

Study of the Internal Morphology of Cation-Exchange Membranes by Means of Electroosmotic Permeability Relaxations

V. M. Barragán,* M. A. Izquierdo-Gil, M. P. Godino, and J. P. G. Villaluenga

Department of Applied Physics I, University Complutense of Madrid, 28040 Madrid, Spain

Received: April 14, 2009; Revised Manuscript Received: July 03, 2009

The effect of an ac sinusoidal perturbation of known amplitude and frequency superimposed to the usual dc applied electric voltage difference on the electroosmotic flow through three cation-exchange membranes with different morphology has been studied. A dispersion of the electroosmotic permeability on the frequency of the applied ac signal has been found for the three membranes investigated, observing that the electroosmotic permeability reaches maximum values for some characteristic values of the frequency. These characteristic frequency values, which are related to relaxation processes in heterogeneous media, depend on the membrane system and permit to obtain information about the different structures of the membrane system. Thus, the study of the electroosmotic permeability relaxation can be used as a method to study the internal morphology of a cation-exchange membrane in a given electrolyte medium.

Introduction

It is well known that the functional properties of a cation-exchange membrane are determined by their structure. For this reason, the study of relationships between the behavior of these membranes and their structure is very important for improving both the membranes properties and the membrane techniques, and the membrane characterization problem continues to attract attentions in current researches with a lot of works carried out in this direction.^{1–6}

The functional properties of membranes and solid-aqueous systems in general are closely connected to the electrochemical processes that occur within the system, so the understanding of the dielectric behavior is useful in improving membrane processes. Thus, the use of ac techniques has been shown as an useful instrument to study electrochemical processes occurring within the interfacial regions between the membrane surface and the bulk electrolyte without disturbing the system. Most of these techniques are based on the dispersion of the impedance with frequency of the alternating fields existing in some kind of systems, revealing that the capacity and the conductance of these systems depend on the frequency of the alternating fields,^{7–10} or on dielectric relaxation spectroscopy measurements.^{11,12}

It is known that when an alternating field is applied to a dielectric medium in the low frequency region, relaxation processes are originated that alter the dielectric constant of the medium.^{7,13} When an electric current circulates across a heterogeneous conductor, it gives rise to several polarization effects in different frequency domains. In biological systems and artificial membranes permeated by ionic solutions at very low frequencies, the dispersions are known as α -dispersions, and they have their origin in diffusion polarization effects occurring in the electrodes, unstirred layers, membrane interfaces, etc. At sufficiently high frequencies, the α -dispersions diminish revealing β -dispersions. These dispersions arise when two contacting phases have different specific conductivities/permittivities and a free charge is formed to provide continuity of the electric current. Because of the diffusion, the charge is

localized in some regions having nonzero thickness within each phase. The interfacial polarization due to the different specific conductivities/permittivities of the two contacting phases is known as Maxwell–Wagner polarization.^{14–16} At even higher frequencies, these β -dispersions also diminish, revealing γ -dispersions that arise from electric field reorientations of molecular dipoles. Molecular dipole-orientation gives rise to a net polarization, which manifests as an enhanced permittivity. Thermal agitation causes a relaxation of the polarization and this results in a dispersion of the dielectric permittivity with frequency.

The electrokinetic phenomena have originated as a consequence of the interaction between matter flux and electric charge flux through porous media. The Classical Irreversible Thermodynamics has been used satisfactorily for their study.^{17,18} In that approach, in the absence of a pressure difference ($\Delta P = 0$) the linear transport equations for matter and electric charge through porous media permit to express the electrokinetic coefficients, L_{12} and L_{22} , by the relations

$$\left(\frac{J_V}{\Delta\phi}\right)_{\Delta P=0} = L_{12} \quad (1)$$

$$\left(\frac{J_V}{I}\right)_{\Delta P=0} = \frac{L_{12}}{L_{22}} = W \quad (2)$$

where J_V is the volume flow, I is the electric current, ΔP is the pressure difference, and $\Delta\phi$ is the electric potential difference. The coefficient L_{22} is the electric conductance, whereas L_{12} , which must be equal to L_{21} according to the Onsager reciprocity relation, is the electrokinetic coefficient. W is the so-called electroosmotic permeability.

On the other hand, it is known that the electrokinetic phenomena can be studied in terms of considering the formation of a double electric layer¹⁹ in the membrane structure. This double layer is formed by a defined part consisting of ions fixed to the solid part, and a diffuse part consisting of free ions in the liquid mass. A slip plane in the double layer is usually envisaged dividing the fixed ions (part) and the free ions (part).

