaCl and CaCl<sub>2</sub> solutions. In all the cases, the ionic diffusion coefficients in the membrane have been chosen as a tenth of those in the solutions for the sake of simplicity. In particular, this choice involves that the ratio of the diffusion coefficients of the ions in the membrane take the same value as in the solutions. If one takes into account that the length unit is approximately 1.37 nm (see Appendix A), the chosen system parameters could correspond to membranes of width 137  $\mu\text{m}$  and fixed-charge concentration 5 M immersed in 100 mM bathing concentrations, being 137  $\mu\text{m}$  the thickness of each DBL.

Fig. 2 shows the voltage-current characteristics of bi-ionic ion-exchange membrane systems with NaCl and CaCl<sub>2</sub> solutions in the left compartment by denoting  $\phi_M = \phi(x = -\delta_L) - \phi(x = d + \delta_R)$  the membrane system potential. These curves are typical of ion-exchange membrane systems [24–28]. The electric potential linearly varies with current for the smallest values of the current. However, the electric potential strongly varies with a small changing in current as the electric

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