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Water sorption and dielectric relaxation spectroscopy studies in hydrated Nafion® (-SO_3K) membranes

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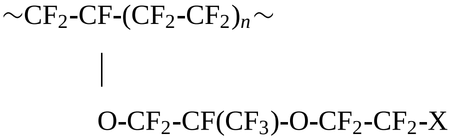
Dynamic and equilibrium sorption isotherm measurements were carried out on hydrated perfluorosulfonate polymer membranes in potassium salt form (Nafion®-SO_3K, 1190 EW), at 22 and 40 °C respectively. Despite the glassy state of the membrane the diffusion process is Fickian with an average diffusion coefficient D in the range $2.8–30 \times 10^{-9}$ cm^2/s. The equilibrium sorption isotherms may be quantitatively analyzed according to the GAB equation for multilayer sorption processes up to the activity value of $\alpha = 0.79$, which corresponds to 1.0 site-bound water molecules per (-SO_3K) group. The analysis of the equilibrium sorption isotherm, using the method of Zimm and Lundberg, suggests clustering of the water molecules for activities $\alpha \geq 0.79$. The apparent polymer-water interaction parameter χ (Flory parameter), was found to have a maximum at $\alpha = 0.79$ $(1.07 \leq \chi \leq 1.95)$. Also, dielectric relaxation studies of the same hydrated Nafion® membranes have been carried out in the frequency range of $10^{-2} - 5 \times 10^6$ Hz and in the temperature range of 223–295 K. Two relaxation mechanisms were observed which both sift to higher frequencies by increasing the water content. The low frequency relaxation mechanism is due to interfacial polarization which takes place in the hydrated ionic regions. The high frequency relaxation mechanism, is a dipolar mechanism which may be attributed to the rotation of (-SO_3^-) group-water complexes at the end of the side chains.

1. Introduction

Perfluorinated ionomer membranes are used or suggested for to be used in many industrial applications, such as battery separators [1], as separators in fuel cells [2] and in photoelectrochemical systems [3]. Nafion® is the trade name of the perfluorosulfonated polymers and was first developed by E. I. Du Pont de Nemours and Co in the 1960's. Nafion® in the sulfonate form has the polymeric structure



$$\sim CF_2\text{-}CF\text{-}(CF_2\text{-}CF_2)_n\sim$$
$$|$$
$$O\text{-}CF_2\text{-}CF(CF_3)\text{-}O\text{-}CF_2\text{-}CF_2\text{-}X$$

where $X = SO_2F$, SO_3H, SO_3Na or SO_3K. The polymeric composition is expressed in terms of equivalent weights EW, defined as the weight in grams of polymer containing 1 eq. of acid. The backbone TFE segment tends to crystallize the structure, while the side groups hinder crystallization. The degree of crystallinity decreases with decreasing EW due to the increasing concentration of side-chain material with decreasing EW.

Small angle X-ray scattering (SAXS) provides evidence for the existence of ionic rich domains or "clusters" and this somewhat ill-defined hydrophobic/hydrophilic micro-phase separation in the form of sulfonate-rich ion clusters (about 4 nm in diameter) embedded in a crystalline perfluorocarbon matrix [4, 5]. It has been proposed that clusters act as multifunctional "electrostatic" crosslinks due to their strong coulombic nature [6] and this results in very good thermal and chemical stability of the perfluorosulfonated polymers. The acid and salt forms are hydrophilic and the most of the absorbed water in Nafion® membranes is located in the hydrophilic ionic regions [7].

In hydrated perfluorosulfonate polymers in potassium salt form, dynamic mechanical and dielectric studies have been carried out by Yeo and Eisenberg [8]. They reported that dynamic mechanical measurements gave α, β and γ relaxation processes. β relaxation which in dry membranes appears at about 423 K, shifts to lower temperatures by the absorption of water, while α and γ relaxations have been found to be unaffected by the absorbed water. In isochronal dielectric measurements two dispersions were observed in the β-relaxation region and both components were found

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to shift to lower temperatures with increasing the water content of the samples [8].

Dielectric measurements have been carried out on dry perfluorocarboxylate polymers in potassium salt form by Perusich *et al.* [9]. Four dielectric relaxation were observed. α-relaxation is related to the motion of the vinyl ether side chain. β-relaxation is due to the ester group (-CO_2K) motion at the end of the side chain. γ- relaxation is related to a crankshaft motion of (-CF_2-) groups along the polymer backbone. The mobile O-K ends of the side group produce δ-relaxation.

In a previous work we studied the dielectric properties of Nafion® membranes in potassium salt form (-SO_3K) (1190 EW), using Thermally Stimulated Depolarization Current (TSDC) spectroscopy [10]. Three dispersion regions have been observed. They were: γ-relaxation, a dipolar relaxation with a contribution from an interfacial polarization mechanism in the β-relaxation region, and a dispersion which could be related to a phase or structural change in which a contribution from electrochemical effects at the electrodes could not be excluded. The two components of the β- relaxation, the dipolar mechanism and the interfacial polarization mechanism were systematically studied. Both processes were found to shift to lower temperatures with increasing the water absorbed by the samples. The TSDC spectroscopy corresponds to measuring dielectric losses as a function of temperature at low frequencies in limited range of frequencies, 0.1–10 mHz [10]. We attributed the dipolar β-relaxation to the rotation of (-SO_3^-) group-water complexes at the end of the side chains. The interfacial polarization takes place in the hydrated ionic regions and is related to the direct current (dc) conductivity of the samples.

In the present work, we continue the investigation of the interaction with water of the Nafion® membranes in potassium salt form (-SO_3K) (1190 EW), the same system as in reference [10]. In this work we study the hydration properties of this Nafion® membranes by means of equilibrium and dynamic water sorption isotherm measurements. We also study the effects of the water absorbed by the material on the molecular mobility of the material by means of dielectric alternating current (ac) measurements.

The hydration properties studied in this work concern the mechanism of the water sorption and desorption, the diffusion coefficient of water in the membranes, the distinction of sorbed water in different states or phases, as well as the effects of sorbed water on the structure of the membranes. The dielectric ac measurements concern the study of the dielectric relaxation mechanisms of the material and the mechanisms related to the direct current (dc) conductivity, such as the interfacial polarization and conductivity relaxation, as well as the influence of the water sorbed by the membranes on the parameters which characterize the dynamics of these mechanisms.