* To whom correspondence should be addressed. E-mail: vmabarra@fis.ucm.es. Fax: +34 91 394 51 91.

TABLE 1: Main Features of the Cation-Exchange Membranes Investigated

membrane	thickness ^b (10 ⁻⁶ m)	solvent uptake ^b (%) (in 0.01 M LiCl)	conductivity ^a (mS cm ⁻¹)	density ^b (g cm ⁻³)	ion exchange capacity (meq g ⁻¹) dry membrane ^a
NAFION 117	183	26	13.3 ^c	1.98	0.94
MK-40	480	55	3.43 ^d	1.12	2.6
CR 65 AZL 412	550	65	8.1 ^c	0.877	2.3

^a Provided by the manufacturer. ^b Measured. ^c Proton conductivity at 30 °C and 100% RH. ^d In 0.1 M NaCl.

The electrical potential in this plane is named ζ -potential, and it has been shown that the electrokinetic coefficients depend on its value. The ζ -potential depends on the dielectric properties of the medium, and therefore a dependence of the electrokinetic phenomena on the dielectric characteristic medium would be expected.

Thus, the origin of the electroosmotic flow arises from the Coulombic interaction between the external electric field and the mobile electric charge localized at the electrolyte-dielectric interface. In classical electrokinetic phenomena, a dc electric field is applied. The electroosmotic flow along a charged solid-liquid interface is generated by interaction of the local tangential components of the applied dc electrical field with the net volume charge in the fluid-side electrical double layer. The slip velocity tangential to the solid interface can be estimated from the Helmholtz-Smoluchowski equation, and it is proportional to the tangential component of the electric field strength. Similar to the dc electroosmosis, fluid motion can also be induced by ac electric fields.²⁰⁻²² Under ac forcing, a flow could be generated by the action of an electric field on its own induce diffuse charge over a polarizable surface. In this case, the normal component induces polarization and the tangential component of the electric field forces the accumulated electric charge to move along the interface. The ac electroosmosis can be observed because then both a nonzero tangential component of the electric field and a nonzero mobile electric charge at the surface are formed. This could be described as an equivalent RC circuit, where the diffusive layers act as capacitors. The sign of the ions in the double layers is always opposite to that of the charges on the corresponding polarizable surfaces, which produces a cumulative effect under ac electric fields, and therefore results in steady state fluid motion.

Previous studies²³⁻²⁵ have shown that the dispersion of the dielectric properties may influence the electrokinetic phenomena and in particular the electroosmotic transport. Under an alternating field, a dispersion with the frequency of the ac perturbation was observed in the electroosmotic transport through a typical ion-exchange membrane. We concluded that the observed dispersion of the electroosmotic permeability on the frequency may be closely related to the phenomena, which cause the dispersion of the permittivity of a membrane system. The typical characteristic frequencies seemed to be very close to the value of the frequencies at which maximum values of the apparent electroosmotic permeability are observed. This fact led us to think that the changes originated in the dielectric properties of the system could have a macroscopic effect in the electroosmotic behavior of the system. Thus, the different maxima observed in the behavior of the electroosmotic permeability versus the ac perturbation frequency would be closely related to the different mechanisms of polarization existing in the membrane system.

With this aim, we can suppose the membrane system is considered as a multilayer electric conductor.⁸ The system includes at least the membrane itself and two adjacent electrolyte solutions. The system would be formed by "fictitious" layers corresponding to the different parts of the system with different

properties, as unstirred layer, Debye layer, membrane pores, among others, and the thickness of each layer would be a characteristic length of that part. The different relaxation times could be roughly evaluated as the characteristic diffusion times attributed to the thickness of the constituent layer. The purpose of this work is to analyze the possibility of using the relaxations of the electroosmotic permeability to obtain information about the internal structure of the membrane under given experimental conditions.

