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Charge and dielectric characterization of nanofiltration membranes by impedance spectroscopy

Miguel Montalvillo [a], Verónica Silva [a], Laura Palacio [a], José I. Calvo [a], Francisco J. Carmona [b], Antonio Hernández [a], Pedro Prádanos [a,*]

[a] *Grupo de Superficies y Materiales Porosos (SMAP, UA-UVA-CSIC), Departamento Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain*

[b] *Departamento de Física Aplicada, Escuela Politécnica, Universidad de Extremadura, 10003 Cáceres, Spain*

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ABSTRACT

The conductance and capacitance of a nanofiltration membrane have been obtained by impedance spectroscopy analysis in a wide range of concentrations of KCl aqueous solutions. The permittivity and conductivity of the electrolyte–membrane system have been determined by means of dielectric analysis and modeling the system with an equivalent circuit that corresponds to the relaxation times experimentally observed.

The volumetric charge in the membrane has been assessed by solving the equilibrium partitioning equations in the membrane that include Donnan, steric and dielectric effects. The mean transport number has been evaluated by the membrane potential method.

It has been proved that the effects of confinement within the narrow pores of nanofiltration pores on the dielectric phenomena arising in such narrow pores are substantial and have to be taken into account in transport models.

In summary by using impedance spectroscopy and membrane potential measurements it has been possible to get the electric and dielectric parameters that should allow the available nanofiltration models to be used as predictive tools.

1. Introduction

The selective transport of charged species through nanofiltration membranes is successfully achieved due to the special properties of nanoporous materials. The normal pore diameters are around 1–2 nm and these membranes show also important electrical contributions to retention. Due to these characteristics, nanofiltration membranes are able to separate multivalent complex ions and transmit small uncharged solutes and low charged ions. Nowadays, there are models able to describe the solute exclusion by steric, Donnan and dielectric partitioning effects in the interfaces and convective, diffusive and electric transport effects in the inner part of the membrane. Within the frame of such models, the characterization of the electric behavior of the membrane is one of the most relevant points to study. Some experimental techniques have been applied with this aim like streaming potential (SP) [1], membrane potential (MP) [2] and impedance spectroscopy (IS) [3,4]. With these methods basically it is possible to obtain the charge developed in the membrane, the mobility of the ions and the permittivity inside the pores.

In both SP and MP there are ion fluxes from one side to the other of the membrane and thus all the transport and partitioning mechanisms are present and both the systems have to be analyzed by using complex models like that presented in previous works [5,6]. It is also possible to use simplified versions like the Teorell–Meyer–Sievers (TMS) model [2], or the usually called Space Charge Model (SCM) [7] but it is important to remind that these models include neither the hindered nature of the ion movement inside NF pores nor the dielectric effects in the interface.

In the IS technique there is no net flux across the membrane so the only contributions to quantify are steric, Donnan, and dielectric effects in the inlet and outlet of the membrane. Even more, the concentration polarization effect is negligible because there is no any net flux through the membrane. The IS technique is usually used to study the electrical properties of complex materials [3,4]. The method consists in introducing an electrical signal and performing a frequency scanning while measuring the impedance of the system. With IS it is possible to obtain the different contributions of each layer of the membrane system. In this technique the system is associated with an equivalent electrical circuit from which it is possible to obtain the resistance and capacity of each layer [8]. A great number of synthetic and biological membranes have been electrically characterized by using this method [9–16].

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[*] Corresponding author. Tel.: +34 983423739; fax: +34 983423013.
E-mail address: pradanos@termo.uva.es (P. Prádanos).

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In this work, MP and IS have been applied to a commercial NF membrane in a wide range of KCl concentrations. First, using MP measurements, the transport numbers of the cation inside the pores has been obtained. On the other hand, IS has been used in this case to obtain the permittivity inside the pores (ε_p) and the conductivity (κ_p) – and their concentration dependence – that actually are two of the most complicated parameters to obtain experimentally. Moreover, using the conductivity results from IS and by modeling the partitioning effect in the interface it is possible to obtain the concentration dependence of the volumetric charge density (X). The respective relevance in the electrical contributions to nanofiltration transport is analyzed.

2. Theory and methods

2.1. Dielectric analysis

A typical IS experiment allows the determination of the electrical impedance of the system under study as a function of the frequency. In the case of a membrane placed between two solutions, the corresponding system is represented by the following scheme:

Electrode–KCl electrolyte–**MEMBRANE**–KCl electrolyte–Electrode

In such complex configurations, several layers and interfaces can be identified. These layers can have different electrical properties and lead to different relaxation times. In general, a system composed by N layers will show $N-1$ relaxation times and can be modeled using an extension of the Maxwell–Wagner theory where the whole (complex) permittivity for a N-layers system is obtained according to Kita [17].

$$\varepsilon^*(\omega)=\varepsilon_{N,\mathrm{h}}+\sum_{i=1}^{N-1}\frac{\varepsilon_{i,\mathrm{l}}-\varepsilon_{i,\mathrm{h}}}{1+(j\omega\tau_i)^{1-\alpha_i}}-j\frac{\kappa_{11}}{\omega} \tag{1}$$

where ε^* is the overall permittivity in the system, $j=\sqrt{-1}$, $\varepsilon_{N,\mathrm{h}}$ is the permittivity at infinite frequency, $\varepsilon_{i,\mathrm{l}}$ and $\varepsilon_{i,\mathrm{h}}$ are the permittivity for each relaxation time, τ_i, at low and high frequencies, ω is the angular frequency and $\kappa_{1,1}$ is the conductivity of the system at low frequency. The α_i are distribution factors characterizing the spread of relaxation time [18], so α_i is 0 (or very near to 0) when the process has a single relaxation time (Debye type) and the corresponding curve in the complex plane plot of relative permitivities is a perfect semicircle. When the curve looks somehow as a flattened semicircle, the value of α_i is different from zero.

