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# THE DIFFERENTIAL CAPACITANCE OF THE ELECTRIC DOUBLE LAYER IN THE DIFFUSION BOUNDARY LAYER OF ION-EXCHANGE MEMBRANE SYSTEMS

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ABSTRACT

The effect of the membrane diffuse layer on the differential capacitance of the diffuse layer in the diffusion boundary layer of an ion-exchange membrane system, as well as on the meaning of this capacitance in the interpretation of the electrochemical impedance, have been investigated. On the one hand, the effect of the diffuse layer in the membrane phase on the electric double layer capacitance is analysed on the basis of the Poisson-Boltzmann equation in the Gouy-Chapman theory for a symmetric binary electrolyte. The results are compared with the analytical expressions obtained by using the Debye-Hückel approximation and by considering ideal membranes with an infinitely thin diffuse layer. On the other hand, the electrochemical impedance of a diffusion layer adjacent to an ideal membrane for a uni-univalent electrolyte has been numerically studied on the basis of the Nernst-Planck and Poisson equations, including a charge transfer resistance between solution and membrane described by a Chang-Jaffé equation, in order to establish the role played by the differential capacitance of the electric double layer. The impedance has been studied by using the network simulation method and the results obtained from the characteristic frequency of the interfacial charge transfer process are compared with the theoretical expressions for the electric double layer capacitance of an ideal system, not only under equilibrium conditions but also by considering the polarization concentration phenomenon.

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## 1. Introduction

The study of the characteristics of the electric double layer (EDL) at a solid-liquid or liquid-liquid interface is a classical scientific research line, which has recently taken a relative importance due to the advanced development of classical electrochemical power sources like supercapacitors [1], of emerging systems to produce capacitive energy by expansion of electric double layers in porous electrodes undergoing salinity differences [2], or promising techniques in the field of environmental engineering to desalination by capacitive deionization by using charged porous materials [3]. In a parallel way, the study of the properties of the transport processes through ion-exchange membranes is receiving special attention because of the use in chemical analysis as ion-selective electrodes [4], in the fields of brackish water or seawater desalination [5], and in that of the renewable energies such as pressure-retarded osmosis and reverse

electrodialysis [6]. In addition, the ion-exchange membranes are often used as separators in fuel cells [7] and redox flux batteries [8], or as elements joined to the porous electrodes in the systems for energy production from salinity differences [9] or capacitive deionization [10].

Nowadays, the properties of the EDL at the electrode-solution interface on the basis of the Poisson-Boltzmann equation, are well known for the different kinds of electrodes [11–13]. The role played by the diffuse layer in the different techniques used for the characterization of electrochemical cells has been widely studied and novel results have been proposed over the years, including among others issues related with the usual transient techniques such as chronopotentiometry or chronoamperometry [14–17], and others more specifics like electrochemical impedance spectroscopy [14,16,18], cyclic voltammetry [19] or large amplitude ac voltammetry [20]. The structure and properties of the EDL at the ion exchange membrane-solution interface are also well known [21–24] and they has also been analysed by considering a number of issues different from those in electrode systems like multi-ionic electrolytes [25], inhomogeneous fixed-charge distributions [26]

and water splitting or other electrokinetic phenomena leading to overlimiting currents [27–29]. In addition, the structure of the diffuse double layers in nanoporous membranes on the basis of the space charge model [30–31] and that in related fluidic micro and nanochannels [32], have been also studied.

The capacitance of the EDL is a parameter that plays a significant role in the characterization of interfacial processes in electrochemical systems. However, it is necessary to distinguish between integral, which is a useful magnitude in systems designed to store electric charge, and differential capacitance, which appears when one uses transient techniques like cyclic voltammetry [33] and particularly impedance spectroscopy [34]. Although one finds certain misunderstandings between integral and differential capacitance in the literature [35], the analytical expressions relating this later magnitude and the transport parameters characteristic of an electrochemical cell are well known by considering the ions as charged points [36] and including the ionic size effects [37–38], the non-electrostatic ion-ion interaction effects [39], the solvent effects [40], non-planar geometries [41–42], or using ionic liquids as electrolytes [43]. In comparison to the electrode systems, the study of the differential capacitance of the EDL at the ion exchange membrane-solution interface is less developed, this being likely due to the more complex nature of this interface because of the presence of two diffuse layers [44]. The differential capacitance of the diffuse layer in the solution phase of an ion-exchange membrane system is used to interpret experimental electrochemical impedances assuming a charge transfer resistance between membrane and solution [45–50] and particularly in ion-selective membrane electrodes [51–52]. Moreover, this capacitance has been interestingly proposed as associated to an intermediate characteristic time scale in ion-exchange membrane systems in addition to the migration and diffusion relaxation times [53–54], which has been used not only in impedance studies [55], but also in studies related to pulsed electric fields [56], and it has been extended to deal with fluidic devices [57]. However, to our knowledge, detail theoretical studies on the differential capacitance of the EDL at the interface between solution and ion-exchange membrane, as well as on their meaning in the interpretation of the electrochemical impedance, are lacking in the literature.

