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Water sorption in Nafion[®] membranes analyzed with an improved dual-mode sorption model—Structure/property relationships

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ABSTRACT

Sigmoid-shaped isotherms for water vapor sorption in fuel cell membranes were analyzed with Feng's new dual-mode model for two series of ionomer systems, Nafion[®] 117 membranes with different counter-ions and protonated Nafion[®] membranes aged under different degrees of humidity. Feng's model appeared to be an excellent sorption model for these sigmoid isotherms and the values of its parameters were used for an analysis of the membrane structure/property relationships. The first model parameter, C_p , corresponds to the number of water molecules strongly sorbed in the first hydration shell of the membrane sulfonic sites. The upward curvature in the isotherms at high water activities, reflected by the A' parameter, appeared to be mainly due to the clustering of new water molecules on those of the first hydration shell. The number of water molecules per ionic site hydration depends on several structural parameters. The counter-ion of high electrostatic power attracts more water molecules per ion site, both in the first hydration shell and in subsequent sorption layers. The qualitative relationships between the membrane structure and its sorption properties obtained by analyzing the New Dual Mode Sorption (NDMS) model parameters make possible different interpretations of several data sets reported in the literature, such as the data on the sorption of different alcohols and the water sorption in Nafion[®] membranes during ageing.

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1. Introduction

Solid polymer electrolytes (SPEs) are polymer systems with complex structures. They generally consist of a dense matrix of ionomers, i.e. highly-polar ionizable groups covalently attached to an organic polymer backbone, which is mainly hydrophobic in nature. The hydrophobic polymer matrix is generally in a glassy state due to the requirements for mechanical stability. Such a structure of SPE systems provides insoluble ionic systems (or polymer electrolytes) in aqueous media, making SPE one of the best materials for membranes destined to fuel cells whose advantages in clean energy production are well known [1].

Since there is simultaneous water generation reaction at the cathode and water evacuation by permeation towards the outer atmosphere, the properties of SPEs in fuel cells depend largely on the degree of water sorption, which is characterized by the water sorption isotherms [2–5]. In fact, the water states and their morphological transitions affect numerous system properties [6]

such as surface wettability, free volume or pore size (i.e. heterogeneous structure in the matrix) and thus the material's conductivity. This has been evidenced for different SPE materials, especially for the best-known polymer electrolytes, Nafion[®]. For instance, there is a water threshold below which there is no ion conductivity, while above it the conductivity follows a power law for the volume fraction of water, in agreement with the percolation theory.

The water sorption isotherms in ionomer membranes generally have a sigmoid shape, i.e. concave to the water activity axis at low activity values and convex to the same axis at high activity values [7]. The sigmoid-shaped isotherm has generally been observed for natural polymer systems such as starch [8], cellulosic materials [9] and complex foodstuffs [10] and has often been simulated by specifically-designed models for that type of isotherm, i.e. BET type II equation, Guggenheim–Anderson–de Boer (GAB) or Park equation. Limited insights have been deduced from the values of the GAB model parameters regarding monolayer and multilayer sorption [11] and a universal model would be useful for the analysis of the sorption phenomena in polymer-penetrant systems with regard to the chemical nature of the components and the structure of the polymer systems.

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Feng [12] has recently developed a new vapor sorption model which describes well all types of isotherms of vapor sorption in glassy polymers. Based on multilayer theory, as is the GAB equation, the new dual mode sorption (NDMS) model has three parameters. The NDMS model has been tested by its author on several series of vapor sorption data reported in the literature on different types of isotherms [12], mainly for the fitting quality aspect. The three-parameter NDMS model appears to be better than other models for the fitting of sigmoid isotherms [12]. It would be interesting to test this new model on polymer systems designed for fuel cells over the entire range of water activity.

The main aim of the present paper is to use the new dual mode sorption (NDMS) model to analyze some vapor sorption data already reported in literature for different fuel cell membranes. We analyze first the absorptions of water and alcohols in Nafion[®] 117 membranes exchanged with different counter-ions [13–15] and that of water in the protonated Nafion[®] membrane during its ageing under different humidity degrees [16]. Next, we analyze copolyimide membranes which are membranes of strong potential for fuel cell use, since copolymerization of sulfonic acid-containing monomers allows for enhanced stability of the proton conducting sites, improved control of the ion exchange capacity (IEC) and therefore control over the proton conductivity, water sorption and morphology of the membranes (*via* their chemical structure). The analyzed copolyimide membranes are those having different chemical structures [17], block copolyimides membrane of different block lengths at a constant ion exchange capacity and the same block copolyimide membrane submitted to different physico-chemical treatments [18].

In analyzing the data on different categories of membranes with this new model, we expect to get a better insight into the influence of the chemical nature and the physical structure of the systems on their water sorption properties. We focus our discussion on the influence of the ion-pair nature on the one hand and that of structure of the polymer backbone bearing the ion-pairs, on the other hand. In the case of the Nafion[®] membrane, the isotherms for alcohol sorption are also compared with the water sorption isotherms to clarify the effect of the sorbate nature. Such work has never been undertaken, as far as we know. There is thus a lack of systematic analysis of the effects of different chemical parameters of the sorbent-sorbate system on the membrane sorption properties, which limits our knowledge of the subtle aspects of the sorption.

1.1. Sorption model background

The sorption models developed with the mean-field approach and statistical calculation (*Flory-type* models) for homogeneous polymers are very convenient for organic compounds in elastomers, but equally well for some systems consisting of water and homopolymers, for which the isotherms are always convex to the activity axis. However, these models do not apply to the micro-heterogeneous systems because the basic assumption, homogeneity in the structure, does not hold. Similarly, the ENSIC model, based on the same assumption, cannot be used for micro-heterogeneous systems, such as the solid polyelectrolytes used for fuel cells. The ENSIC model, in which the affinity of a penetrant molecule with a polymer is different from its affinity with another sorbed penetrant molecule, describes the isotherms that are highly convex to the activity axis better than the Flory model [19]. In the following description, we focus on the sorption models, based on the sorption site, which can fit concave, convex or sigmoid-type isotherms.

Depending on the nature and the strength of the interactions between the penetrant and heterogeneous materials, various types

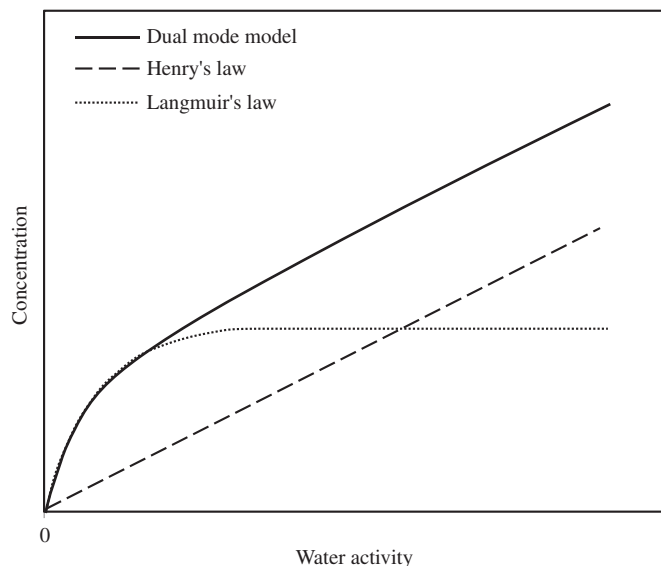


Fig. 1. Type 1 sorption isotherm in glassy polymers: dual mode isotherm which is the combination of Langmuir and Henry isotherms.

of isotherms, commonly called BET isotherms, can be identified and classified according to Rogers [20] and Brunauer [21].

There are three main types of sorption isotherms in this classification that can describe the vapor sorption isotherms in glassy polymers [12]. Type 1 is concave to the activity axis at low activities and almost linear at higher activities. Type 2, referred to as BET type II, is a sigmoid isotherm which is concave to the abscissa at low activities and convex at high activities. And type 3 is always convex to the activity axis and concerns only a few vapor sorption isotherms in glassy polymer materials.

1.1.1. Type 1: dual mode sorption model

Fig. 1 represents the type 1 sorption isotherm, that is to say the dual-mode sorption isotherm which is a combination of Langmuir (the first part of the curve, i.e. concave to the activity axis) and Henry isotherms (the second part, i.e. linear to the activity axis). This model assumes that penetrant molecules are partitioned into two distinct populations that are in dynamic equilibrium with each other: (i) first, the penetrant molecules are sorbed on specific sites (Langmuir's population) that are mainly microvoids in the glassy matrix and second, (ii) the penetrant molecules are sorbed by a dissolution mechanism in the dense polymer matrix (Henry's law population). The penetrant concentration in a glassy polymer is expressed analytically as the sum of two contributions to penetrant sorption [22–25]:

$$C = C_H + C_L = k_H a_w + \frac{A_L b_L a_w}{1 + b_L a_w} \quad (1)$$

where C is the total water vapor concentration, C_H the concentration of Henry's law species, C_L the concentration of Langmuir species, k_H the Henry's law constant, A_L the Langmuir capacity constant (i.e. the concentration of the specific sorption sites), b_L the Langmuir affinity constant and a_w the water activity.