The conductance (G) and capacity (C) of the system are related to the conductivity and permittivity respectively as,

$$G_i=\kappa_i\frac{S}{\Delta x} \tag{2}$$

$$C_i=\varepsilon_i\frac{S}{\Delta x} \tag{3}$$

S is the effective area and Δx is the thickness of the layer considered in each relaxation process. Therefore, combining Eqs. (2) and (3) in Eq. (1), the whole (complex) capacitance of the system can be obtained according to a Cole–Cole relaxations scheme [18],

$$C^*(\omega)=C(\omega)+\frac{G(\omega)}{j\omega}=C_{N,h}+\sum_{i=1}^{N-1}\frac{C_{i,\mathrm{l}}-C_{i,\mathrm{h}}}{1+(j\omega\tau_i)^{1-\alpha_i}}-j\frac{G_{11}}{\omega} \tag{4}$$

$\tau_i=1/2\pi f_i$ and f_i is the frequency at the maximum value in the corresponding lobe in the complex capacitance plane plot (or the inflection point in the C or G versus frequency plots). $C_{N,\mathrm{h}}$ is the capacitance at infinite frequency, $C_{i,\mathrm{l}}$ and $C_{i,\mathrm{h}}$ are the capacitances for each relaxation time at low and high frequency. The relaxation time is also related with these parameters and the corresponding conductances by $\tau_i=(C_{i,\mathrm{l}}-C_{i,\mathrm{h}})/(G_{i,\mathrm{h}}-G_{i,\mathrm{l}})$.

For multilayer systems there are some connections in Eq. (4) that must be fulfilled, they are

$$C_{i,\mathrm{h}}=C_{(i+1),\mathrm{l}} \quad \text{for} \quad i=1,\ldots,N-1 \tag{5}$$

$$G_{i,\mathrm{h}}=G_{(i+1),\mathrm{l}} \quad \text{for} \quad i=1,\ldots,N-1 \tag{6}$$

Using experimental results of complex capacitance C^* (equivalently on both $C(\omega)$ and $G(\omega)$) it is possible to identify the dielectric parameters $C_{N,\mathrm{h}}$, $G_{1,\mathrm{l}}$, $C_{i,\mathrm{h}}$, $G_{i,\mathrm{h}}$ and α_i. The relation between these parameters and the parameters of the corresponding layers were presented by Li and Zhao [19]. They assume that when a certain relaxation is not ideal it can be separated in two Debye perfectly ideal relaxations (two layers) with similar properties leading to quite similar response times. Each of these layers should correspond to a resistance in parallel with a capacitance and electrically should be placed in series with the corresponding circuits for the other layers.

When some of the relaxations are assumed to consist in the convolution of two perfect or ideal (Debye's) ones – this can be interesting for $\alpha_i \neq 0$ – a deconvolution can be made by using the equations shown in Table 1. This procedure can be interpreted as the discovery of two very similar phases or layers in our case. These equations are deduced by taking into account the rules of addiction for two complex capacitances in series and extrapolating for high and low frequencies and finally solving the resulting system of equations for capacitances and conductances of the two elemental circuits [19].

2.2. Partitioning equilibrium at the interfaces

In an IS experiment, both sides of the membrane are in contact with the same concentration of electrolyte then the only mechanisms in action are those related with the thermodynamic equilibrium at the interfaces. When this equilibrium is reached, a difference of solute concentration is generated at each side of the interface, according to

$$\frac{c_{i,\mathrm{p}}}{c_{i,\mathrm{b}}}=\varnothing_i\frac{\gamma_{i,\mathrm{b}}}{\gamma_{i,\mathrm{p}}}\exp(-z_i\Delta\Psi)\exp(-\Delta W_{i,\mathrm{B}}{}')\exp(-\Delta W_{i,\mathrm{im}}{}') \tag{7}$$

$$\sum_i c_{i,\mathrm{b}}z_i=0 \tag{8}$$

$$\sum_i c_{i,p}z_i+X=0 \tag{9}$$

where X is the volumetric charge density.

Table 1
Relation between phase and dielectric parameters [19].

$\omega=\frac{G_\mathrm{h}-G_\mathrm{l}}{C_\mathrm{l}-C_\mathrm{h}}=2\pi f$	(1.1)
$B=\omega+\frac{G_\mathrm{h}}{C_\mathrm{h}}$	(1.2)
$D=\sqrt{B^2-4\frac{G_\mathrm{l}\omega}{C_\mathrm{h}}}$	(1.3)
$A=\frac{B-D}{2} \quad b=B-A$	(1.4)
$C_\mathrm{m}=C_\mathrm{h}\frac{D}{\omega-A} \quad \varepsilon_\mathrm{m}=C_\mathrm{m}\frac{\Delta x}{S\varepsilon_0}$	(1.5)
$C_\mathrm{w}=C_\mathrm{h}\frac{D}{b-\omega} \quad \varepsilon_w=C_w\frac{L}{S\varepsilon_0}$	(1.6)
$G_\mathrm{m}=AC_\mathrm{m} \quad \kappa_\mathrm{m}=G_\mathrm{m}\frac{\Delta x}{S}$	(1.7)
$G_\mathrm{w}=bC_\mathrm{w} \quad \kappa_\mathrm{w}=G_\mathrm{w}\frac{L}{S}$	(1.8)

The subscripts h and l refer to the high and low frequencies and m and w refer to inside and outside each membrane system layer.