This paper re-examines the properties of the differential capacitance of the diffuse layer in the solution phase of an ion-exchange membrane system. On the one hand, the effect of the diffuse layer in the membrane phase on the differential capacitance of the diffuse layer in the solution is analysed on the basis of the Poisson-Boltzmann equation in the Gouy-Chapman theory for a symmetric binary electrolyte, ions being considered as charged points. The results are compared with the analytical expressions obtained by using the Debye-Hückel approximation and by considering ideally selective membranes with an infinitely thin diffuse layer. On the other hand, we have numerically simulated the electrochemical impedance of a diffusion boundary layer (DBL) adjacent to an ideal membrane for a uni-univalent electrolyte on the basis of the Nernst-Planck and Poisson equations, including the interfacial transfer kinetics between solution and membrane described by a Chang-Jaffé equation, in order to established the role played by the differential capacitance of the EDL. The impedance has been numerically studied by using the network simulation method [58], which is based on a finite differences scheme, and the results obtained from the characteristic frequency of the interfacial charge transfer process are compared with the theoretical expressions for the differential capacitance of the diffuse layer in the DBL of an ideal system, not only under equilibrium conditions but also by considering the polarization concentration phenomenon.

## 2. The differential capacitance of the diffuse layer in the diffusion boundary layer

We will consider the system constituted by an ion-exchange membrane and a DBL adjacent to the membrane. The membrane-solution interface is placed at $x = 0$, the DBL is extended from $x \rightarrow -\infty$ to $x = 0$, i.e., for $x < 0$, while the membrane is a cation-exchange one, with the fixed-charge concentration $X$, and it is extended from $x = 0$ to $x \rightarrow \infty$, i.e., for $x > 0$. The system is bathed by a $z$:$z$ symmetric binary electrolyte, $c_0$ being the ionic concentration in the solution bulk, and it is in an equilibrium steady-state. Ions are treated as point charges and the ionic size effects are neglected.

Fig. 1 shows a sketch of the system. The EDL is formed by a diffuse layer in the solution phase and another diffuse layer in the membrane phase. Since we consider the values of the bathing ionic concentration, $c_0$, to be smaller than that of the fixed-charge concentration inside the membrane, $X$, the electric charge stored in the diffuse layer in the solution phase is positive and it arises from the accumulation of cations in the solution region close to the interface. Conversely, the electric charge stored in the membrane diffuse layer is negative and it is due to the depletion of counterions in the interfacial zone of the membrane. In this way, if we consider the origin of the electric potential at $x \rightarrow \infty$, the total electric potential, $\phi_T$, is positive throughout the system and it can be expressed as the sum of the potential difference in the solution phase, $\phi_S$, and that in the membrane phase, $\phi_M$, i.e.:

$$\phi_T = \phi_S + \phi_M \tag{1}$$

and the absolute values of the surface electric charge stored in the solution, $\sigma_S$, and the membrane, $\sigma_M$, diffuse layers must be identical:

$$\sigma_S = -\sigma_M \tag{2}$$

Since the equilibrium ionic concentrations are given by the Boltzmann equation [59], from the Poisson equation is followed that the surface charge density, $\sigma$, stored in a region of the diffusion boundary layer ($x < 0$) extended from a point of potential $\phi = \phi_T$ to another of potential $\phi$, is given by [59]:

$$\sigma = \sqrt{8 c_0 \varepsilon_S R T} \sinh\left[\frac{z F (\phi_T - \phi)}{2 R T}\right] \tag{3}$$

where $\varepsilon_S$ is the electric permittivity of the solution phase, and $F$, $R$ and $T$ are Faraday constant, ideal gas constant and absolute temperature, respectively. The surface electric charge stored in the solution diffuse layer is obtained by doing $\phi = \phi_M$ in the above equation and it is given by:
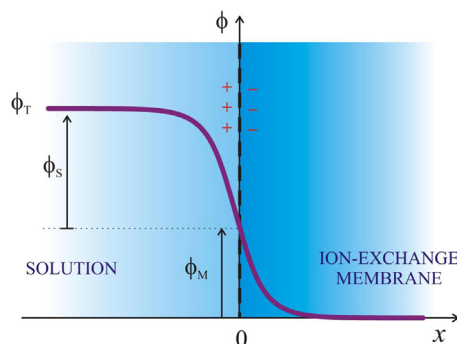


**Fig. 1.** Sketch of the system corresponding to the ion exchange membrane-solution interface.