1.1.2. Type 2: the sigmoid sorption isotherm

Fig. 2 represents a sigmoidal isotherm which reflects a complex combination of several sorption modes; this usually occurs with water sorption in hydrophilic polymers.

1.1.2.1. BET type II model. The first theoretical equation to interpret these shapes is the well-known BET (Brunauer–Emmett–Teller model) relation [26]: the BET type II sorption isotherm is a

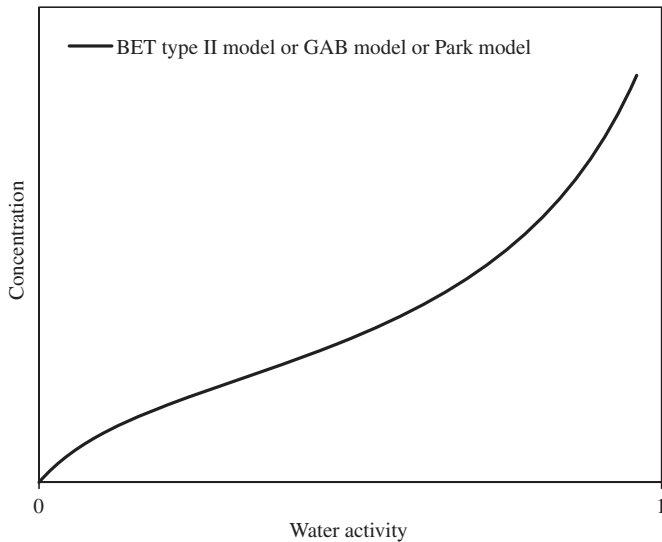


Fig. 2. Type 2 sorption isotherm in glassy polymers.

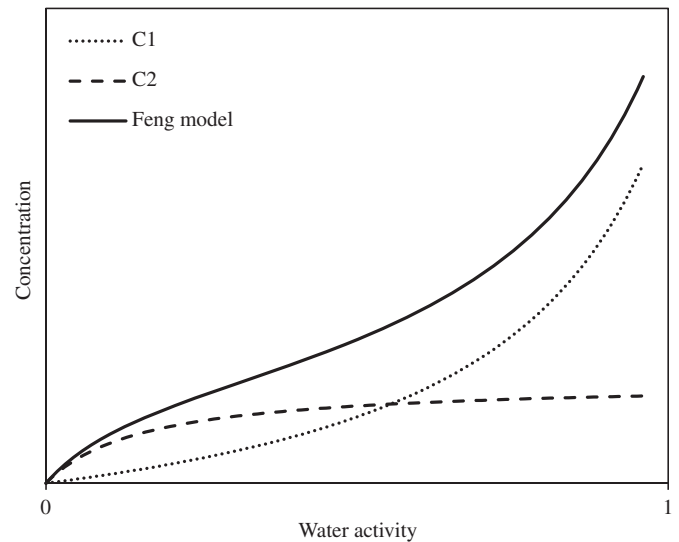


Fig. 3. Schematic representation of the new dual mode sorption (NDMS) model [12].

combination of Langmuir (the first part of the curve, i.e. concave to the activity axis) and Flory–Huggins isotherms (the second part, i.e. convex to the activity axis) [27]. It is established to describe the adsorption phenomena at the surface of very diverse materials [28,29]. The BET model considers that water molecules condense in several layers on adsorption surfaces and assumes that beyond the second layer, their evaporation–condensation properties are the same as in the liquid state

$$C = C_m \frac{C_{BET} \times a_w}{(1-a_w)((1-a_w) + C_{BET} \times a_w)} \quad (2)$$

where C_m is the water concentration sorbed on monolayer and C_{BET} the energy constant, related to the difference of free enthalpy of the water sorbed molecules in the pure liquid state and in the monolayer. This model is limited to water activities up to about 0.4–0.5 [30].

1.1.2.2. GAB model. The GAB model also considers the assumption of localized physical adsorption into a multilayer (the number of layers being limited) with no lateral interactions [31]. The molecules in the so-called multilayer have interactions with the penetrant which range in energy levels somewhere between those of the monolayer molecules and the bulk liquid. Successive layers of water molecules increasingly exhibit bulk liquid properties. The GAB model represents a refinement over the BET type II model, shares with it the two original BET constants (C_m and C_{BET}) and owes its major versatility to the introduction of a third constant [11]:

$$C = C_m \frac{C_G \times K \times a_w}{(1-K \times a_w)((1-K \times a_w) + C_G \times K \times a_w)} \quad (3)$$

where C_G is defined as the ratio of the partition function of the first molecule sorbed on a site and the partition function of molecules sorbed beyond the first molecule in the multilayer. It is a measure of how strongly water binds to the primary binding sites. The larger C_G is, the stronger water is bound in the monolayer and the larger the difference in enthalpy between the monolayer molecules and multilayer molecules. K is defined as the ratio of the partition function of molecules in bulk liquid to the partition function of molecules sorbed in the multilayer. K is called a correction factor, since it corrects the properties of the multilayer molecules relative to the bulk liquid. When K approaches 1, there is almost no distinction between multilayer molecules and liquid molecules. In that case the water molecules beyond the monolayer are not structured in a

multilayer, but have the same characteristics as the molecules in the bulk liquid. The GAB equation is thus reduced to the BET equation for sorption. The more structured the sorbed molecules in a multilayer, the lower the value for K . C_m is called the monolayer value. It is a measure of the availability of active sites for water sorption by the material [31].

1.1.2.3. Park model. The Park model for sigmoidal isotherms of water vapor [32] considers three mechanisms: Langmuir's sorption on special sites (the first part of the curve), non-specific sorption of Henry's type (the second part) and water-molecule aggregation or clustering (the third part, i.e. convex to the activity axis) at high water activity based on the equilibrium $n\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_n$:

$$C = \frac{A_L \times b_L \times a_w}{(1 + b_L \times a_w)} + k_H \times a_w + n \times k_H^n \times K_a \times a_w^n \quad (4)$$

where K_a is the equilibrium constant for the clustering reaction and n the mean number of water molecules per cluster. This model for multi-mode sorption Eq. (4) fits sigmoid isotherms very well. Since it requires a large number of adjustable parameters (five), the interpretation of the values of the parameters on the basis of physico-chemical interactions is rather difficult.

1.1.3. New dual mode sorption (NDMS) model

This new model is deduced from the GAB equation and is thus based on multilayer sorption theory. Four assumptions are made for this new model: (i) the sorption site in a glassy polymer material can be divided into two different species; one is located in the matrix region of the polymer and the other in the microvoids, (ii) all the molecules in the matrix region of the polymer have the same partition functions, (iii) there is GAB sorption in the microvoid region of the polymer, (iv) the molecules in the layers other than the first layer in the microvoid region have the same partition function as those in the matrix region.

The sorption is a contribution of two modes, as shown in Fig. 3, one of which occurs in the matrix region of the glassy polymers and follows C_1 which has an upward curve similar to that in rubbery polymers; the other occurs in the microvoids and follows C_2 which has a downward trend. The penetrant concentration in

the polymer is given by

$$C = C_1 + C_2 = C_p \frac{k' \times a_w}{1 - k' \times a_w} + C_p \frac{(A' - 1) \times k' \times a_w}{1 + (A' - 1) \times k' \times a_w} \quad (5)$$

where C_p is the weighted mean value of the sorption capacity of the polymer for the penetrant (a constant at a given temperature); it mainly depends on the structure and the state of the polymer. k' is the difference between the interaction of vapor molecules with each other and with a polymer molecule segment; it is essentially an indication of the interaction between the vapor molecule and the polymer segment. Larger k' indicates stronger interaction between the vapor and the polymer. A' is the difference between the interactions of a microvoid with the first layer of penetrant molecules sorbed on it and the interactions of the penetrant molecules that sorb later in the successive layers; in other words, it is a measure of the interaction of the vapor molecule and the microvoid [12].

The NDMS model leads to a shape for the sorption isotherms that is similar to the original GAB model. The GAB equation assumes that all the sorption sites are equivalent, while there are two different types of sorption sites in the NDMS model. From the physical viewpoint, the NDMS model seems to be more appropriate to polymer systems in which there are different phases/sites with which the sorbate molecules can interact. The NDMS model is compatible with sigmoid isotherms, concave isotherms (i.e. Langmuir's or classical dual-mode type), or convex isotherms (i.e. Flory–Huggins' type) for vapor sorption in polymers. Henry's isotherm is the limiting case of very low interactions between the vapor and the polymer ($k' \ll 1$), while the concave isotherm is the limiting case where the vapor-microvoid interactions are strong ($A' > 1$) and the convex isotherm is the limiting case of a rubbery polymer without microvoids (A' value should be close to 1).