Experimental Procedures

Materials. Three different commercial cation-exchange membranes with similar electric properties but different morphology were tested in this work. The Nafion 117 membrane (NF117) from Dupont de Nemours, U.S.A. with a nominal equivalent weight of 1100 g/eq is a homogeneous cation-exchange membrane consisting of a polytetrafluoroethylene backbone and long fluorovinyl ether pendant side chains regularly spaced, terminated by a sulfonate ionic group. There are no cross-links between the polymers. The MK-40 membrane (MK40), produced by Schekinzot, Russia, is a sulfonic polystyrene divinylbenzene cation-exchange membrane of heterogeneous type prepared by the inclusion of a finely ground ion-exchange resin in a PE binder. The CR65 AZL 412 membrane (ICR65), from Ionics, U.S.A. is a heterogeneous cross-linked sulfonated copolymer of vinyl compounds cast in homogeneous films on synthetic reinforced fabrics. Table 1 shows the main characteristics of these membranes. They all are representative membranes, used often in different membrane processes fields. The study of the Nafion membranes structure has been the purpose of many papers, and it is a very appropriate membrane to check the viability of the present method to study the internal morphology of a membrane.

The material employed in the experiments was 10⁻² mol/liter aqueous solutions of lithium chloride. Pure proanalysis-grade chemicals and pure water (deionized, doubly distilled, doubly filtrated, and degassed) were used.

Apparatus and Procedures. The apparatus used in this work and the methodology employed were substantially similar to those described in earlier publications.²⁶ The membrane surface exposed to the flow was 5.7 cm². A Ag/AgCl electrode with a large active surface was introduced in each chamber on both sides of the membrane to inject an electric current.

All the experiments were carried out under isothermal conditions at 297.7 K. Temperature requirements were achieved by immersing the cell in a water thermostatted bath. In order to improve the uniformity of the temperatures and concentrations inside each chamber, the solutions were stirred by a magnetic stirrer assembly. The stirring rate in all the experiments was 365 rpm. Under these conditions, the temperature was constant within ± 0.1 K.

Prior to each experiment, the membranes were immersed for a minimum of 24 h in the solution in order to achieve equilibrium.

The volume flow, J_v , originated by the pass of an electric current, I , was determined by measuring the volume change

rates of the cathodic and anodic compartments, ΔV_c and ΔV_a , respectively. Taking into account the volume change due to the electrochemical reactions at the Ag/AgCl electrodes, this volume flow can be expressed as²⁶

$$J_v \text{ (ml/s)} = \frac{|\Delta V_a| + |\Delta V_c|}{2} + 1.6 \times 10^{-4} \text{ (ml/C)} I \quad (3)$$

where I is expressed in amperes.

It was checked that the electric current passing through the system was constant up to the hundredth or tenth part of milliamperes, during the measurement time. When the electric potential was applied, a steady current was reached after a few seconds. If an ac perturbation was superimposed to the dc signal, a steady effective dc current was also observed, with this value being similar to the one obtained in the absence of ac perturbation under the same conditions. Only for frequencies below 10 Hz, a small oscillation of the dc current around a mean value was observed. This mean value was similar to the value in the absence of ac perturbation under the same conditions. In these cases, this mean value was taken as effective dc current, I^* , in order to calculate the correction of the reaction volume change to the volume flow in eq 3.

In this situation, from eqs 2 and 3, the effective apparent electroosmotic permeability, W^* , can be estimated as follows

$$W^* \text{ (m}^3\text{/C)} = \frac{|\Delta V_a^*| + |\Delta V_c^*|}{2I^*} + 1.6 \times 10^{-10} \text{ (m}^3\text{/C)} \quad (4)$$

where ΔV_c^* and ΔV_a^* are, respectively, the volume change rate of the anodic and cathodic compartments in the presence of the ac perturbation, and I^* is expressed in amperes.

Results and Discussion

In previous studies,^{23,24} we checked the validity of the linear phenomenological eq 1 in the presence of an ac perturbation. The results obtained showed that a linear relation existed between the volume flow and the applied dc voltage under all the studied conditions. It was observed that for the same dc voltage applied, the effective continuous component of the current was the same within the experimental accuracy for all the frequencies, and so the effective ion transport does not seem to be significantly affected by the ac signal in the studied frequency range. It was also checked that there were no changes in the described qualitative behavior when the same electrodes were used to measure the dc current as well as the dc voltage. In all cases, it was observed that the presence of an ac perturbation did not influence the linear behavior range, but it affected the value of the slope, depending on the frequency of the ac perturbation. No significant influence of the amplitude on the effective apparent electroosmotic permeability could be observed under the established experimental conditions.

Thus, in the present study, the effective apparent electroosmotic permeability has been measured as a function of the frequency of a small ac perturbation for three membrane systems at the same dc voltage, 9.7 V, with a 10^{-2} mol/liter LiCl electrolyte.