2. Experimental procedure

Measurements were carried out on Nafion® membranes of E. I. Du Pont in perfluorosulfonate potassium salt form (1190 EW). The Nafion® membranes were sheets of about 0.063 mm thickness.

The method adopted for the determination of the dry weights was that of drying the samples in vacuum (5×10^{-2} Torr) at 380 K for 2 days. The water content n, have been defined as the ratio (H_2O/SO_3K) of the number of H_2O molecules to the number of SO_3K groups.

Equilibrium water sorption isotherms were measured at 40 °C. The sample was allowed to equilibrate in atmospheres of different water activities, which were monitored between 0.06 and 1, using different saturated salt solutions in various dessicators. The water regain, was measured by periodic weighing on a A200S Sartorius analytic balance, until the sample reach equilibrium (sample weight changes less than 0.1 mg).

Dynamic water sorption isotherm measurements, were carried out at 22 °C, to study the kinetics of sorption and desorption. Samples after drying, were allowed to equilibrate in sealed jars of water activity $\alpha = 0.08$ for the sorption measurements and of 0.95 for the desorption measurements. They were then allowed to equilibrate to the environment water activity ($\alpha \approx 0.5$), while their weights were continuously recorded.

The dielectric relaxation measurements were carried out using two different experimental set ups. In the frequency range 10^{-2}–10^{6} Hz and at room temperature a Schlumberger frequency response analyzer SI 1260 was used, supplemented by a buffer amplifier of variable gain. The sample was clamped between gold electrodes. In the frequency range 10^2–5×10^6 Hz and temperature range 223–278 K a Hewlett Packard HP 4192A impedance analyzer was used. The samples were clamped between stainless steel electrodes in a three-terminal electrode configuration. The water content was adjusted over saturated salts solution in sealed jars at controlled relative humidities and after weighing were rapidly enclosed between the electrodes and cooled to 223 K in order to minimize water loss. For both set ups we performed complex admittance measurements.

The uncertainties were about ± 0.01 eV (± 1 kJ/mole) in the activation energy and ± 0.1 H_2O/SO_3K in the water content.

3. Result and discussion

3.1. Dynamic water sorption isotherms

Fig. 1 shows the normalized dynamic water sorption isotherm of a Nafion® membrane at 22 °C. The normalized dynamic water uptake (or loss), M_t/M_∞, is defined as the water uptake or loss at time t (sorption or desorption respectively), divided by the corresponding limiting value at equilibrium. d is the thickness of the sample, presumed constant over the whole sorption or desorption process. The observed linearity extending to at least $M_t/M_\infty = 0.6$ and the curvature concave to the abscissa axis following the initial linear increase, suggest that the sorption and desorption processes are controlled by a simple Fickian diffusion [11]. Systems in the glassy state, as the Nafion® membranes, usually do not follow a simple Fickian diffusion process [12].

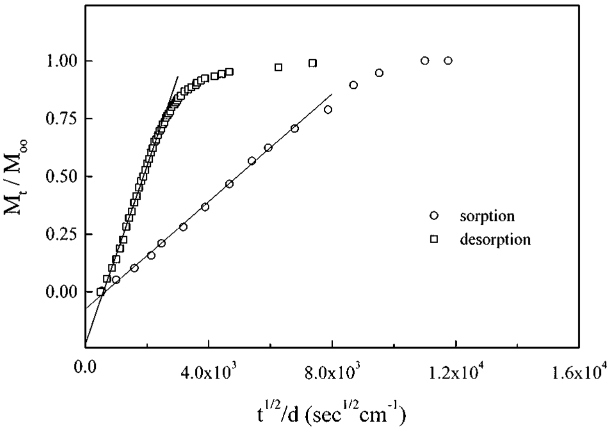

Figure 1 Sorption and desorption curves of a perfluorosulfonate membrane in potassium salt form at 22°C.

The values of diffusion coefficient, D, were calculated from the initial slope ($M_t/M_\infty \leq 0.6$) of the plots by using the relation [11]

$$\frac{M_t}{M_\infty} = \left(\frac{16D}{\pi}\right)^{1/2} \frac{t^{1/2}}{d} \tag{1}$$

The diffusion coefficient for the desorption experiment was found to be 3.0×10^{-8} cm^2/sec, one order of magnitude higher than that found for the sorption experiment, 2.8×10^{-9} cm^2/sec. The experimental error for D have been estimated to about 10–15%. A value of about 1.6×10^{-6} cm^2/sec has been reported [8] for the sorption isotherm process of a Nafion® membrane in acid form (1155 EW), which is three orders of magnitude higher than the value of D calculated above for the Nafion® membrane in potassium salt form, at the same temperature. The difference between the sorption and desorption isotherm diffusion coefficient, which is often observed in glassy systems, suggests a definite dependence of the diffusion coefficient upon the permeant concentration. Generally, the diffusion coefficient of diluents in polymers was found to increase significantly with increasing diluent water concentration [13, 14]. Free volume concepts have been applied to describe the concentration dependence of D, both, above and below the glass transition temperature [15, 16].

3.2. Equilibrium water sorption isotherm

Fig. 2 shows the sorption and desorption isotherm of a Nafion® membrane at 40 °C. The desorption isotherm process exhibits a hysterisis with respect sorption. For water activities less than 0.8, the water content decreases slightly by decreasing activity and at the lower value ($\alpha = 0.06$) the membrane retains 1.6 H_2O/SO_3K. This result suggests a modification of the physical structure of the Nafion® membrane caused by the sorbed water.