The main aim of the present paper is to use the new dual mode sorption (NDMS) model to analyze some vapor sorption data already reported in literature for two types of fuel cell membranes. We analyze first the water absorption in the Nafion[®] 117, then in a copolyimide membranes exchanged with different counter-ions [14,15,27]. Copolyimide membranes are membranes of strong potential for fuel cell use, since copolymerization of sulfonic acid-containing monomers allows for enhanced stability of the proton conducting sites, improved control of the ion exchange capacity (IEC) and therefore controlled properties of the membranes via their chemical structure. Finally, we analyze the isotherms of water sorption in the protonated Nafion[®] membrane during its ageing under different humidity degrees [16].

In analyzing the data on different categories of membranes with this new model, we expect to get a better insight into the influence of the chemical nature and the physical structure of the systems on their water sorption properties. We focus our discussion on the influence of the ion-pair nature on the one hand and that of structure of the polymer backbone bearing the ion-pairs, on the other hand. Furthermore, we compare the sorption isotherms for alcohols with different alkyl lengths with those for water in the Nafion[®] 117 membrane to clarify the effect of the sorbate nature. Such a work seems not to have been undertaken so far. There is thus a lack of systematic analysis of the effects of different chemical parameters of the sorbent-sorbate system on the membrane sorption properties, which limits our knowledge of the subtle aspects of the sorption.

2. Experimental methods

2.1. Materials

The polymer materials used for the sorption and water uptake measurements are described in the papers specifically referenced

in Section 3. The different counter-ion forms were generally obtained by boiling first the ionomer dense films under reflux in 2N chlorhydric acid, then immersed in a 2N solution of the appropriate alkaline solution of counter-ion.

2.2. Vapor sorption experiments

Either IGA2 (Hidden Analytical, Warrington, UK) or DVS (Cahn D200 with a mass resolution of 0.1 µg, Surface Measurement Systems Ltd., London, UK) electronic microbalances were used for the data collections for Rouen University group. The two microbalances were checked with the same sample and sorption program: they generally gave consistent data to within 5%, except for very low sorbed amounts. A typical sorption protocol consists first in drying the sorption chamber, where the membrane sample is hanged from the microbalance beam, by high vacuum pumping (IGA) or nitrogen flushing (DVS) to a constant sample weight. Then, a vapor at constant pressure is admitted in the sorption chamber whose temperature is controlled by enclosing the entire system in a temperature-controlled incubator for the DVS or by circulating water from a constant water bath for the IGA. The partial vapor pressure in the sorption chamber is controlled by mixing water-saturated nitrogen and dry nitrogen using electronic mass flow controllers. The sorption kinetics are obtained from the mass gain versus time and the sorbed amount at equilibrium is obtained from the extrapolated value for infinite time of the sorption curve. The vapor pressure is then increased step-wise and the sorption curve is recorded up to a pressure close to the saturation pressure. Care is taken to avoid vapor condensation for vapor pressures close to saturation.

Besides our own sorption data, the experimental sorption isotherms collected in the literature under the form of scanned graphs are digitalized by ImageJ public software (rsbweb.nih.gov/ij/).

The measured mass of sorbate w_s are converted to the number of sorbed molecules per ion pair with

$$\lambda = \left(\frac{w_s/M_s}{IEC \times m} \right) \quad (6)$$

where M_s is the sorbate molecular-weight (g/mol), IEC is the membrane ion-exchange capacity (equivalent ion/g of dry membrane) and m is the mass of the dry membrane sample.

The digitalized “ λ versus solvent activity” isotherms are fitted with Feng's equation by using “Table curve 2-D” software (Systat Software Inc.).

3. Results and discussion

First of all, to compare categories of polymer systems with ionomer structures easily, we will not use the content in penetrant to express the extent of sorption as usual, but the parameter, usually called λ , that represents the number of water molecules per sulfonic site in the dry material. By doing this, we assume that the water sorption occurs around the highly hydrophilic ionic sites and that there is a negligible sorption elsewhere into the polymer matrix. Such an assumption would hold for the majority of ionomer systems designed for fuel cells, which generally have a matrix formed of hydrophobic segments to ensure correct mechanical properties. The C_p parameter in the NDMS model has thus the same unit as λ , i.e. the number of sorbed water molecules per sulfonic site in the dry polymer. Among the water molecules around the ionic site in the polymer, there could be two populations of molecules, those that are strongly bound to the acid site of the polymer and those that are more weakly bound to the ionic sites, which are more able to distribute between regions of the

swollen system. The former must correspond to the value of the C_p parameter, which represents the water molecules strongly sorbed (in a Langmuir-site sorption way), while the latter must correspond to those sorbed in subsequent layers on the first-sorbed water layer.

We further assume, in the discussion, a bi-phasic structure with hydrophilic and hydrophobic domains for ionomer membranes destined to fuel cells like Nafion[®] and sulfonated copolyimides, as shown in different works [33].

3.1. Water sorption isotherms for Nafion[®] [13–15] and copolyimide [27] membranes with different counter-ions

In a previous work [15], we studied the influence of the water activity and the nature of the membrane counter-ions on the water sorption and diffusion properties. Such an influence is very important in the passive transport of permeants as well as in the facilitated transport of gases through Nafion[®] membranes loaded with ionic carriers. The λ versus activity isotherms for water sorption in Nafion[®] membrane under the H, Li and Cs counter-ion forms are well fitted with new dual-mode sorption model (Fig. 4a). We treated in the same way the sorption isotherms reported in the literature by Jalani and Datta [14] and obtained similar results. However, Table 1 shows different values of the model parameters for the data sets with two different Nafion[®] samples.

In order to know whether the polymer nature has a significant effect on the behavior of counter-ions, we applied the NDMS model to copolyimide membranes. Multiblock-copolymers of sulfonated and non-sulfonated polyimides synthesized for fuel cell membranes [34,35] have provided materials of progressively varied structure for a fundamental study of water sorption. In a previous work [36], a dense film of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA)-diphenylene-2,2'-disulfonic acid (BDSA)/oxydianiline (ODA) (3/7) prepared from NTDA with BDSA and ODA was studied under different counter-ion forms in water vapor sorption. Again, the experimental water vapor sorption isotherms for naphthalenic sulfonated co-polyimide membranes (Pims) with different ionic forms are well fitted with the NDMS model (Fig. 4b), although they were already well fitted with the Park model [27]. While the latter required five adjustable parameters, the NDMS model requires only three parameters, providing then a better model than Park's.

The good fitting of these sigmoid-shape isotherms prompts us to interpret the water sorption in Nafion[®] and copolyimide membranes by using the values of the NDMS parameters. When the counter-ion of Pims membrane changes from H⁺ to Cs⁺, then to mono-protonated ethylene diamine (EDAH⁺), the k' and A' values decrease from 0.72 to 0.64 and from 14.4 to 9.6, respectively (Table 1); the C_p value decreases from 4.3 for H⁺ to 3.4 for Cs⁺, but it is higher for EDAH⁺ (3.5) than for Cs⁺. The water sorption isotherms exhibit a different behavior at low water activity for the Nafion[®] membranes exchanged with proton and alkali counter-ions, in comparison with that of the Pims membrane (Fig. 4a) and b). The concave part at low water activities characterizing the Langmuir-site sorption is smaller when the counter-ion size increases. When exchanging the H⁺ counter-ion to Cs⁺, the C_p value decreases much more for the Nafion[®] membranes than for the Pims membranes (Table 1).