The effective apparent electroosmotic permeability was estimated from eq 4. In all cases, the value of the applied dc voltage was selected in such a way that the electric current circulating through the system was far away from the corresponding limiting values. These limiting values were reported

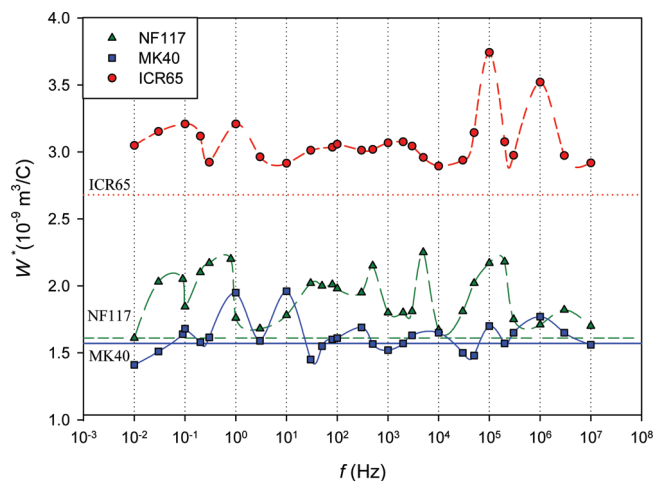


Figure 1. Effective electroosmotic permeability as a function of the frequency of the ac perturbation for the three membrane systems investigated. The data correspond to a dc voltage of 9.7 V. The horizontal lines represent the electroosmotic permeability values in the absence of an ac perturbation. Dotted lines are only a visual guide.

TABLE 2: Characteristic Relaxation Frequencies, f^* , for the Electroosmotic Permeability of the Membrane Systems Investigated

frequency (Hz)	NF117	MK40	ICR65
f^{*1}	0.09	0.1	0.1
f^{*2}	0.8	1	1
f^{*3}	3×10^1	1×10^1	
f^{*4}	5×10^2	3×10^2	1×10^2
f^{*5}	5×10^3	1×10^4	2×10^3
f^{*6}	1×10^5	1×10^5	1×10^5
f^{*7}	3×10^6	1×10^6	1×10^6

in a previous paper for these same membrane systems.²⁷ The values obtained for the limiting current density were 54, 56, and 62 A/m² for NF117, MK40 and CR65 membranes, respectively. The effective electric current was always lower than 8 A/m². These voltage and electrolyte concentration values are adequate to consider negligible the Joule-heating effects. It is well known that the so-called Joule heating is generated when an electric field is applied across conductive liquids. Such Joule heating not only could cause temperature increase but also may create temperature gradient.^{28–31} However, under the applied conditions, no positive deviation from linearity in Ohms plots was observed, and relation (1) is valid, indicating that the Joule heating can be neglected in the systems investigated.³¹

The results obtained for the electroosmotic permeability as a function of the ac perturbation are shown in Figure 1 for the different membrane systems investigated. The horizontal lines correspond to the values of the apparent electroosmotic permeability in the absence of ac perturbation. In all cases, the measurements were reproducible within the experimental accuracy.

The experimental results show that the presence of the ac perturbation seems to increase, as a general trend, the value of the electroosmotic flow with respect to the value in the absence of the ac signal. Moreover, for the three membrane systems, it is possible to observe that maximum values are reached at certain values of the ac signal frequency. These characteristic frequencies, f^* , depend on the membrane considered, but they appear in the same frequency ranges for the three studied membrane systems. These values are given in Table 2. Two of them, named f^{*1} and f^{*2} , appear at low values of the frequency, in the 0.01–1 Hz range. In this frequency range, the spectrum

is very similar for the three systems studied. In the 10–10 000 Hz frequency interval, a group of maxima are observed at different characteristic frequencies, named f^{*3} , f^{*4} , and f^{*5} , depending on the membrane system considered. In this 10–10 000 Hz frequency interval, three maxima are observed for membranes NF117 and MK40, but only two for ionics membrane. At higher frequencies, for a characteristic frequency around of 100 kHz other maximum can be observed for the three membranes. Another maximum value is also observed at frequencies of the order of megahertz. These results are in agreement with those obtained in previous works^{23,24} with an ionics membrane, where a similar spectrum was reported for the electroosmotic permeability in different experimental conditions.

Following the treatment of Zholkovski for multilayer membranes,⁸ for a 1:1 electrolyte solution the characteristic frequency of a medium containing two charged species, 1 and 2, is given by

$$f^* = \frac{1}{d^2} \frac{2D_1D_2}{D_1 + D_2} \quad (5)$$

where D_1 and D_2 are the diffusion coefficients of the two charged species, and d is the thickness of the layer considered. Thus, one characteristic layer of thickness d_i can be associated to each characteristic frequency f^{*i} . The low-frequency dispersion region here is attributed to the contribution of charge accumulation at the different interfaces.