The sigmoidal-like shape of the sorption isotherm allows us to analyze the data according to the Guggenheim-Anderson-De Boer (GAB) equation [17]

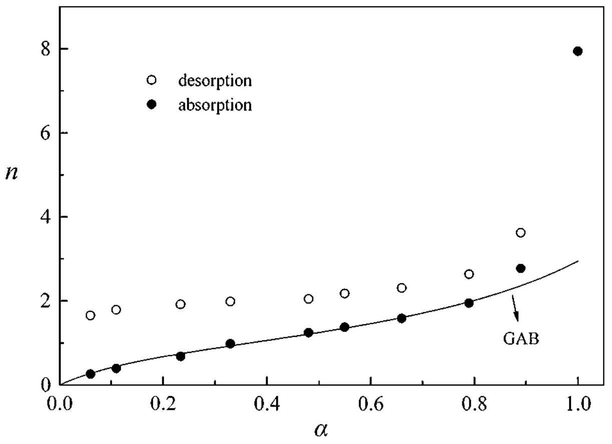

Figure 2 Sorption and desorption isotherms of a perfluorosulfonate membrane in potassium salt form at 40°C. Open points represent desorption while closed points represent sorption. The line is calculated according to GAB equation (Equation 2).

$$n = n_{\mathrm{m}} \frac{kf\alpha}{(1 - f\alpha)(1 + (k-1)f\alpha)} \tag{2}$$

n is the number of sorbed water molecules per -SO_3K group. n_{m} is the number of sorption sites per (-SO_3K) group (first monolayer sorption capacity). k is the ratio of the binding constants of a water molecule directly bound to the sorption site in the first layer and of one indirectly bound in the succeeding liquidlike layers. f is the ratio of the standard chemical potential of the indirectly bound water molecule to that of the molecule in the bulk liquid state.

The values of the parameters have been derived from the sorption isotherm data by using the linear form of Equation 2 [18]. After optimization of the parameter f [18] were found $n_{\mathrm{m}} = 1.0(\pm 0.1)$, $k = 8.4(\pm 0.3)$ and $f = 0.67(\pm 0.02)$. Thus in the first monolayer capacity corresponds one molecule of water per (-SO_3K) group. Taking into account that only the (-SO_3K) groups are hydrophilic in the structure of the membrane, one of the water molecules corresponding to the first monolayer capacity, could be attached to each (-SO_3K) group. It must be noted here that in our previous report [10], it was found that a water content of about 1 H_2O/SO_3K is needed to form a stable dipolar unit at the end of the side chains. The value of k is similar to that found in poly(zwitterions) [19, 22]. This seems inconsistent with the classification proposed by Galin-Galin [22] for the strength of the specific site binding, according to which strength for ion pair-H_2O should be greater than that for zwitterion-H_2O. However, it must be taking into account that the interactions between the side groups in the ionic regions could reduce the strength of the specific site binding, because of the microphase separated morphology of the Nafion® membranes. Also, the value of f is relatively low compared with these reported in the literature [17, 19, 22] and that is an indication of a higher stability tendency of the indirectly bound water. This low value of the parameter f probably could be related to the observed hysterisis of the desorption isotherm with respect to the sorption (Fig. 2).

However, the GAB equation fits the experimental data (Fig. 2) up to $\alpha = 0.79$, a value for which the water content corresponds to the completion of about two layers of water molecules. The sorption of water increased slowly after the completion of a monolayer ($\alpha \sim 0.35$–0.79) and increased rapidly at activities $\alpha > 0.79$. This large degree of upturn observed at higher activities may suggest clustering of water molecules. Zimm and Lundberg's theory [20] describes a mathematical approach for determination of the tendency of penetrant molecules to cluster formation in a polymer. This theory based on a quantity called cluster integral, G_{11}, which can be calculated from the equilibrium sorption isotherm data by the following Equation [20]

$$\frac{G_{11}}{V_1} = -(1-\varphi_1)\left[\frac{\partial\left(\frac{\alpha}{\varphi_1}\right)}{\partial\alpha}\right]_{P,T} - 1 \qquad (3)$$

where V_1, φ_1 is the partial molar volume and the volume fraction of the penetrant water respectively, while α is the water activity of the polymer environment. At a given water activity the value of φ_1 can be calculated from the equilibrium sorption isotherm by the following equation

$$\varphi_1 = \frac{vR}{1+vR} \qquad (4)$$

where R is the equilibrium sorption regain (g water/g polymer) and v is the ratio of the density of the polymer to the density of water.

The quantity $\varphi_1 G_{11}/V_1$ is the number of water molecules in excess of the mean concentration of water molecules in the neighborhood of a given water molecule. Thus, clustering of water molecules is indicated when $\varphi_1 G_{11}/V_1$ is greater than zero. Fig. 3 shows $\varphi_1 G_{11}/V_1$ as a function of activity α. The values of $\varphi_1 G_{11}/V_1$ have been calculated from the equilibrium sorption data (Fig. 2), by using a 6th order polynomial fitting to the α/φ_1 vs α plot, and taking the derivative at the corresponding values of α. The values of $\varphi_1 G_{11}/V_1 > 0$ for $\alpha \geq 0.79$ suggest clustering of water molecules. The mean number of water molecules per cluster, $(\varphi_1 G_{11}/V_1) + 1$, at activity $\alpha = 1$ has been estimated to be 12.0, which is higher than the water content per (-SO_3K) group at the same activity, 8 H_2O/SO_3K (Fig. 2). This result is in accordance with experimental evidence [4, 5] leading to the conclusion that the sulfonated side groups of the Nafion® membranes form sulfonate-rich ion "clusters", because only these regions are hydrophilic in the structure of the membrane. Making the assumption that all the absorbed water molecules exist in the ionic regions and taking into account that two bound water molecules correspond to each (-SO_3K) group, then it can be estimated that the mean number of the (-SO_3K) groups per ionic region is 2. Otherwise, if the most of the absorbed water molecules are located at the ionic regions [7], then it can be estimated that 2–3 (-SO_3K) groups correspond in each ionic region.

The Flory-Huggins theory assumes that the water vapor and the polymer segments are randomly distributed throughout the volume of the solution. The isotherm equation is [21]

$$\ln\alpha = \ln\varphi_1 + (1-\varphi_1) + \chi(1-\varphi_1)^2 \qquad (5)$$

where φ_1 is the volume fraction of water and χ is the interaction parameter for the water-polymer system. Althought this theory does not describe a multilayer sorption process, it is interesting to point out any concentration dependence of the apparent interaction parameter χ [17, 22, 23].

Fig. 4 shows the dependence on the activity α of the interaction parameter χ, for the experimental data of the sorption process (Fig. 2). The parameter χ is an increasing function of the activity up to $\alpha = 0.79$ which means a decrease of water-polymer interactions, while for activities $\alpha > 0.79$, χ decreases showing a corresponding increase of water-polymer interactions. Such a behaviour were already observed in some systems such as poly(zwitterions) [22], poly(2-hydroxyethylmethacrylate) [17] and stoichiometric polyion complex poly(acrylic acid)-poly(4-vinylpyridine) [23].