In the original NDMS model, C_p represents the mean sorption capacity of polymer for the sorbate (in g of sorbate per g of polymer); it takes into account both the matrix region and the microvoids, where the Langmuir-site sorption occurs at low vapor activities. In the new data representation (with the number of water molecules per sulfonic site), C_p corresponds to the mean number of water molecules sorbed on Langmuir sites (ion pair), since the sorption in the hydrophobic matrix is assumed to be

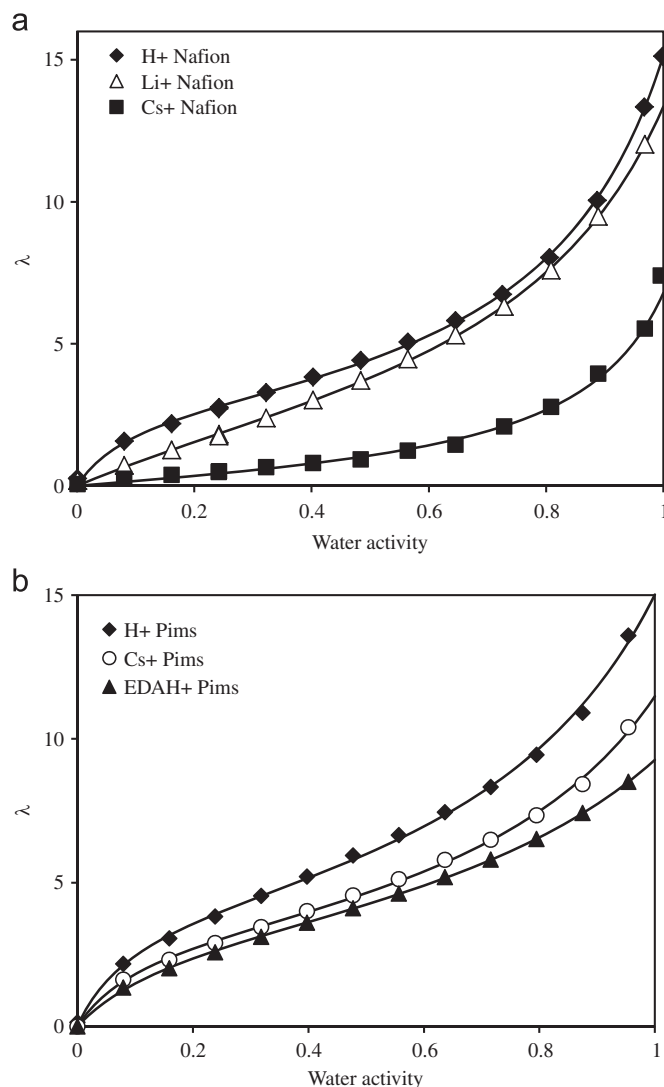


Fig. 4. Water sorption isotherms (experimental points) and best fit curves (lines) obtained with Feng's NDMS model for: (a) Nafion[®] membranes with different ionic forms at 25 °C [15] and (b) naphthalenic sulfonated multiblock co-polyimide membranes [27].

Table 1

Values of the NDMS model parameters for water vapor sorption at 25 °C in two Nafion[®] membranes successively put in H⁺ and alkali ion forms, and the naphthalenic sulfonated multiblock co-polyimide membrane (Pims) successively put in the H⁺, Cs⁺ and EDAH⁺ (mono-protonated ethylene diamine) forms.

Polymer system	C_p	k'	A'	r^2
Nafion[®] 117 [15]				
Nafion [®] -H ⁺	3.1	0.80	11.4	0.999
Nafion [®] -Li ⁺	3.1	0.80	3.1	0.992
Nafion [®] -Cs ⁺	0.9	0.89	2.5	0.996
Cast and hot-pressed Nafion[®] [14]				
Nafion [®] -H ⁺	2.7	0.77	47.0	0.993
Nafion [®] -Li ⁺	2.1	0.76	9.4	0.995
Nafion [®] -K ⁺	1.6	0.86	0.6	0.997
Nafion [®] -Cs ⁺	0.7	0.81	2.2	0.997
Pims [27]				
Pims-H ⁺	4.3	0.72	14.4	0.999
Pims-Cs ⁺	3.4	0.71	12.7	0.999
Pims-EDAH ⁺	3.5	0.64	9.6	0.999

negligible. As the Langmuir-type sorption occurs readily at low water activities (low driving force for sorption), C_p must correspond to the water molecules that are strongly bound via electrostatic forces to the ion pair, i.e. to the water molecules of the first hydration layer of the (sulfonic) ion pair.

The value of the mean number of strongly-sorbed water molecules per ion pair is a measure of the affinity of the ion pair in its chemical and physical environment in the material. It is thus logical that C_p (Table 1) is larger for the counter-ion which attracts more polar molecules like water, due to its higher electrostatic field ($H^+ > Li^+ > Cs^+$). The latter is higher for a cation of higher hydration energy and of smaller size of the counter-ion: H^+ has a very high hydration energy, i.e. -1090 kJ/mol and the smallest size (that of a proton); Li^+ , a hydration energy of -515 kJ/mol and a 0.069 nm radius and Cs^+ , a hydration energy of -290 kJ/mol and a 0.170 nm radius [37], respectively. Such a variation in the C_p value for the membranes with different counter ions reflects both the difference in the polar character of the ion pairs in the two membranes [14] and the effect of the chemical nature of backbone. The sulfonic acid in Nafion[®] ionomers is known to be more polar than those in the sulfonated copolyimide, due to the perfluoroether environment that reinforces the sulfonic polarity. This normally leads to a stronger interaction of Nafion[®] sulfonic acid with water than the one for aromatic sulfonic groups, as shown by a very low pK_a constant for Nafion[®] sulfonic acid compared with that for an aromatic sulfonic acid (i.e. -6 compared with -1) [38]. Thus, the Na- or Cs-sulfonate groups in Nafion[®] must exhibit stronger interactions with water molecules at lower water activities than those in Pims. Such a difference in the affinity of sulfonate-alkali ion pair in the perfluoroether (Nafion[®]) and the aromatic (Pims) membranes was evidenced in an infrared study of these membranes [39,6]. In fact, the C_p values in Table 1 show an anomalous behavior with a reverse trend for the sulfonic ion pairs in the two types of membranes.

Before discussing this surprising behavior, note that the C_p values found for the Nafion[®] membranes were under-estimated due to the presence of one residual water molecule per sulfonic acid site [40,41] in the Nafion[®] samples at the beginning of the sorption experiments after the sample drying under vacuum in the sorption chamber until a constant weight is reached, while the Pims membranes were practically dry under the same conditions. Such a difference in behavior is again explained by the high polarity of the sulfonic group linked to a fluoroether segment compared with that linked to an aromatic ring. Several authors [7,40,41] reported the difficult removal of the last water molecule from the fluoroether-sulfonic acid group in Nafion[®] by vacuum at room temperatures. Unfortunately, a sample drying at high temperatures is not possible in our microbalances.

Ludvigsson et al. [41] found a big change in the water-OH stretching band between the infrared spectra of the Nafion[®] membranes with one and two water molecules in the form of a large shift of this band towards higher wave numbers. They inferred that there is only one water molecule in the evacuated Nafion[®] film at room temperature, and that this water molecule is in the form of the H_3O^+ ion resulting from a transfer of the proton to water. For other sulfonic membranes, the first water molecule would only hydrate the whole SO_3H ion pair without proton transfer [42]. The different behaviors between the sulfonic acid group linked to a perfluoroether group (in Nafion[®]) and that linked to an aromatic ring resides in the presence of the electro-attractive fluorine atom close to the SO_3H group. If we take into account the presence of one water molecule in the Nafion[®]- H^+ membrane before the sorption, the C_p values for its sulfonic acid group will be ca. 4, in agreement with that recently found by Zhao et al. [54] by using another approach. The close C_p values found for the Nafion[®] and the Pims- H^+ membranes (Table 1) suggest that,

except for the first water molecule, both these membranes had similar first hydration shell of four water molecules around the dissociated sulfonic acid. This hydration shell would consist of one hydronium ion H_3O^+ that is hydrogen-bonded with three water molecules [43], although ab-initio electronic structure calculations showed a spontaneous dissociation for molecular models of Nafion[®] and aromatic sulfonic acid structures after the sorption of only three water molecules [44].

It should be noted that almost all ionomer membranes designed for fuel cells have phase-separated morphology. Nafion[®] is known as a polymer of homogeneous chemical structure which exhibits a phase-separated morphology in the matrix of the dense polymer: it consists of nanometer-size hydrophilic domains of ion clusters and fluorocarbon matrix domains [45]. However, as the hydrophilic sulfonic groups are covalently bound to the hydrophobic chains, their organization into domains is not free and more void spaces (or free volume) must be left in the vicinity of the sulfonic groups due to hindered organization of rigid chains [46]. One might expect that the more rigid the chain backbone, the larger the void spaces and the greater the number of sorbed water molecules per ionic group in the first hydration shell, provided that the chemical driving force for sorption is high enough. In all cases, the chemical driving force for water sorption decreases when the SO_3^- counterion is exchanged to a bigger one, so that the drastic reduction in the C_p value for the Nafion[®] membranes compared with the Pims one (Table 1) cannot be explained on the interaction (enthalpic) basis. In fact, for both membranes with the same SO_3^- counterion pair, the affinity to water is always higher for Nafion[®] than for Pims due to the greater acid strength of the SO_3H groups in the former membrane.

The stronger decrease in the C_p value with the counterion size is here attributed to the smaller space available for sorbed water molecules in the Nafion[®] membrane after the exchange with a bigger cation, because of the easier organization of fluorocarbon chains into a more compact structure than that of aromatic chains. Such higher flexibility of the polymer segments in the Nafion[®] ion cluster domains can be seen in the lower glass transition (ca. 120 °C [47]) compared with that in the polyimide membranes (around 200 °C [48,49]); the location of the sulfonic group on the rigid aromatic Pims chain and at the end of flexible pendant chains for Nafion[®] may eventually enhance the effect.