At the lowest frequencies, the α -dispersions have their origin in diffusion polarization effects occurring in the unstirred layers formed between bulk solution and electrode, and between bulk solution and membrane. In the first case, the so-called electrode polarization, the estimation of the diffusion layer for the electrode solution interface can be made by considering that the diffusion occurs across a region parallel to the interface, that is, across a Nernst diffusion layer of effective thickness δ_{elec} . For typical Ag/AgCl electrodes, the thickness is about 10^{-4} m.^{32,33} In the second case, the so-called concentration polarization, the thickness of these polarization layers, δ_p , can be estimated from the classical polarization theory by the equation of Levich

$$\delta_p = \frac{FDc_0}{\Delta t_+ I_L} \quad (6)$$

where c_0 is the concentration corresponding to the bulk solution, I_L is the limiting current density, D is the salt diffusion coefficient, $\Delta t_+ = \bar{t}_+ - t_+$ is the difference between the cation transport numbers in the membrane and in the free solution, and F is the Faraday constant. Using the values of D and t_+ found in the literature³⁴ for a LiCl 0.01 mol/liter aqueous solution at 298 K and the values of the limiting current density and the membrane transport number estimated in a previous study²⁷ for the same membrane systems, the values of δ_p can be estimated from eq 6. The results obtained for the three studied systems are given in Table 3.

From eq 5 and taking into account that in the polarization layers $D_1 = D_2 = D$, we can estimate the thickness, d_i , of the

TABLE 3: Thickness of the Electrode, d_1 , and Concentration Polarization, d_2 , Layers, Estimated from the Corresponding Relaxation Frequency and Equation 7, Together with the Concentration Polarization Thickness, δ_p , Estimated from Equation 6

	NF117	MK40	ICR65
d_1 (10^{-4} m)	1.21	1.14	1.14
d_2 (10^{-5} m)	4.0	3.6	3.6
δ_p (10^{-5} m)	4.1	3.5	3.7

polarization layer associated to the characteristic frequency, f^{*i} , by means of the expression

$$f^{*i} = \frac{D}{d_i^2} \quad (7)$$

The values obtained are also shown in Table 3. As can be observed, in the case of f^{*1} , the order of magnitude of the corresponding layer, d_1 , is 10^{-4} m. This value is nearly the same for the three membrane systems, in agreement with the data reported for δ_{elec} in the literature.³³ In the case of f^{*2} , the thickness of the corresponding layer, d_2 , is very close to the thickness of unstirred layer, δ_p , obtained from eq 6. This fact suggests that these both maxima are due to the electrode and concentration polarization effects and originated in the same mechanism as the α -permittivity dispersions observed in this kind of systems.

At sufficiently high frequencies, β -dispersions appear due to the interfacial polarization effect in heterogeneous systems containing two contacting phases with different specific conductivities/permittivities. An ionic charge distribution, called electrical double layer^{8,35} is always formed on a charge surface in an electrolyte. The electric charge is distributed between both phases and it is localized in a region with a thickness characterized by the Debye screening length, l_D . Maxwell polarization is usually seen at frequencies about 100 kHz. As can be observed in Figure 1, for the three membrane systems a maximum value of the electroosmotic permeability is observed at approximately 100 kHz, named f^{*6} .

For a high fixed charge membrane, $D = \bar{D}_1$ (diffusion coefficient of counterions inside the membrane) must be written in eq 5, and by analogy with eq 7 the following equation can be written

$$f^* = \frac{\bar{D}_1}{l_D^2} \quad (8)$$

where l_D is the thickness of this layer, which can be estimated by the corresponding Debye length given by the expression²⁸

$$l_D^{-1} = \sqrt{\frac{F^2}{\epsilon RT} \bar{c} z^2} \quad (9)$$

where \bar{c} is the electrolyte concentration inside the membrane, z its valence, ϵ its permittivity, T the absolute temperature, and R is the gas constant. As the value of the fixed charge of the membrane is known, it is possible to estimate \bar{c} for each experimental situation. For a 0.01 M bulk solution, the electrolyte concentration inside the membrane practically coincides with the membrane concentration of fixed ionic groups. The values obtained for \bar{c} are shown in Table 4. The value of