The increase of the parameter χ with increasing activity up to $\alpha = 0.79$ can be explained by he fact that the increase of the water content, in this range of activities, decreases the number of sorption sites per (-SO_3K) group (first and second layer capacity) and thus the

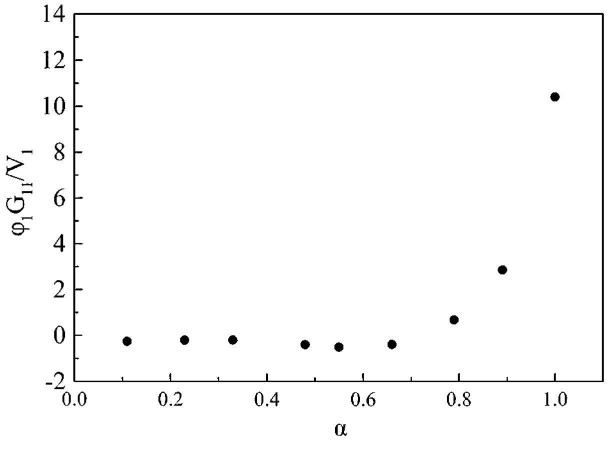

Figure 3 $\varphi_1 G_{11}/V_1$ as a function of the activity, α, at 40°C. Clustering of the water molecules is indicated for $\alpha = 0.79$, where $\varphi_1 G_{11}/V_1 > 0$.

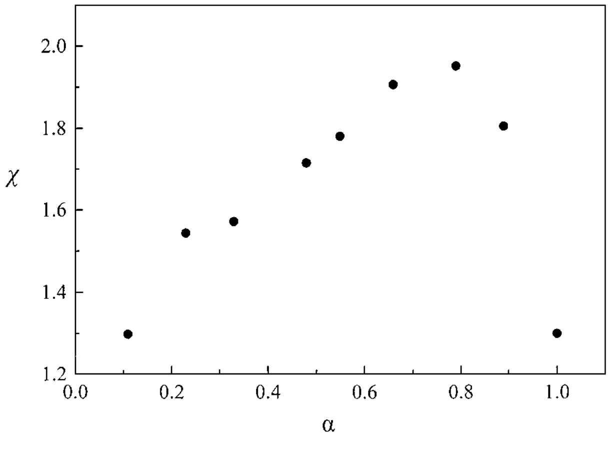

Figure 4 The interaction parameter χ, as a function of the activity α, at 40°C.

water-polymer interactions are reduced. The decrease of the parameter χ for $\alpha > 0.79$, is related to the clustering of water molecules, according to Zimm-Lundberg theory [20]. When the clustering starts the interactions between the water molecules, through hydrogen bonding, apparently are favored over water-polymer interactions. For $\alpha > 0.79$, additional water molecules decrease progressively the electrostatic interactions between the side groups, making them more flexible [10]. The increase of the mobility of the side groups could result in the generation of available volume in the ionic regions, which means new hydration sites. Also, additional water molecules, for $\alpha > 0.79$, increase the cluster size and this results in an increase of the degree of interconnectivity between the hydrated ionic regions.

Three unrelated theories were used for the examination of the sorption isotherms data. The GAB equation is based on the view of a localized multilayer sorption, while the Flory-Huggins equation is based on the assumption of random mixing. Both theories can be considered as complementary views of the water sorption in hydrophilic polymers. The Zimm-Lundberg theory, is a general statistical theory of binary liquid mixtures, independent of any physical model views. For all the above theories the value of $\alpha = 0.79$ is a characteristic value of the water activity. The interpretations of the sorption isotherm data of the Nafion® (-SO_3K) membranes which derived from one of these theories are consistent with those derived from the others.

3.3. Dielectric relaxation spectroscopy measurements

The dielectric behavior of a material is usually described by using the dielectric function, $\varepsilon^*(= \varepsilon' - i\varepsilon'')$. $\varepsilon^* = Y^*/i\omega C_0$, where Y^* is the measured admittance of the sample, ω is the angular frequency ($\omega = 2\pi f$) and C_0 is the equivalent capacitance of the sample holder. Fig. 5 shows the typical overall dielectric behavior in log-log plot of the imaginary part of ε^*, ε'', versus frequency, f, of a Nafion® membrane with water content 0.9, at 295 K. At low frequencies, the linear part of the plot, the behavior is dominated by the presence of effects related to the long range ion displacements (dc conductivity), which are at the origin of the high values of ε''. At higher frequencies two dielectric loss peaks are observed, one at about 10^2 Hz, named the low frequency (l.f.) peak, and another at about 5×10^4 Hz, named the high frequency (h.f.) peak. In order to analyze the plot into its components and find their characteristic parameters, the experimental data are fitted by two Havriliak-Negami expressions [24] for the two loss peaks and by the conductivity term $A\omega^{-s}$ for the linear part of the plot (excluding the lowest frequency points because of the electrode polarization contribution)

$$\varepsilon''(\omega) = A\omega^{-s} + \sum_{i=1}^{2} \frac{\Delta\varepsilon_i' \sin(\beta_i\phi_i)}{\left\langle 1 + 2(\omega\tau_{0i})^{1-\alpha_i}\sin(0.5\pi\alpha_i) + (\omega\tau_{0i})^{2(1-\alpha_i)}\right\rangle^{\frac{\beta_i}{2}}} \qquad (6)$$

where

$$\phi_i = \arctan\left(\frac{(\omega\tau_{0i})^{1-\alpha_i}\cos(0.5\pi\alpha_i)}{(1 + (\omega\tau_{0i})^{1-\alpha_i}\sin(0.5\pi\alpha_i))}\right)$$

A and s are constants ($0 < s < 1$), $\Delta\varepsilon_i'$ is the contribution to the real part of the dielectric function of each relaxation mechanism, ω is the angular frequency with $\omega = 2\pi f$, α_i and β_i are fit parameters denoting the symmetric and asymmetric broadening of the relaxation function of each mechanism. τ_{0i} is a characteristic relaxation time which is closely related to the relaxation time $\tau_{\max}$ with $\tau_{\max} = 1/2\pi f_{\max}$, where $f_{\max}$ is the frequency at the maximum dielectric loss for each mechanism.

