

## Influence of effective membrane fixed charge on electrolyte concentration-polarization in nanoporous alumina membranes with similar pore size

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Solid structures with accurate nanopore diameters and narrow pore size distributions are necessary for the study of confined diffusion, since they facilitate the control and modeling of molecular transport which is of great interest in different applications [1]. Particularly, Nanoporous Alumina Membranes (NPAMs) fabricated via electrochemical anodization, which present a well-defined pore structure with rather high density of uniform nanopores while their dimensions and porosity can easily be controlled by the anodization process [2], are used in nanofluidics, solution purifications and drug delivery devices [3]. These applications are associated with motions of molecules or ions inside the membrane nanopores, which are usually investigated by performing diffusion experiments at a given concentration gradient using Fick law, independently of the neutral or charged character of the solutes or the higher or lower fixed charge of the membranes [4-5]. On the other hand, solution stirring is not usually considered in many of the experimental systems used in drug delivery characterization devices [5-6], which can favour the solute accumulation on the membrane surface or concentration-polarization effect schematically shown in Fig. 1(a) and to mask the effective concentration gradient. However, these factors could be among the reasons associated to the significant reduction in diffusion coefficients across NPAMs with pore size between 20 and 40 nm reported by different authors when diffusive transport of charged species (macromolecules and ions) is analyzed [5-7].

In this study, the influence of membrane equivalent fixed charge on concentration-polarization at the solution/membrane interface is considered. Diffusive transport across two nanoporous alumina membranes (NPAMs) fabricated by the two-step anodization process [2] with similar pore size (~ 20 nm) and thickness (~ 60  $\mu\text{m}$ ) was determined. One of the studied membranes is commercial (Anopore<sup>®</sup>) and it has a porosity between 25-50 % (indicated by supplier), while the other is experimental (AL1) and with a porosity of 16-20 % [4]. This latter membrane was fabricated using a constant anodization potential of 25 V applied between the Al foil and a Pt counter-electrode in a 0.3 M sulfuric acid solution. Membranes behaviour was analyzed by measuring membrane potentials at different NaCl solution concentrations ratio ( $C_f/C_v$  ranging between 0.2 and 10) and hydrodynamic conditions (solutions stirring rate of 0 rpm and 540 rpm).

Differences in the electrical behaviour of both membranes can be determined by comparing membrane potential values obtained for both membranes at the same solutions concentration ratio and hydrodynamic condition. The analysis of these data by using the TMS model [8-9] allows us the estimation of both the effective membrane fixed charge ( $X_{\text{ef}}$ ) and cation transport number ( $t_+$ ) and their values are indicated in Table 1. These results clearly show the almost neutral character of the Anopore membrane ( $t_+ \sim$  solution cation transport number  $t_+^0 = 0.38$ ) and the more electropositive character of the AL1 membrane when compared with the Anopore one. This fact affects both ion transport and interfacial effects as it is schematically represented in Fig. 1(b).

Table 1

Effective fixed charge concentration,  $X_{\text{ef}}$ , and cation transport number,  $t_+$ , for both studied membranes

membrane	$X_{\text{ef}}$ (M)	$t_+$
Anopore	$1.0 \times 10^{-3}$	0.35
AL1	$10.0 \times 10^{-3}$	0.25

The comparison of membrane potential values obtained for the practically neutral Anopore membrane at the same solutions concentration ratio but different hydrodynamic conditions does not show almost differences, while solution stirring significantly affects membrane potential values in the case of the charged AL1 membrane, which is an indication of the contribution of concentration-polarization in the values obtained with this membrane (see Fig. 1(b)).

This effect might also be affected by slight surface differences between both membranes related with the fabrication process as well as by the lower porosity of the AL1 membrane, which should also be taken into account. Particularly, the effect of membrane porosity has separately been considered by comparing results obtained from diffusion measurements, which were performed with a neutral solute (tritiated water radiotracer) to avoid any electrical contribution able to mask pure diffusion data. Moreover, due to the similar pore size of both membranes comparable frictional/steric effects can be assumed.

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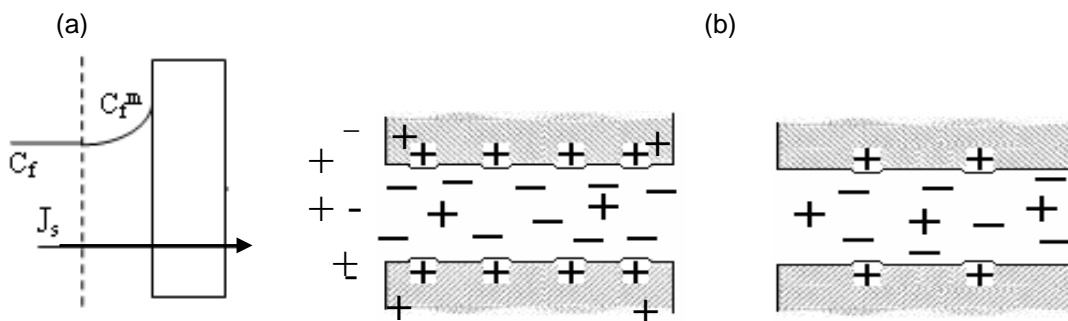


Fig. 1: Schematic representation of: (a) concentration-polarization at the membrane/solution interface; (b) effect of membrane charge on ion transport and interfacial effects.