TABLE 4: Membrane Charge Fixed Concentration, \bar{c} , Debye Length, l_D , and Membrane Cation Diffusion Coefficient, \bar{D}_1 , Estimated from Equation 8 and Maxwell Relaxation Frequency, f^{*6}

	NF117	MK40	ICR65
\bar{c} (kmol/m ³)	1.37	1.29	0.64
l_D (10 ⁻¹⁰ m)	3.37	3.47	4.93
\bar{D}_1 (10 ⁻¹⁴ m ² /s)	1.13	1.21	2.43

TABLE 5: Thickness of the Interfacial Polarization Structures Inside Membrane Estimated from Equation 8 and the Corresponding Relaxations Frequencies, and Effective Pore Radii, r , Estimated from Equation 10

	NF117	MK40	ICR65
d_3 (10 ⁻⁹ m)	19	35	
d_4 (10 ⁻⁹ m)	4.8	6.3	16
d_5 (10 ⁻⁹ m)	1.5	1.1	3.5
r (10 ⁻⁹ m)	0.65	3.7	4.1

the permittivity is $\varepsilon = \varepsilon_r \varepsilon_0$, where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of the vacuum and $\varepsilon_r = 66$ is the medium relative permittivity. From eq 9, it is possible to calculate the Debye length for each electrolyte at a concentration \bar{c} and temperature T . The results are also given Table 4. We have no information about the value of the diffusion coefficient of the counterion in the membrane phase. On the basis of previous results,^{23,24} it can be assumed that this characteristic frequency is associated with the electrical double layer. In this case, by using eq 8 and supposing that the maximum observed is due to the Maxwell polarization, we can estimate the value of \bar{D}_1 using the experimental f^{*6} frequencies. The results obtained for \bar{D}_1 are shown in Table 4. As can be observed, the value of \bar{D}_1 is higher at higher membrane solvent uptakes, probably due to a decrease of the ion interaction with the fixed charge of the membrane.

As can be observed, other maximum values are found in the frequency interval characteristic of the α -dispersion. It can be speculated that these peaks may be due to the existence of an internal porous structure in the membrane, and the creation of a double layer due to a charge distribution in these pores. Kuang and Nelson³⁶ showed that a dielectric dispersion mechanism arises from membrane pores within artificial membranes. Theoretical analysis showed that a low-frequency dielectric dispersion would be produced in the same frequency range as the α -dispersion.

If we consider the diffusion coefficient in the membrane phase previously estimated in eq 8 and the values of the experimental characteristic frequencies, f^{*3} , f^{*4} , and f^{*5} , given in Table 2, we can use an analogue expression to eq 8 to estimate the associated length to each relaxation frequency observed. This analysis is useful to check the viability of the present method to study the internal morphology of the membrane. With this aim, the results obtained here are compared with those reported in the literature for the Nafion membrane.

In Figure 1, three maxima are observed at 30, 500, and 5000 Hz, respectively, for the Nafion membrane. The thickness of the corresponding layers can be estimated by using eq 8. The results are given in Table 5. These results seem to indicate that three structures exist inside the membranes. The dimensions of these structures are in agreement with the structure data found in the literature for Nafion membrane. The Nafion structure is described with a cluster model of ionic aggregation with pores of 5 nm of diameter connected by narrow channels of 1–2 nm, aggregating to form cluster agglomerates with size from 5 to 30 nm.^{37–39} This allows to state that the study of the electroosmotic permeability relaxations gives information about the

internal structure of the membrane, showing the existence of clusters, narrow channels and the formation of aggregations around the previous structures.

For MK40 membrane, three maxima also appear at similar frequency values, 10, 300, and 10 000 Hz, indicating that the internal structure of both membranes is very similar. This result is in agreement with papers found in the literature, where models can be applied to these two kind of membranes, indicating the existence of microstructure in both, heterogeneous and homogeneous membranes.⁶ In the case of membrane MK40, the aggregations are greater than that of Nafion membrane.

In the case of ICR65 membrane, only two maxima are observed in the same frequency interval, and thus only two internal structures are found for this kind of membrane. Moreover, the maxima are slighter than for the other two membranes.