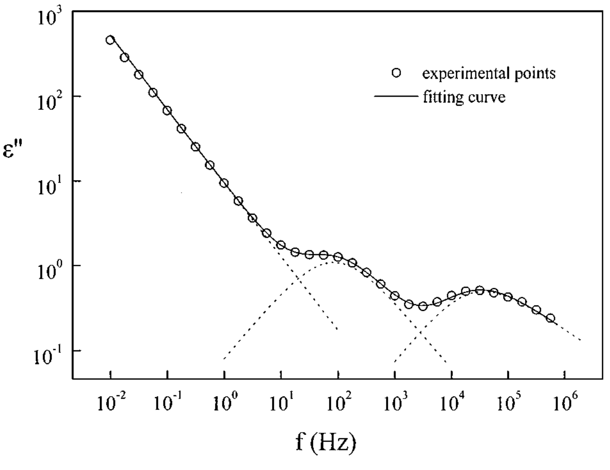

Figure 5 The imaginary part ε'', of the dielectric function versus frequency f, of a Nafion® membrane with water content $n = 0.9$, at 295 K. The solid line is a fit according to Equation 6. The dotted lines show the contribution of the two relaxations and the long-range conductivity processes to the total spectrum.

The parameters obtained from the best fit are: $\alpha_1 = 0.20$, $\beta_1 = 1$, $\tau_{01} = 1.89 \times 10^{-3}$ s, $\Delta\varepsilon_1' = 3.0$ for the low frequency peak (l.f.), and $\alpha_2 = 0.18$, $\beta_2 = 0.57$, $\tau_{02} = 7.80 \times 10^{-6}$ s, $\Delta\varepsilon_2' = 1.69$ for the high frequency peak (h.f.). Thus the l.f. peak is described by a symmetric distribution of the relaxation times (Cole-Cole behaviour, $\beta_1 = 1$), while the h.f. peak by an asymmetric one.

The fit parameters for the conductivity term are: $A = 46.922$, $s = 0.87$. The parameter s reflects the degree of interconnectivity of conducting elements [25] which in our case are the hydrated ionic regions. In the case of "pure" dc conductivity the parameter s takes the value of $1(\varepsilon'' = A\omega^{-1})$ and corresponds to the ideal charge drift across the sample. The value of $s = 0.5$ corresponds to tortuous conducting pathways where the diffusion of charges is dominant. The value of s found, $0.5 < s = 0.87 < 1$, indicates that the Nafion® membrane has random charge conducting paths across the sample that may or may not intersect each other [26].

Fig. 6a and b show the dielectric loss tangent, $\tan\delta$ ($\tan\delta = \varepsilon''/\varepsilon'$), as a function of frequency, f, for samples with water content 0.9 and 2.2 H_2O/SO_3K respectivelly, at differente temperatures. As we can see, two peaks apear in these plots which correspond to the low frequency (l.f.) and high frequency (h.f.) peaks of Fig. 5.

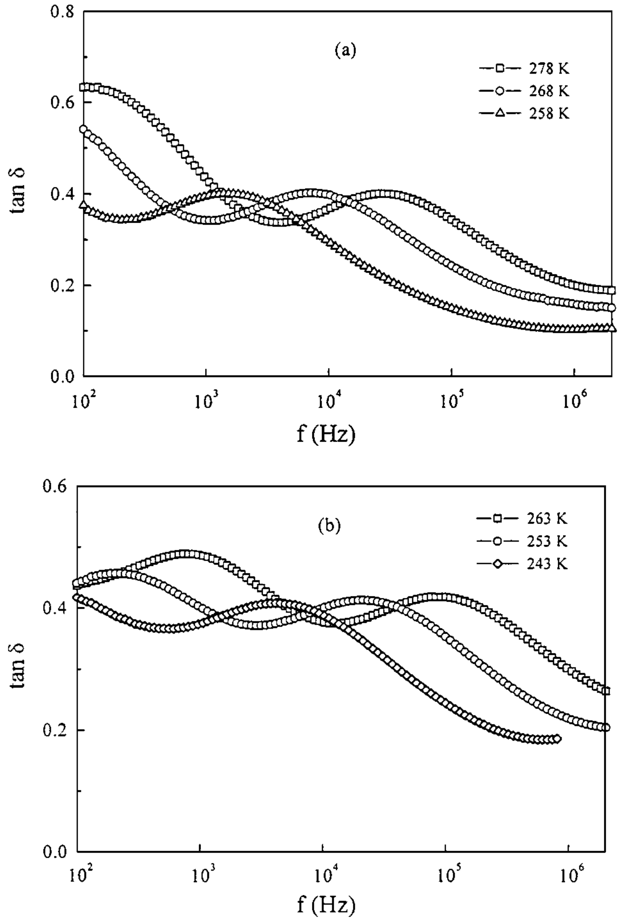

Figure 6 Loss tangent tan δ, versus frequency f, of a Nafion® membrane at $n = 0.9$ (a) and $n = 2.2$ (b), for several temperatures given in the plot.

The magnitude of the h.f. mechanism, which is a measure of the number of the relaxing units, does not seem to change by increasing the water content or by increasing the temperature, it remains almost constant at a value of about 0.4. The magnitude of the l.f. mechanism increases by increasing the temperature but no systematic change by increasing the water content has been observed. Both relaxation mechanisms become faster, by increasing the water content. This means that water acts as a plasticizer increasing the mobility of the relaxing units which are responsible for the l.f. and h.f. loss peaks. These results present a manifestation of the temperature-frequency-hydration (T-f-h) superposition principle proposed for hydrated polymers [27, 28]. It states that the plasticizing effect of increasing water content at constant temperature is equivalent to the effect of increasing temperature at constant moisture, both leading to increased segmental mobility of the polymeric chains [28].

