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Experimental determination of the streaming potential across cation-exchange membranes with different morphologies

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ABSTRACT

Liquid uptake and streaming potential have been determined in aqueous sodium chloride solutions for five different commercial sulfonated polymer cation-exchange membranes. The selected membranes have distinct morphologies and electrochemical properties. Differences in the liquid uptake properties of the membranes have been found, which have been analysed on the basis of the structure and the chemical properties of the membranes. In most of the membranes analyzed, the higher the liquid content of the membranes, the lower the effective concentration of fixed charges in the membranes. The streaming potential across the membranes increases linearly with the established pressure difference, and it is larger in heterogeneous membranes than in homogeneous ones. In general, the higher the membrane liquid content, the higher the streaming potential across the membranes.

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1. Introduction

When an ion-exchange membrane separating two electrolyte aqueous solutions is subject to one or more driving forces, transport phenomena of electro-kinetic character can be originated through the membrane. For instance, a pressure difference across a membrane is able to drive both a volume flux and an electric charge flux through the membrane. This electro-kinetic phenomenon indicates that mass and electric charge transport processes can be coupled. Coupling means that a mass flux can be caused by an electric potential difference, and that an electric charge flux can be originated by a pressure difference alone.

If an excess hydrostatic pressure is applied to the solution on one side of an ion-exchange membrane, the liquid is forced to move across the membrane along the pressure difference. This liquid carries along a net electric charge, as a consequence of the excess of counter-ions with respect to the co-ions, towards the low-pressure membrane side, which acquires the same charge as the counter-ions, while the high-pressure membrane side acquires the charge of the fixed groups. Accordingly, an electric potential difference appears between the two sides of the membrane, which is known as streaming potential.

The streaming potential acts over the electrically charged liquid inside the membrane, partly balancing the effect of the pressure and thus reducing the flow across the membrane. The streaming potential also accelerates the co-ions and slows down the counter-

ions in such a way that, despite their different concentrations, both of them transfer equivalent amounts of electric charge in the same time. However, the effect of applied pressure is stronger than the one produced by the developed electric field and thus, relative to the membrane matrix; both ionic species are carried out along with the solvent flux.

According to the linear non-equilibrium thermodynamics approach, the phenomenological equations for modelling the transport of mass and electric charge across an ion-exchange membrane are [1]

$$J_V = L_{11}\Delta P + L_{12}\Delta\psi \quad (1)$$

$$I = L_{21}\Delta P + L_{22}\Delta\psi \quad (2)$$

where J_V is the volume flux, I is the electric current, ΔP is the pressure difference across the membrane, and $\Delta\psi$ is the difference of electric potential across the membrane. The coefficients L_{11} and L_{22} are the hydraulic permeability and the electric conductance, respectively, whereas L_{12} and L_{21} are the electro-kinetic coefficients that take into account the coupling phenomenon.

Coupling can be studied in terms of the so-called pressure coefficient β and electro-osmotic permeability W , which can be defined, from Eqs. (1) and (2), as follows:

$$\beta \equiv \left(\frac{\Delta\psi}{\Delta P}\right)_{I=0} = -\frac{L_{21}}{L_{22}} \quad (3)$$

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$$W \equiv \left(\frac{J_V}{I}\right)_{\Delta P=0} = \frac{L_{12}}{L_{22}} \quad (4)$$

The Onsager's reciprocity relation implies that $L_{12}=L_{21}$, it then follows that $W = -\beta$. This relation, which can be expressed as

$$\left(\frac{J_V}{I}\right)_{\Delta P=0} = -\left(\frac{\Delta\psi}{\Delta P}\right)_{J=0} \quad (5)$$

is known as Saxén's law.

In order to determine experimentally the streaming potential, a pressure difference between the two sides of an ion-exchange membrane is established, and the electric potential difference $\Delta\psi$ across the membrane is measured as a function of time t . A typical plot of $\Delta\psi$ vs. t shows an initial sudden rise in the electric potential difference, when $\Delta P \neq 0$, which represents the potential arising from the pressure difference, when the two bulk solution concentrations are equal. This is the electrical potential difference, $\Delta\psi_0$, in the absence of concentration polarization because there is no liquid flow through the membrane in this stage. As the process takes place, a concentration difference between the two sides of the membrane is also originated. It has been found [2] that this term is proportional to $t^{1/2}$. Thus, the contribution of the concentration polarization to the electric potential difference can be removed by determining the streaming potential as an intercept at $t=0, \Delta\psi_0$ from the plot of the experimental curves of $\Delta\psi$ vs. $t^{1/2}$, i.e., the streaming potential is obtained in the initial time of the diffusion step

$$-\Delta\psi = -\Delta\psi_0 + At^{1/2} \quad (6)$$

where the constant A can be related to the hydrodynamic permeability in the membrane [3].