The different C_p values for the two types of Nafion[®] membranes (commercial and lab-cast, Table 1) are likely due to differences in the microstructures formed in their respective processing. Our data [15] concern a commercial Nafion[®] 117 membrane made by extrusion, while those of Jalani and Datta [14] concern a solvent-cast membrane annealed at 170 °C under 10 t of mechanical pressure (hot-pressed membrane). The latter process makes the chain re-organized into more entangled network, with higher crystallinity [50]. Such a processing imparts better mechanical properties but modifies the water sorption. The C_p value which is systematically smaller for the hot-pressed membrane compared with the commercial Nafion[®] suggests smaller spaces for sorbed molecules in the immediate vicinity of the sulfonic group of the hot-pressed Nafion[®].

At higher vapor activity, the long-range electrostatic field of the hydrated ion pairs drives additional water molecules onto the first hydration layer of the ion pair for subsequent water molecule layers. The stronger interaction of water with the sulfonic site in the first hydration layer compared with that in the further hydration layers is reflected by a higher sorption enthalpy observed at low water activities compared with that at high water activities [7]. Note that the water sorption in the hydrophilic ion-cluster domains requires a swelling, i.e. a volume expansion of the ion-cluster domains. The absence of swelling in the hydrophobic domains, which was confirmed by a mechanical study of swollen Nafion[®] membrane [51], does not mean that these domains remain fixed in the material frame. A swelling of the sole dispersed hydrophilic domains

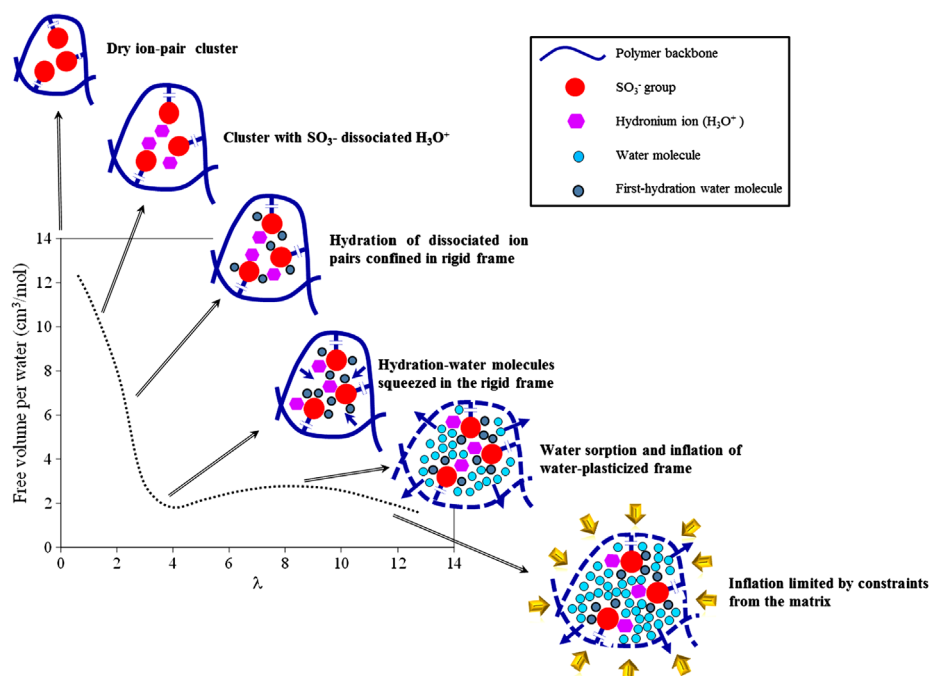


Fig. 5. Schematic representation of the water-hydrophilic domain structure in the cast Nafion[®] 117 membrane (1100 EW) at 80 °C and different water contents λ shown in parallel with the water free volume curve [47].

transmits the swelling to the whole water-ionomer system, in much the similar way as the swelling of semi-crystalline polymers due to the swelling of the sole amorphous domains.

The upturn curvature at higher water activity, reflected by the A' parameter value, logically follows the same trend as the C_p value, i.e. the highest for the smallest counter-cation, H^+ (Table 1) [7,14]. In fact, the A' value decreases much less with the increase of the counter-ion size for the Pims membrane than for the Nafion[®] membrane. Again, such behavior is attributed to the more rigid polyimide chains compared with Nafion[®] fluorocarbon chains. The chain rigidity can affect the amount of secondarily sorbed water in different ways: (i) by its stronger resistance, under a given chemical driving force, to water molecule addition on the sulfonic sites, as more space is to be created to house these water molecules, or (ii) by its larger frozen space in the glassy hydrophilic domains around the hydrated sulfonic sites in Pims, due to the hindering effect of the rigid chains on the chain packing.

In summary, the polymer chain organization at different levels in the membranes and its changes upon water sorption affect critically sorption behavior, hence membrane properties. Besides the here-discussed effect of local organization in ion-cluster domains, it should be noted that the strong anisotropy of the mesoscopic structure of the Nafion[®] ion domains suggested by the recent studies, (either cylindrical pores [38,52] or locally flat around polymer ribbons [53]) must also influence water sorption behavior, particularly at high water activities.

3.2. Effect of water sorption on the membrane dilation/excess free volume

In a recent study, Zhao et al. [54] measured the swelling strain of the Nafion[®] 117 membrane in the sorption of water vapor at different activities and found a surprising pattern of the variation of the excess free volume per sorbed water molecule as a function of λ : the excess free volume decreases sharply with the number of water molecule per sulfonic site to a minimum point at 4 water

molecules then increases slightly to pass a maximum before decreasing again (curve in Fig. 5). These authors suggest that the minimum point of swelling strain at $\lambda=4$ water molecules per sulfonic acid corresponds to a strong bonding between water molecules and the sulfonic acid, i.e. to the first solvation shell of sulfonic acid. The second stage of water sorption corresponds more weakly bound water (further solvation shells). Let us interpret such behavior in the Nafion[®] swelling with arguments based on the changes in the physical properties of the glassy hydrophilic domains.

In classical theories of polymer swelling, when a polymer network is placed into a fluid, the solvent tends to diffuse into it due to a negative total free energy (sum of a mixing and an elastic free energies [55] $\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{elastic}}$), resulting in a swelling strain. In the case of ionomers where the interactions of ionic groups and water are favoured, ΔG_{mix} has a large negative value and $\Delta G_{\text{elastic}}$ has a small positive value due to the energy expense to expand the polymer network against its elastic resistance. As swelling proceeds, however, ΔG_{mix} becomes less negative and $\Delta G_{\text{elastic}}$ turns more positive and the swelling stops when the two quantities are equal in magnitude and opposite in signs. At this point, $\Delta G_{\text{mix}} + \Delta G_{\text{elastic}} = 0$; there is no more driving force for swelling. For glassy polymers, the elastic resistance to polymer deformation is higher than for rubbery polymers so that the polymer inflation by solvent molecules is more limited. As the water content in the system is higher at a higher water activity, at a certain value of the latter, the water molecules in the hydrophilic domains increases enough the free volume of these domains according to the phenomenon of polymer plasticization to make easier further swelling. Such a “solvent-induced plasticization” phenomenon was observed in Nafion[®] membranes at temperatures lower than the transition temperature of 70–100 °C [56] which is often assigned to the glass transition in the ionic domains [6]; it occurs locally in the hydrophilic domains and in the case of the biphasic Nafion[®] (and similar) membranes dilate the polymer network as a whole to allow for a higher rate of polymer swelling at high water activities, as experimentally observed. In other

words, the local swelling stress in well- dispersed ion domains by plasticization appears to be capable of pushing the hydrophobic matrix outward for an overall volume expansion.

Although the ionomer membranes studied here are not chemically cross-linked, their hydrophobic domains with entangled chains in a glassy state, which are inert to water, can act as physical crosslinks. The swelling of such an ionomer structure is thus similar to that of a semi-crystalline polymer whose crystallites play the role of non-inflatable domains that restrict the expansion of the inflatable amorphous domains [57]. Although there are similar high rates of polymer swelling in the high water activity range for both types of polymers, the swelling behavior of semi-crystalline polymers is different from that of ionomers in the low water activity range by the absence of the Langmuir-like sorption pattern (see for instance Ref. [58] for semi-crystalline poly(vinyl alcohol)).

Let us examine now the swelling mechanism at a microscopic scale of such systems. In a dry polymer system, besides the free volume non-occupied by the hard cores of the chain unit, there is the excess free volume due to the presence of “holes” of different sizes, which is usually formed when the polymer is frozen into a non-equilibrium glassy state. Both these void spaces are more easily occupied by solvent molecules at low solvent activities in the external phase, i.e. at low sorption driving force. Therefore, in the glassy state (i.e. the state of low chain mobility), the largest void spaces are the first ones to be occupied in a sorption experiment followed by the others in sequence of size and accessibility.