Fig. 7a and b show the frequency of maximum losses, $f_{\max}$, versus reciprocal temperature (Arrhenius plots) for the l.f. and h.f. peaks at several water contents. The values of the activation energy E were obtained by least-square fittings of the Arrhenius equation

$$f_{\max} = f_0\, e^{-\frac{E}{kT}} \tag{7}$$

where k is the Boltzmann's constant and f_0 a pre-exponential parameter. By increasing the water content the activation energy, E, for the l.f. peak changes from 0.77 to 0.74 eV (from 74 kJ/mole to 71 kJ/mole) for

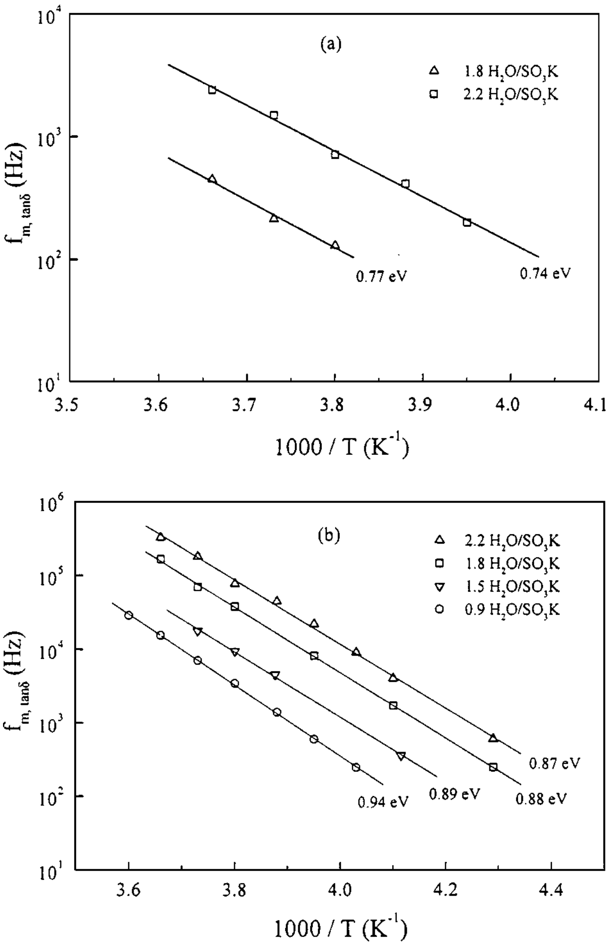

Figure 7 Arrhenius plots of the maximum frequency of the tan $\delta(f)$, for the low frequency peak (a) and the high frequency peak (b), at several water contents given in the plot.

$n = 1.8$ and 2.2 H_2O/SO_3K respectively. For $n = 1.5$, only two experimental points were available giving a value of activation energy of 1.34 eV (129 kJ/mole). The value of the activation energy for the h.f. peak varies from 0.94 eV (91 kJ/mole) for $n = 0.9$ to 0.89 eV (86 kJ/mole) for $n = 1.5$ and it remains almost constant, 0.89–0.87 eV (86–84 kJ/mole), up to water content of 2.2 H_2O/SO_3K. The sift to higher frequencies by increasing water content is related to the change of the pre-exponential parameter f_0 and not to activation energy change. In the rate theory, the Eyring equation [29] correlates f_0 with the activation entropy ΔS of the relaxing units by the relation

$$f_0 = \frac{kT}{2\pi h}\, e^{\frac{\Delta S}{k}} \tag{8}$$

where h is the Planck constant, k is the Boltzmann's constant and T is the absolute temperature. So, the change of the parameter f_0, by increasing the water content, reflects the change of the molecular environment of the relaxing units which contribute to the h.f. relaxation mechanism, in the sense that this change increases the number of the possible ways for rotation of these units.

In our previous report [10], using dielectric Thermally Stimulated Depolarization Current (TSDC) measurements, hydrated Nafion® membranes have been studied. One of the main dielectric dispersion (dispersion II in the β-relaxation region) in the TSDC spectrum obtained from Nafion® membranes has been analysed in two components; one due to dipolar polarization and an other due to interfacial polarization. We attributed the dipolar component of the dispersion II to the rotation of (-SO_3^-) group-water complexes formed at the end of the side chains [10]. It was found that water content of about 1 H_2O/SO_3K is needed for the formation of a stable dipolar unit at the end of the side chains and that the absorption of more water acts only as a plasticizer without changing the polarization of this dipolar mechanism. The interfacial polarization mechanism, which take place in the hydrated ionic regions, has been found to be related to the dc conductivity [10]. The interfacial polarization mechanism becomes faster and its magnitude is increasing by increasing the water content. This behavior enabled us to relate the conduction mechanism with the water existing in the ionic regions. The dipolar mechanism appears to be faster than the interfacial polarization mechanism. The reason for that is that the dipole rotations are local motions, while interfacial polarization is related to the migration of charges in longer distances through the hydrated ionic regions between the hydrophilic/hydrophobic phase boundaries.

Thermal Sampling (TS) analysis of the TSDC spectrum obtained from a Nafion® membrane with a water content $n = 0.9$, gave for the dipolar mechanism a main component located at $T_m = 198$ K with an activation energy of 0.88 eV (85 kJ/mole) and a pre-exponential factor of 2.28×10^{-21} s, and for the interfacial polarization mechanism a main component located at $T_m = 218$ K with an activation energy of 0.93 eV (90 kJ/mole) and a pre-exponential factor of 2.23×10^{-20} s [10].

Fig. 8 shows an Arrhenius plot ($\log \tau$ vs $1/T$) for the h.f. peak of a membrane with $n = 0.9$, in which a point from TS measurement is included. The TSDC point corresponds to the position $T_m = 198$ K and its characteristic relaxation time (calculated from the Arrhenius equation $\tau = \tau_0 \exp(E/kT)$) of the dipolar component mentioned above. The linear relationship in Fig. 8 is an indication that the dipolar component observed in the TSDC spectrum (dispertion II) and the high frequency peak of the Fig. 5 may be due to the same dipolar mechanism.