If we consider the membrane as a simple array of parallel capillaries, it can be shown⁴⁰ that the equivalent pore radii can be estimated by means of the equation

$$r = \left(\frac{8\eta\sigma Lp}{S} \right)^{1/2} \quad (10)$$

where σ is the specific conductivity of the solution, η its absolute viscosity, Lp is the hydraulic permeability, and S is the membrane surface. Using this capillary model, the effective pore radii can be estimated from permeation measurements. In a previous work,⁴¹ the Lp coefficients were determined for these three kind of membranes in similar experimental conditions. From these values, the effective pore radii, r , has been determined. The results are given in Table 5 for the three membranes investigated. On the other hand, if spherical pores are considered from the obtained values of d_i , an estimation of a mean effective radii, \bar{r} , for the internal structures of the membrane can be made. Only in the case of the membrane ICR65, there is an agreement between both values, $r = 4.1$ nm and $\bar{r} = 4.9$ nm. This suggests that in the case of membranes Nafion and MK40, the capillary model is not applicable, probably due to the higher densities of these membranes. In the case of the ionics membranes, the permeation transport seems to take place through both structures.

At frequencies higher than 1 MHz, γ -dispersions arisen from electric field reorientations of molecular dipoles are originated. The characteristic frequency of these dispersions is 20 MHz for water. This frequency is related to the time that the molecules spend in reorientating in the electric field. The presence of the electrolyte must affect this time since the water molecules are hydrating the ions in the solutions forming the hydration shell of the ions, and thus the water polarization is affected.^{42,43} The reorientating time is expected to be greater in an ionic medium, and lower frequencies should be found in agreement with the results obtained for f^{*7} .

Conclusions

1. The effect of an ac sinusoidal perturbation, of known angular frequency and small amplitude, superimposed to the usual applied dc electric voltage difference on the electroosmotic behavior of a cation-exchange membrane system has been studied for three membrane systems of different structures. In all the studied cases, the experimental results show that the presence of the ac perturbation influences the electroosmotic permeability value, and this effect depends on the membrane structure.

2. A dispersion of the electroosmotic permeability on the frequency of the ac signal applied has been found for the three membranes studied, observing that the electroosmotic permeability reaches maximum values for some characteristic values of the frequency. These characteristic values depend on the membrane considered, but they appear in the same frequency domains for the three membranes.
3. The electroosmotic permeability spectrum has been related to the different relaxation processes in heterogeneous media and permits one to obtain information about the different polarization layers of the systems. Thus, electroosmotic permeability relaxation could be used as a method to study the internal nanoscale structure of cation-exchange membranes.

Acknowledgment. Financial support from the University Complutense of Madrid under Project No. PR1/08-15918-A is gratefully acknowledged. Professors C. Larchet and V. Nikonenko are gratefully acknowledged for donating MK40 samples.