For the specific case of water sorption into glassy ionomers, the penetrant molecules at low water activities first sorb without significant dilation of the pre-existing void spaces of the inflatable hydrophilic domains, at least up to the filling of the frozen void spaces. The ionic domains in the glassy polymer must resist strongly to the osmotic pressure generated by the water-hydrophilic group interactions. We suggest that the incoming water molecules must squeeze up into already occupied pre-existing void spaces in the hydrophilic domains, leading to a reduction in their free volume of the sorbed water phase to the minimum point. At high water activities, the sorption occurs with a proportional increase in swelling with the amount of sorbed water molecules, i.e. with a constant free volume. This mechanism explains well the strong decrease in the free volume per sorbed water molecule in the region of low water activities and the constant free volume in the region of high water activities reported by Zhao et al. for water sorption in Nafion® [54].

The high excess free volume for the first water molecule absorbed per sulfonic group is more difficult to interpret. According to Zhao [56], the excess free volume is the difference between the volume of the mixture and the sum of the molar volumes of Nafion® and water. Its sudden increase upon incorporation of the first water molecule of ca. 150% of its own volume would cause a significant deformation of the Nafion® membrane which is in its most glassy state. We speculate that such a deformation was caused by the splitting of the SO₃H ion pair in close contact into separated SO₃[−] and H₃O⁺ of larger free volume. The largely negative sorption enthalpy (−83 kJ/sulfonic site [59]) must provide enough driving force for the chains around the ion cluster to expand. The frozen void volume which is present in each ionic domain but not inside the ion pairs aggregated in ion clusters cannot share much of its volume. In other words, the strong affinity of water with the dry SO₃H ion pair in the sorption of one water molecule induces a spontaneous splitting of the close-contact ion pair into anion and the bigger H₃O⁺ and a jump in volume.

When the amount of sorbed water in these domains is high enough to plasticize the hydrophilic domains and to impart sufficient polymer segment mobility in these domains for their swelling, a chain relaxation and an inflation of the hydrophilic domains can occur. The increase in free volume observed by Zhao

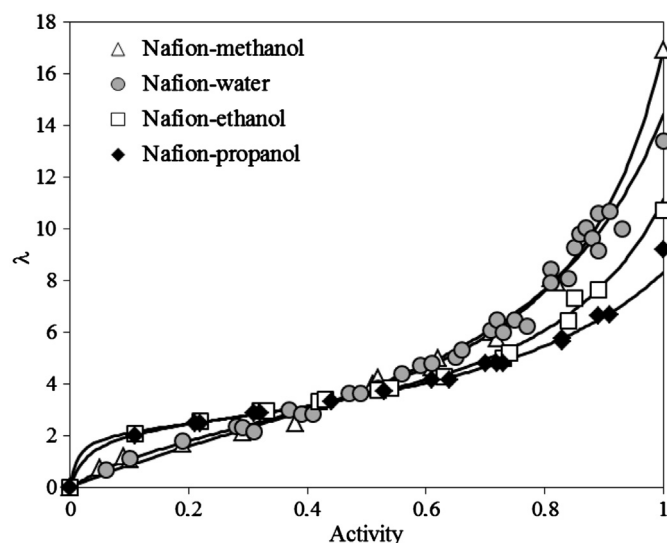


Fig. 6. Alcohol vapor sorptions (experimental points) and best fit curves (lines) obtained with Feng's NDMS model of Nafion® 117 membranes at 20 °C. The mass gain data from Ref. [13] are converted into the mean number of solvent molecules per sulfonic group for the plots as indicated in the experimental part.

Table 2

Values of the NDMS model parameters for alcohol vapor sorption in the Nafion® 117 membrane at 20 °C. The mass gain data from Ref. [13] are converted into the mean number of solvent molecules per sulfonic group for the plots as indicated in the experimental part. The membrane sample was dried under dry nitrogen stream at room temperature before sorption. Thus, the residual water molecule would be in the dissociated sulfonic acid group before solvent vapor sorption. The total number of water molecules per sulfonic site must be the reported *C_p* values plus one.

Solvent	<i>C_p</i>	<i>k'</i>	<i>A'</i>	<i>r</i> ²
Water	3.3	0.79	3.8	0.982
Methanol	2.6	0.85	6.6	0.992
Ethanol	2.3	0.78	40.0	0.993
Propanol	2.4	0.72	44.2	0.998

et al. would be due to a chain relaxation in the glass–rubber transition region, because of a progressive plasticization of the different hydrophilic domains. The slight decrease in free volume at further increase in the external water activity observed by these authors [54] reflects the network elastic forces that oppose more and more to a further swelling. A schematic representation (Fig. 5) of the water-hydrophilic domain structure in the cast Nafion® 117 membrane at different water contents is given, in parallel with the excess water free volume curve [54].

3.3. Effect of the solvent polarity on solvent sorption in Nafion® membranes

The data on the sorption isotherms of other solvents than water, in fuel cell membranes, are scarce in the literature. The most complete sorption data on the same sample (of Nafion® membranes), are from Rivin et al. [13] and Jalani and Datta [14] who reported a series of alcohol mass gain data as a function of alcohol activities, together with those for water. In converting Rivin's sorption data into the number of sorbed solvent molecules per sulfonic group, we obtain close sorption isotherms for two pairs of solvents, water–methanol and ethanol–propanol, respectively (Fig. 6). In fact, they diverge from each other only at high solvent activities, i.e. at values exceeding ca. 0.8. The values of the NDMS model parameters, shown in Table 2, indicate a decrease in *C_p* value with the decrease in the hydrophilicity of the

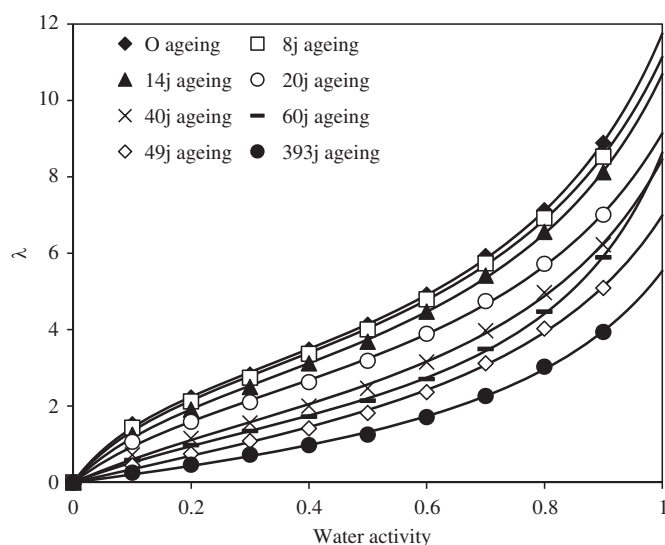


Fig. 7. Water sorption isotherms (experimental points) and best fit curves (lines) obtained with Feng's NDMS model of Nafion[®] 112 membranes at different ageing at 80 °C and 80% RH. The water uptake data from Ref. [16] are converted into the mean number of solvent molecules per sulfonic group for the plots as indicated in the experimental part.

alcohols. Such a decrease in C_p value is consistent with the decrease in the affinity of the ionic groups for the solvent molecules whose polarity follows the order: propanol < ethanol < methanol < water. Such a decrease in the affinity of the ionic groups to the alcohol molecules was evidenced in a previous study of the solvation of the Nafion[®] membrane by alcohols [39] by infrared spectroscopy. This study also showed that upon contact with pure alcohols, the ion-pairs in the Nafion[®] membrane are completely dissociated and alcohol molecules and solvated, contrary to the sulfonic groups on aromatic rings which remain un-dissociated due to their weaker dissociation power. One may thus expect a different behavior for alcohol sorption in aromatic sulfonic membranes.

At high solvent activities, the increase in the swelling with the solvent hydrophobicity, as reflected the A' value (Table 2), is large. This behavior contrasts with that for water and membranes with different counter-ions: there, A' increases with the affinity between the ion pairs and the solvent molecules, as expected. We infer that the increase in swelling at high solvent activities is mainly caused by a larger swelling of the hydrophobic domains by the organic solvent, due to hydrophobic interactions. This interpretation is consistent with the data from SAXS [60] and Fluor 19-nuclear magnetic resonance [61,62] experiments. Elliott et al. [60] came to the conclusion that, in an ethanol-water mixture, ethanol plasticises the Nafion[®] fluorocarbon matrix, allowing the ionic material to be redistributed into smaller and more numerous clusters than in membranes swollen with water alone. A similar behavior can occur in ethanol and propanol sorption in Nafion[®] 117 at high solvent activities where the synergy in swelling is due to the solvation of both the ionic domains and the fluorocarbon domains by these solvents.

We did not analyze Jalani and Datta data [14] because of the complex shape of their isotherms of alcohol sorption, which make their fittings with the NDMS model impossible. Such a complex shape probably resulted from the membrane preparation process, which involved a hot-pressing treatment of the membrane.