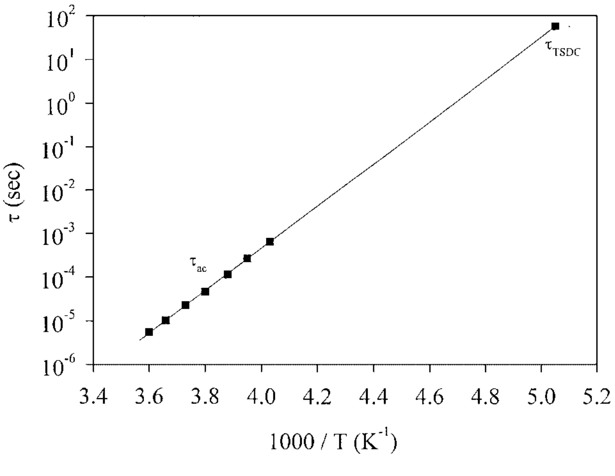

Figure 8 Arrhenius plot of the relaxation time, τ, for the high frequency peak at $n = 0.9$. The open point is from TSDC measurements (details in the text).

Fig. 6a shows that the low frequency peak has a maximum at about 100 Hz at a temperature of 278 K, from which a mean relaxation time of about 1.59×10^{-3} s can be calculated. Assuming an Arrhenius behavior of the main component of the interfacial polarization in the TSDC spectra mentioned above, a relaxation time of about 1.62×10^{-3} s can be calculated for the temperature of 278 K. The good agreement of these values of the relaxation time suggests that both relaxations may have the same origin. This means that the low frequency peak of the ac measurements (Fig. 5) may be due to the interfacial polarization which takes place in the hydrated ionic regions.

l.f. and the h.f. peaks, correspond to the higher and lower temperature peaks respectively, observed by Yeo and Eisenberg [8], in isochronal dielectric measurements of hydrated ($n > 1$) perfluorosulfonate membrane in potassium salt form. The above two peaks dominate in the β-relaxation region for water content $n > 1$ [8]. As Fig. 5 shows at the lower frequency region (linear part of the plot) the long-range conductivity becomes dominant. This conductivity mechanism is related to the hopping of ions between the hydrated ionic regions. A similar behavior in perfluorosulfonate membranes equilibrated in aqueous $ZnSO_4$ solutions, has been reported [25]. In these membranes a polymer chain polarization mechanism has not been observed [25]. This may be due to the fact that in the respective frequency region, the conductivity contribution to the ε'' is dominant and covers any chain polarization contribution.

The electric modulus is defined as $M^* = M' + iM'' = 1/\varepsilon^*$ and it has been proposed to be used in the description of electrical relaxation phenomena [30]. In the M^* formalism, the existence of the conductivity term $A\omega^{-s}$ in a $\log \varepsilon''$ vs $\log \omega$ plot, usually reveals a peak in the plot of M'' versus $\log \omega$, related to the long-range conductivity relaxation mechanism [30]. In Fig. 9 we show the M'' vs $\log f$ plot, by expressing the results of Fig. 5 in M^* formalism. A third peak appears at lower frequencies, which may be related to the long-range

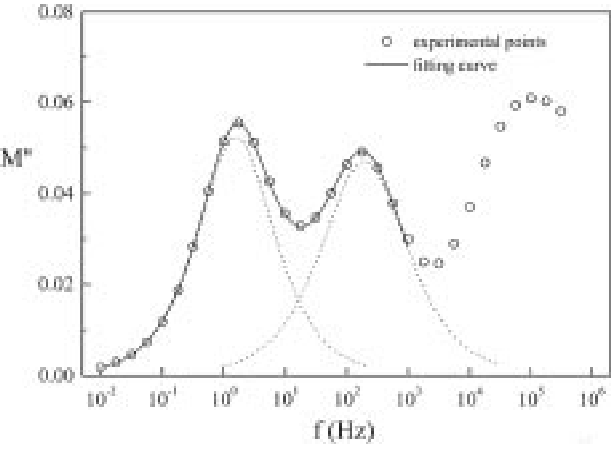

Figure 9 Imaginary part M'', of the electric modulus versus frequency f, for a Nafion® membrane with water content $n = 0.9$, at 295 K. The solid line is a fit according to Equation 9 for the long-range and the short-range conductivity relaxation process, taking into account the contribution of the higher frequency relaxation process. The dotted lines show the contribution of each relaxation process to the total spectrum.

conductivity relaxation mechanism. This peak corresponds to the linear part ($A\omega^{-s}$) of Fig. 5. In the same figure we show the best fit of the sum of two Cole-Cole expressions [23]

$$M''(\omega) = \sum_{i=1}^{2} \frac{\Delta M_i'\left((\omega\tau_{0i})^{1-\alpha_i}\cos(0.5\pi\alpha_i)\right)}{1+2(\omega\tau_{0i})^{1-\alpha_i}\sin(0.5\pi\alpha_i)+(\omega\tau_{0i})^{2(1-\alpha_i)}} \tag{9}$$

for the conductivity relaxation and the interfacial polarization mechanisms respectively. $\Delta M_i'$, τ_{0i} and α_i are the contribution to the real part of M^*, a characteristic relaxation time and a shape parameter of the relaxation mechanisms. The values of the parameters obtained by the best fit are: $\Delta M_1' = 0.133$, $\alpha_1 = 0.15$, $\tau_{01} = 0.099$ s (1.6 Hz) for the conductivity relaxation mechanism and $\Delta M_2' = 0.134$, $\alpha_2 = 0.22$, $\tau_{02} = 8.2 \times 10^{-4}$ s (194.7 Hz) for the interfacial polarization mechanism. So, the long-range and the short-range conductivity relaxation mechanisms can be described by a symmetric distribution of the relaxation times. According to the values of the shape parameter α the short-range conductivity relaxation mechanism should be considered as more broadly distributed. This result could be related to the broad size distribution of the ionic regions.

The complex impedance formalism $Z^* = Z' - iZ'' = 1/Y^*$ is usually used in the form of Z'' versus Z' plots in order to separate the bulk from the electrode-material interface phenomena and to determine effective dc resistance of the materials [31]. The electrode-material interface phenomena are highly capacitive phenomena and are, therefore, characterised by larger relaxation times than the conductivity relaxation and the polarization mechanisms in the bulk. Fig. 10 shows the Z'' vs Z' plot obtained by the transformation of the data of Fig. 5 in Z^* formalism. We can distinguish the bulk from the electrode-material interface phenomena (low frequency region). The same figure also shows the best-fit for the semicircular portion (excluding points of the low frequency region where electrode effects are strong or dominant) which is described by the Cole-Cole expression [32].