The value of the streaming potential $\Delta\psi_0$ found as explained above does not coincide with the real value. The use of reversible electrodes involves the correction of the measured potential due to the pressure difference. When an electrode Ag/AgCl is used, the true streaming potential $\Delta\psi_r$ can be obtained by subtracting a contribution from the experimentally determined value as follows:

$$\Delta\psi_r = \Delta\psi_0 - \frac{1}{F}(v_{\text{AgCl}} - v_{\text{Ag}})\Delta P \quad (7)$$

where F is Faraday's constant, and v_{AgCl} and v_{Ag} are the molar volumes of AgCl and Ag, respectively [4].

This work is a contribution of the application of linear non-equilibrium thermodynamics theory to the study of the transport processes in charged membranes. This work is concerned to the search of relations between polymer membrane properties and morphology. With this aim, the liquid uptake and the streaming potential have been experimentally determined for several cation-exchange membranes with different structures and electrochemical properties.

2. Experimental

2.1. Membrane and materials

The main characteristics of the commercial cation-exchange membranes used in this study are given in Table 1. Nafion-115 membranes (hereafter named NF115) are films consisted of a polytetrafluoroethylene backbone and long fluorovinyl ether pendant side chains regularly spaced, terminated by a sulphonate ionic groups. There are no cross-links between the polymers. MK-40 membranes (hereafter named MK40) are composites formed from the cation-exchange resins KU-2 (polystyrene matrix cross-linked

Table 1

Ion exchange capacity (IEC), density (ρ_m), thickness (d_m), water content (s_w), wet membrane porosity (ε_w), FH interaction parameter (χ_w), and parameter λ in water, of cation-exchange membranes used in this study.

Membrane	IEC (meq/g) ^a	ρ_m (g/cm ³) ^a	d_m (μm) ^a	s_w ^b	ε_w ^c	χ_w ^d	λ ^e
MK40	2.6	1.12	480	0.53	0.37	0.91	11
CR65	2.3	0.877	550	0.56	0.33	0.98	14
RXC	2.2	0.817	650	0.64	0.34	0.96	16
CMX	1.7	1.0	170	0.30	0.23	1.18	10
NF115	1.0	2.0	130	0.20	0.29	1.05	11

^a Provided by the manufacturer. IEC (meq/g dry membrane); ρ_m (g/cm³) dry membrane.

^b Estimated from Eq. (8).

^c Estimated from Eq. (12).

^d Estimated from Eq. (13).

^e Estimated from Eq. (9).

with divinylbenzene and fixed groups), polyethylene and nylon. Membranes CR65-CZL-412 (hereafter named CR65) are cross-linked sulfonated copolymers of vinyl compounds cast in homogeneous films on synthetic reinforced fabrics. Neosepta CMX membranes (hereafter named CMX) are composites prepared on the base of polystyrene and divinylbenzene, and reinforced with polyvinylchloride. Ralex CMH-PES membranes (hereafter named RXC) are composites formed from ion-exchange resins, polyethylene and polyamide as the reinforcing material. The membranes can be divided with respect to their structure and preparation into two categories: MK40, CR65 and RXC are considered as heterogeneous membranes, whereas NF115 and CMX are considered as homogeneous membranes. Based on the type of fixed charge group, the five membrane-types are classified as strong acid base membranes because contain sulphonate groups as charged group.

2.2. Liquid uptake measurements

In order to determine the liquid uptake by the membrane, a liquid swelling study was performed by using a water solution with a concentration of 0.01 M NaCl. Before the experiments, the membrane samples were dried under vacuum at 30.0 ± 0.1 °C for 24 h and weighted. After that, the samples were immersed in a closed bottle containing the solution and allowed to equilibrate. The bottle was placed in an oven thermostatted at 25.0 ± 0.1 °C. After several days of immersion, when no more liquid is sorbed, the swelling is considered to be completed and the swollen membrane was taken out of the liquid, wiped carefully with filter paper and weighted again. The increase in weight was equal to the weight of the liquid sorbed by the membrane. The liquid uptake was estimated from the weight of the swollen and the dry membrane sample according to the following expression:

$$s = \frac{m_w - m_d}{m_d} \quad (8)$$

where m_w and m_d are the weights of the swollen and dry membrane, respectively. The water content of the membrane can be expressed as the average number of water molecules per conducting functional group, λ , determined by [5]

$$\lambda = \frac{s}{IEC \cdot M_w} \quad (9)$$

where IEC represents the ion-exchange capacity (i.e. the ionizable hydrophilic functional groups content per gram of polymer, eq/g) and M_w is the molecular weight of water.

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