3.4. Influence of hygrothermal aging of a Nafion[®] membrane

In a recent work, Collette et al. [16] determined a series of water sorption isotherms for a Nafion[®] 112 membrane submitted to a hygrothermal aging. The isotherms of Nafion[®] 112 aged at 80 °C in

Table 3

Values of the NDMS model parameters for water vapor sorption at 50 °C in the Nafion[®] 112 membrane at different aging times at 80 °C under 0.8 water activity [16]. The C_p and A' parameter values refer to the initial sulfonic group. No specifications were given for the initial sample drying in the sorption experiments.

Aging time	C_p	k'	A'	r^2
0 (initial)	3.1	0.75	9.5	0.9997
8-day aging	3.1	0.74	8.6	0.9997
14-day aging	2.9	0.74	7.4	0.9997
20-day aging	2.6	0.73	6.3	0.9991
40-day aging	2.3	0.75	4.1	0.9987
49-day aging	2.1	0.74	2.3	0.9985
60-day aging	1.8	0.81	4.3	0.9994
393-day aging	1.7	0.75	1.6	0.999

water vapor of 80% RH show a progressive change in their shape with time, namely a progressive decrease in the sorption extent and in the sigmoid-shape characterizing the Langmuir sorption part at low water activities (Fig. 7) [16].

In analyzing the chemical structure of the aged membrane with different techniques, the authors found that the sulfonic groups changed to sulfo-anhydride groups by condensation. On the basis of a model combining a Langmuir sorption on ionic sites and a Henry sorption modified with a quadratic term in water activity for water sorption isotherms, they concluded that the Langmuir sites disappear in the sulfonic-acid condensation reaction. The modeling of the same data with the NDMS leads to another conclusion. The number of water molecules per initial sulfonic site in the first hydration shell (C_p value) decreases quasi-linearly with time during the early period of aging from 3.1 and levels-off at a floor value of 1.7 (Table 3), with a parallel decrease in the A' value. According to the NDMS model data, the Langmuir sites are still present but with a decrease in the number of water molecules per initial sulfonic site in the first hydration shell. By taking into account the residual water molecule in the initial membrane sample, the C_p value change corresponds approximately to a halved number of strongly sorbed water molecules per initial hydrophilic (sulfonic) group, i.e. the double of the anhydride-group number when all the acid groups are converted (Table 3).

We suggest that the polar sulfo-anhydride groups remain in the former hydrophilic domains, where they are formed by condensation of sulfonic groups and cause the Langmuir type sorption. With two polar groups ($\sim\text{SO}_2\text{--O--SO}_2\sim$) on each anhydride site, an average number of water molecules per site of 1.7 seems to be plausible (Table 3). In our opinion, such a strong water binding to polar anhydride site is more compatible to the physico-chemistry of polymer-solvent interactions. Furthermore, as the ionized groups endowed with long-range interaction fields are completely converted into neutral anhydride groups [16], the aged membrane exhibited a lower affinity to water, thus less multilayer water sorption at high water activities (i.e. lower A' values when the membrane is aged, Table 3). The Henry sorption mode suggested by Collette et al. is generally suitable for gas sorption in liquids, for gas and vapor sorption in polymers where the dispersive-type interactions with the sorbate are low; it can only lead to a weak and random sorption. This is not the case for the sulfo-anhydride membrane.

4. Conclusion

Feng's NDMS model describes quite well all sorption isotherms of sigmoid shape with only three adjustable parameters. The first parameter, C_p , represents the mean number of strongly-sorbed water molecules per ionic group, those in the first-shell around the ion site. This number depends on several physico-chemical parameters, such as the nature of the ion pair and its environment

in the ionomer system. The upward curvature in the isotherms of all the studied ionomer systems at high water activities appears to be mainly due to the water molecule clustering into multiple layers on the first hydration shell of the ionic sites.

The analysis of the data obtained with the NDMS model sheds light on the relationships between the membrane structure and its detailed sorption properties. The water sorption in the membrane hydrophobic domains is negligible for ionomer systems, compared to that in the ionic domains. While the water sorption in the first hydration shell occurs in the available frozen spaces of the hydrophilic domains, the sorption at high water activities occurs in a multilayer way on the first hydration site in inflating the hydrophilic domains. The inflation of the latter is made possible by an increase in local polymer-segment mobility which is induced by sorbed water molecules (phenomenon known as solvent-induced plasticization). The consecutive inflation of the whole system is similar to that observed in the swelling of semi-crystalline polymer, whose non-inflatable crystallites play a similar role as the hydrophobic domains of ionomers. In the case of alcohol sorption, the sorption in the hydrophilic domains decreases, but that in the hydrophobic domains increases, when the length of the hydrophobic alkyl part in the alcohol increases.

The specific sigmoid shape of the isotherms for each solvent-ionomer system depends on the specific environment of the hydrophilic groups together with the microstructure and the segment rigidity. These parameters can greatly affect the detailed solvent sorption in rigid-chain ionomer membranes via cooperative effects that result from a complex interplay between the driving force and the response of these biphasic materials whose microstructure and local physical properties change with the change in the driving force during sorption.

The qualitative relationships between the membrane structure and its sorption properties obtained in analyzing the NDMS model parameters allowed us to interpret some data on the solvent sorption in Nafion[®] membranes reported in the literature [13,16,54].