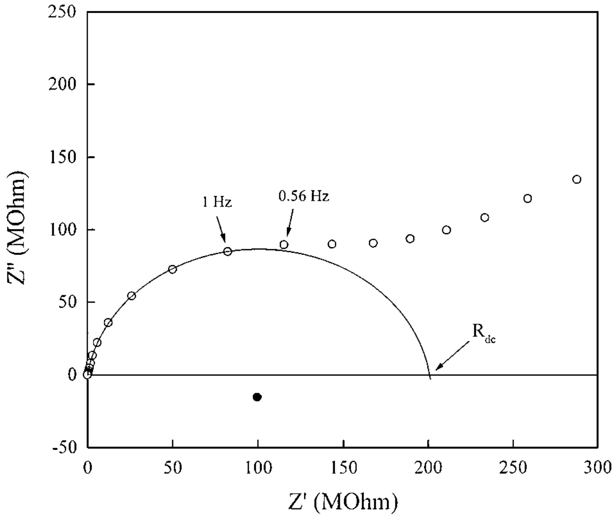

Figure 10 Complex impedance plot for a Nafion® membrane with water content $n = 0.9$ at 295 K. The solid line is the best fit of the Cole-Cole depressed arc. The closed point is the centre of the circle.

$$Z^* = \frac{R}{1+(i\omega\tau_0)^{1-\alpha}} \tag{10}$$

In Equation 10 α is a shape parameter, R is the effective dc resistance and τ_0 is a characteristic relaxation time. The best-fit was a circle with its centre below Z' axis and the effective dc resistance, R, was then calculated from the intercept of the depressed arc with Z' axis. Using the dimensions of the sample, thickness d and effective area S, a value of the electrical conductivity, σ, of 4.5×10^{-10} S/m has been calculated using the relation $\sigma = d/SR$. In order to check this value, the dc conductivity of the same sample was measured by a HP 4339 high resistance meter and found to be 4.7×10^{-10} S/m. Also, a value of about 5×10^{-10} S/m has been estimated from the low frequency plateau in the $\log \sigma_{ac}$ vs $\log f$ plot, taking into account the electrode polarization effect which occurs at the lowest frequencies.

The shape parameter α of the Cole-Cole expression was found to be 0.10 and the characteristic relaxation time τ_0, which corresponds to the maximum of the semicircular portion, was found to be 0.118 s (an equivalent frequency of 1.35 Hz). The value of τ_0 is very close but a little higher than that obtained by the electric modulus formalism, as expected for the case of non-"pure" dc conductivity [33]. In the case of "pure" dc conductivity the characteristic relaxation time is expected to take the same value in both, electric modulus and impedance formalism [33].

The lower frequency region in Fig. 10 is described by the impedance $Z_e^* = Z_e(i\omega\tau_e)^{-a}$. The slope of the plot $\log Z''$ vs $\log \omega$ was found to be $a = 0.19$. This behavior (with $\alpha > 0$) indicates that the impedance Z_e^* may be of the capacitative type, caused by double layers in the electrode-material interface [34].

In the Z-plot of Fig. 10 there is no evidence for the contribution of the short-range conductivity relaxation mechanism. This evidence implies that the resistance corresponding to this conductivity mechanisms must be orders of magnitude smaller than that corresponding to the long-range conductivity relaxation mechanism.

The fact that the conductivity relaxation mechanism is relatively slow ($f_{\max \cdot M''} = 1.6$ Hz at $T = 295$ K for $n = 0.9$), combined with the limited available frequency range (10^{-2}–10^{6} Hz) and the restrictions in temperature (the upper limit must be well bellow the room temperature to avoid water loss), makes it difficult, almost impossible, to study the temperature dependence of the electrical conductivity in Nafion® (-SO_3K) membranes containing different amounts of water ($n \geq 1$).

4. Conclusions

Dynamic and equilibrium sorption isotherm measurements were carried out in perfluorosulfonate polymer membranes in potassium salt form. Although the membrane is in glassy state the diffusion process is found to be Fickian.

The equilibrium desorption isotherm process presents a hysterisis with respect to the sorption isotherm, which suggests that the sorbed water molecules affect the physical structure of the membrane.

The equilibrium sorption isotherm may be quantitatively analyzed according to the GAB equation up to the activity value of $\alpha = 0.79$, which corresponds to 1.0 site-bound water molecules per (-SO_3K) group. As only the (-SO_3K) groups are hydrophilic in the structure of the Nafion® membrane, from these site-bound molecules one water molecule should be attached to each (-SO_3K) group.

Clustering of water molecules, according to the Zimm-Lundberg theory, is observed for activities $\alpha \geq 0.79$. The calculated mean number of water molecules per cluster is 12.0, at the maximum activity, $\alpha = 1$. Also the mean number of (-SO_3K) groups per ionic region is estimated to be 2–3.

The polymer-water interaction parameter, χ (Flory parameter), is an increasing function of water content up to $\alpha = 0.79$ while for $\alpha > 0.79$ is decreasing, showing that the clustering of the water molecules increases the hydrophilicity of the Nafion® membrane.

Two relaxation mechanisms were observed in isothermal dielectric relaxation measurements on hydrated membranes. Both mechanisms shift to higher frequencies by increasing the water content. The low frequency relaxation is attributed to an interfacial polarization mechanism, produced by the migration of charges through the hydrated ionic regions, between the hydrophilic/hydrophobic phase boundaries. In a previous work, using TSDC measurements we obtained evidence that the interfacial mechanism must be related to the dc conductivity and that the water located in the ionic regions should be related to the conduction mechanism.

The high frequency relaxation mechanism is a dipolar mechanism and may be attributed to the rotation of (-SO_3^-) group-water complexes at the end of the side chains. This is supported by the fact that according to the GAB analysis one site-bound water molecule is attached to each (-SO_3K) group. Also, the activation energy of this dipolar mechanism, remains practically constant by changing the water content in the range of $n = 1.5$–2.2. The magnitude of the dissipation factor ($\tan\delta$) of the dipolar mechanism also remains almost constant, by changing the temperature or the water content in the range of $n = 0.9$–2.2. Using the electric modulus, M^*, and the impedance, Z^*, formalism the conductivity mechanism has been studied. A long-range conductivity relaxation mechanism related to long-range ion displacements has been identified.

Acknowledgements

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