References and Notes

- (1) Choi, J.-H.; Kim, S.-H.; Moon, S.-H. *J. Colloid Interface Sci.* **2001**, *241*, 120.
- (2) Gnsin, N. P.; Berezina, N. P.; Kononenko, N. A.; Dyomina, O. A. *J. Membr. Sci.* **2004**, *243*, 301.
- (3) She, F. H.; Gao, W. M.; Peng, Z.; Hodgson, P. D.; Kong, L. X. *J. Chin. Inst. Chem. Eng.* **2008**, *39*, 313.
- (4) Le, X. T. *J. Colloid Interface Sci.* **2008**, *325*, 215.
- (5) Chaabane, L.; Bulvestre, G.; Larchet, C.; Nikonenko, V.; Deslouis, C.; Takenouti, H. *J. Membr. Sci.* **2008**, *323*, 167.
- (6) Berezina, N. P.; Kononenko, N. A.; Dyomina, O. A.; Gnusin, N. P. *Adv. Colloid Interface Sci.* **2008**, *139*, 3.
- (7) Coster, H. G. L.; Chilcott, T. C. *Surface Chemistry and Electrochemistry of Membranes*; Sørensen, T. S., Ed.; Marcel Dekker, Inc.: New York, 1999; Chapter 19.
- (8) Zholkovskij, E. K. *Surface Chemistry and Electrochemistry of Membranes*; Sørensen, T. S., Ed.; Marcel Dekker, Inc.: New York, 1999; Chapter 20.
- (9) Zhao, K.; Li, Y. *J. Phys. Chem. B* **2006**, *110*, 2755.
- (10) Sistat, P.; Kozmai, A.; Pismenskaya, N.; Larchet, C.; Pourcelly, G.; Nikonenko, V. *Electrochim. Acta* **2008**, *53*, 6380.
- (11) Sørensen, T. S. *Surface Chemistry and Electrochemistry of Membranes*; Sørensen, T. S., Ed.; Marcel Dekker, Inc.: New York, 1999; Chapter 18.
- (12) Tsouos, C.; Apekis, L.; Pissis, P. *J. Mater. Sci.* **2000**, *35*, 5957.
- (13) Böttcher, C. J. F.; Bordewijk, P. *Theory of Electric Polarization*; Elsevier, Ed., 1996, Vol. II.
- (14) Maxwell, J. C. *A Treatise of Electricity and Magnetism*; Dover: New York, 1954.
- (15) Wagner, K. W. *Arch. Electrotech.* **1914**, *2*, 371.
- (16) Wagner, K. W. *Arch. Electrotech.* **1914**, *3*, 67.
- (17) Prigogine, I. *Introduction to Thermodynamics of Irreversible Processes*, 3rd ed.; Wiley: New York, 1968.
- (18) De Groot, S. R. *Thermodynamics of Irreversible Processes*, 4th ed.; North Holland Publishing Co.: Amsterdam, 1966.
- (19) Lakshminarayanaiah, W. *Transport Phenomena in Membranes*; Academic Press: New York, 1969.
- (20) Ramos, A.; Morgan, H.; Castellanos, A. *J. Phys. D: Appl. Phys.* **1998**, *31*, 2338.
- (21) Morgan, H.; Green, N. *AC Electrokinetics: Colloids and Nanoparticle*; Research Studies Press LTD.: Hertfordshire, England, 2003.
- (22) Wang, D.; Sigurdson, M.; Meinhart, C. D. *Exp. Fluids* **2005**, *38*, 1.
- (23) Barragán, V. M.; Ruiz-Bauzá, C. *J. Colloid Interface Sci.* **2000**, *230*, 359.
- (24) Barragán, V. M.; Ruiz-Bauzá, C. *J. Colloid Interface Sci.* **2001**, *240*, 182.
- (25) Barragán, V. M.; Ruiz-Bauzá, C.; Imaña, J. L. *Desalination* **2002**, *142*, 235.
- (26) Barragán, V. M.; Ruiz-Bauzá, C.; Villaluenga, J. P. G.; Seoane, B. *J. Membr. Sci.* **2004**, *236*, 109.
- (27) Barragán, V. M.; Villaluenga, J. P. G.; Godino, M. P.; Izquierdo-Gil, M. A.; Ruiz-Bauzá, C.; Seoane, B. *J. Colloid Interface Sci.* **2009**, *333*, 497.
- (28) Tang, G. Y.; Yang, C.; Chai, J. C.; Gong, H. Q. *Int. J. Heat Mass Transfer* **2004**, *47*, 215.
- (29) Kang, Y.; Yang, C.; Huang, X. *Langmuir* **2005**, *21*, 7598.
- (30) Gagnon, Z. R.; Chang, H. *Appl. Phys. Lett.* **2009**, *94*, 024101.
- (31) Chen, G.; Tallarek, U.; Seide-Morgenstern, A.; Zhang, Y. *J. Chromatogr., A* **2004**, *1044*, 287.
- (32) Bagotzky, V. S. *Fundamentals of Electrochemistry*; Plenum Press: New York, 1993.
- (33) Bockris, J. O.; Reddy, A. K. N.; Gamboa-Aldeco, M. *Modern Electrochemistry*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 2000; Vol. 2A.
- (34) Lobo, V. M. M. *Electrolyte Solutions: Literature Data on Thermodynamics and Transport Properties*; Coimbra Editora, Lda.: Coimbra, Portugal, 1975.
- (35) Helfferich, F. *Ion-Exchange*; McGraw-Hill: New York, 1962.
- (36) Kuang, W.; Nelson, S. O. *J. Colloid Interface Sci.* **1997**, *193*, 242.
- (37) Mauritz, J. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535.
- (38) Rollet, A. L.; Diat, O.; Gebel, G. *J. Phys. Chem. B* **2002**, *106*, 3033.
- (39) Rubatat, L.; Rollet, A. a.; Gebel, G.; Diat, O. *Macromolecules* **2002**, *35*, 4050.
- (40) González-Caballero, F.; De las Nieves, F. J. *J. Membr. Sci.* **1983**, *16*, 225.
- (41) Barragán, V. M.; Ruiz-Bauzá, C. *J. Non-Equilib. Thermodyn.* **1997**, *22*, 374.
- (42) Bucher, D.; Kuyucak, S. *J. Phys. Chem. B* **2008**, *112*, 10786.
- (43) Moon, M. J.; Jhon, M. S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1215.

JP903414Z