References

- [1] B. Smitha, S. Sridhar, A.A. Khan, Solid polymer electrolyte membranes for fuel cell applications—a review, *J. Membr. Sci.* 259 (2005) 10–26.
- [2] F.G. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
- [3] M.R. Tant, K.A. Mauritz, G.L. Wilkes, *Ionomers: Synthesis, Structure, Properties and Elasticity*, Chapman and Hall, London, 1997.
- [4] A. Eisenberg, J.S. Kim, *Introduction to Ionomers*, John Wiley and Sons, New York, 1998.
- [5] M. Bass, V. Freger, Hydration of Nafion and Dowex in liquid and vapor environment: Schroeder's paradox and microstructure, *Polymer* 49 (2008) 497–506.
- [6] K.A. Mauritz, R.B. Moore, State of understanding of Nafion, *Chem. Rev.* 104 (2004) 4535–4585.
- [7] M. Escoubes, M. Pineri, Water absorption studies of carboxylic and sulfonic ionomers: correlation with their microstructure, in: Pineri, Eisenberg (Eds.), *Structure and Properties of Ionomers*, NATO ASI Series, Dordrecht, 1987.
- [8] C. Masclaux, F. Gouanvé, E. Espuche, Experimental and modeling studies of transport in starch nanocomposite films as affected by relative humidity, *J. Membr. Sci.* 363 (2010) 221–231.
- [9] S. Belbekhouche, J. Bras, G. Siqueira, C. Chappey, L. Lebrun, B. Khelifi, S. Marais, A. Dufresne, Water sorption behavior and gas barrier properties of cellulose whiskers and microfibrils films, *Carbohydr. Polym.* 83 (2011) 1740–1748.
- [10] S. Furmaniak, A.P. Terzyk, R. Gołembiewski, P.A. Gauden, L. Czepirski, Searching the most optimal model of water sorption on foodstuffs in the whole range of relative humidity, *Food Res. Int.* 42 (2009) 1203–1214.
- [11] E.O. Timmermann, J. Chirife, H.A. Iglesias, Water sorption isotherms of foods and foodstuffs: BET or GAB parameters? *J. Food Eng.* 48 (2001) 19–31.
- [12] H. Feng, Modeling of vapor sorption in glassy polymers using a new dual mode sorption model based on multilayer sorption theory, *Polymer* 48 (10) (2007) 2988–3002.
- [13] D. Rivin, C.E. Kendrick, P.W. Gibson, N.S. Schneider, Solubility and transport behavior of water and alcohols in Nafion[™], *Polymer* 42 (2) (2001) 623–635.
- [14] N.H. Jalani, R. Datta, The effect of equivalent weight, temperature, cationic forms, sorbates, and nanoinorganic additives on the sorption behavior of Nafion[®], *J. Membr. Sci.* 264 (1–2) (2005) 167–175.
- [15] M. Legras, Y. Hirata, Q.T. Nguyen, D. Langevin, M. Métayer, Sorption and diffusion behaviors of water in Nafion 117 membranes with different counter ions, *Desalination* 147 (2002) 351–357.
- [16] F. Collette, C. Lorentz, G. Gebel, F. Thominette, Hygrothermal aging of Nafion, *J. Membr. Sci.* 330 (2009) 21–29.
- [17] T. Watari, J. Fang, K. Tanaka, H. Kita, K. Okamoto, T. Hirano, Synthesis, water stability and proton conductivity of novel sulfonated polyimides from 4,4'-bis (4-aminophenoxy)biphenyl-3,3'-disulfonic acid, *J. Membr. Sci.* 230 (1–2) (2004) 111–120.
- [18] N. Cornet, G. Beaudoin, G. Gebel, Influence of the structure of sulfonated polyimide membranes on transport properties, *Sep. Purif. Technol.* 22–23 (2001) 681–687.
- [19] E. Favre, Q.T. Nguyen, P. Schaetzel, R. Clement, J. Néel, Sorption of organic solvents into dense silicone membranes. Part 1. Validity and limitations of Flory–Huggins and related theories, *J. Chem. Soc. Faraday Trans.* 89 (1993) 4339–4346.
- [20] C.E. Rogers, *Physics and Chemistry of the Organic Solid State*, Interscience Publishers, New York, 1965.
- [21] S. Brunauer, *The Adsorption of Gases and Vapor*, Oxford University Press, London, 1944.
- [22] S. Kanehashi, K. Nagai, Analysis of dual-mode model parameters for gas sorption in glassy polymers, *J. Membr. Sci.* 253 (2005) 117–138.
- [23] R.M. Barrer, Diffusivities in glassy polymers for the dual sorption model, *J. Membr. Sci.* 18 (1984) 25–35.
- [24] Y. Tsujita, Gas sorption and permeation of glassy polymers with microvoids, *Prog. Polym. Sci.* 28 (2003) 1377–1401.
- [25] J.S. Wang, Y. Kamiya, A method of validation and parameter evaluation for dual-mode sorption model, *J. Membr. Sci.* 154 (1999) 25–32.
- [26] E.O. Timmermann, Multilayer sorption parameters: BET or GAB values? *Colloids Surf. A* 220 (2003) 235–260.
- [27] V. Detallante, D. Langevin, C. Chappey, M. Métayer, R. Mercier, M. Pinéri, Water vapor sorption in naphthalenic sulfonated polyimide membranes, *J. Membr. Sci.* 190 (2) (2001) 227–241.
- [28] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- [29] R.B. Anderson, Modifications of the Brunauer, Emmet and Teller Equation, *J. Am. Chem. Soc.* 68 (1946) 686–691.
- [30] J. Blahovec, S. Yanniotis, GAB generalized equation for sorption phenomena, *Food Bioprocess Technol.* 1 (2008) 82–90.
- [31] E.J. Quirijns, A.J.B. Van Boxtel, W.K.P. Van Loon, G. Van Straten, Sorption isotherms, GAB parameters and isosteric heat of sorption, *J. Sci. Food Agric.* 85 (2005) 1805–1814.
- [32] E.A. Guggenheim, *Application of Statistical Mechanics*, Clarendon Press, Oxford, 1966.
- [33] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M., Soluble sulfonated naphthalenic polyimides as materials for proton exchange membranes, *Polymer* 42 (2001) 359–373.
- [34] H. Bi, S. Chen, X. Chen, K. Chen, N. Endo, M. Higa, K. Okamoto, L. Wang, Poly (sulfonated phenylene)-block-polyimide copolymers for fuel cell applications, *Macromol. Rapid Commun.* 30 (21) (2009) 1852–1856.
- [35] H.S. Lee, A.S. Badami, A. Roy, J.E. McGrath, Segmented sulfonated poly(arylene ether sulfone)-b-polyimide copolymers for proton exchange membrane fuel cells. I. Copolymer synthesis and fundamental properties, *J. Polym. Sci. Part A: Polym. Chem.* 45 (21) (2007) 4879–4890.
- [36] S. Faure, N. Cornet, G. Gebel, R. Mercier, M. Pineri, B. Sillion, Proceedings of the Second International Symposium on New Material Fuel Cell Modern Battery System II, Montreal, 1997.
- [37] H.H. Girault, *Électrochimie physique et analytique, Solutions électrolytiques—Presses Polytechniques et Universitaires Romandes*, Lausanne, 1997.
- [38] K.D. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, *J. Membr. Sci.* 185 (1) (2001) 29–39.
- [39] W. Kujawski, Q.T. Nguyen, J. Néel, Infrared investigations of sulfonated ionomer membranes. I. Water–alcohol compositions and counterions effects, *J. Appl. Polym. Sci.* 44 (6) (1992) 951–958.
- [40] N.J. Bunce, S.J. Sondheimer, C.C. Fyfe, Proton NMR method for the quantitative determination of the water content of the polymeric fluorosulfonic acid Nafion-H, *Macromolecules* 19 (1986) 333–339.
- [41] M. Ludvigsson, J. Lindgren, J. Tegenfeldt, FTIR study of water in cast Nafion films, *Electrochim. Acta* 45 (2000) 2267–2271.
- [42] G. Zundel, Hydration and intermolecular interaction, *Angew. Chem.* 8 (1966) 499–509.
- [43] H.G.M. Edwards, F.R. Brown, J.R. Dale, S. Plant, Raman spectroscopy studied of acid dissociation in sulfonated poly(styrene)resins, *J. Mol. Struct.* 595 (2001) 11–125.
- [44] S.J. Paddison, The modeling of molecular structure and ion transport in sulfonic acid based ionomer membranes, *J. New Mater. Electrochem. Syst.* 4 (1999) 197–207.
- [45] S.S. Jang, V. Molinero, T. Cagin, W.A. Goddard, Nanophase-segregation and transport in Nafion 117 from molecular dynamics simulations: effect of monomeric sequence, *J. Phys. Chem. B* 180 (2004) 3149–3157.
- [46] S.J. Paddison, J.A. Elliott, The effects of backbone conformation on hydration and proton transfer in the 'short-side-chain' perfluorosulfonic acid membrane, *Solid State Ionics* 177 (2006) 2385–2390.
- [47] S.H. de Almeida, Y. Kawano, Thermal behavior of Nafion membranes, *J. Therm. Anal. Calorimetry* 58 (2004) 569–577.

- [48] C. Marestin, G. Gebel, O. Diat, R. Mercier, Sulfonated polyimides, *Adv. Polym. Sci.* 216 (2008) 185–258.
- [49] J.F. Blachot, O. Diat, J.L. Putaux, A.L. Rollet, L. Rubatat, C. Vallois, M. Müller, G. Gebel, Anisotropy of structure and transport properties in sulfonated polyimide membranes, *J. Membr. Sci.* 214 (2003) 31–42.
- [50] Y. Yang, A. Siu, T.J. Peckham, S. Holdcroft, Structural and morphological features of acid-bearing polymers for PEM fuel cells, in: G.G. Scherer (Ed.), *Advanced in Polymer Science—Fuel Cells I*, Springer-Verlag, Berlin, 2008, p. 73.
- [51] T. Ishida, Y. Kasai, K. Urayama, T. Takigawa, Structure and mechanical properties of nafion membranes, *J. Soc. Mater. Sci.* 56 (11) (2007) 1005–1009.
- [52] K. Schmidt-Rohr, Q. Chen, Parallel cylindrical water nanochannels in Nafion fuel-cell membranes, *Nat. Mater.* 7 (2008) 75–83.
- [53] L. Rubatat, A.L. Rollet, G. Gebel, O. Diat, Evidence of elongated polymeric aggregates in Nafion, *Macromolecules* 35 (2002) 4050–4055.
- [54] Q. Zhao, P. Majsztrik, J. Benziger, Diffusion and interfacial transport of water in Nafion, *J. Phys. Chem. B* 115 (2011) 2717–2727.
- [55] P.J. Flory, The elastic free energy of dilation of a network, *Macromolecules* 12 (1979) 119–122.
- [56] Q. Zhao, Structures and Properties of Sulfonated Ionomers Probed by Transport and Mechanical Measurements, Ph.D. Dissertation, Princeton University, 2012, p. 31.
- [57] H.R. Brown, Flory–Huggins–Rehner theory and the swelling of semicrystalline polymers by organic fluids, *J. Polym. Sci. Polym. Phys.* 16 (1978) 1887–1889.
- [58] L. Perrin, Q.T. Nguyen, R. Clément, J. Néel, Sorption and diffusion of solvent vapours in poly(vinylalcohol) membranes of different crystallinity degrees, *Polym. Int.* 39 (1996) 251–260.
- [59] P.J. Reucroft, D. Rivin, N.S. Schneider, Thermodynamics of Nafion–vapor interactions. I. Water Vapor, *Polymer* 43 (2002) 5157–5161.
- [60] J.A. Elliott, S. Hanna, A.M.S. Elliott, G.E. Cooley, The swelling behavior of perfluorinated ionomer membranes in ethanol/water mixtures, *Polymer* 42 (2001) 2251–2253.
- [61] N.G. Boyle, V.J. McBrierty, A. Eisenberg, NMR investigation of molecular motion in Nafion membranes, *Macromolecules* 16 (1983) 80–84.
- [62] S. Schlick, G. Gebel, M. Pineri, F. Volino, ¹⁹F NMR spectroscopy of acid nafion membranes and solutions, *Macromolecules* 24 (1991) 3517–3521.