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

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## ARTICLE INFO

## 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
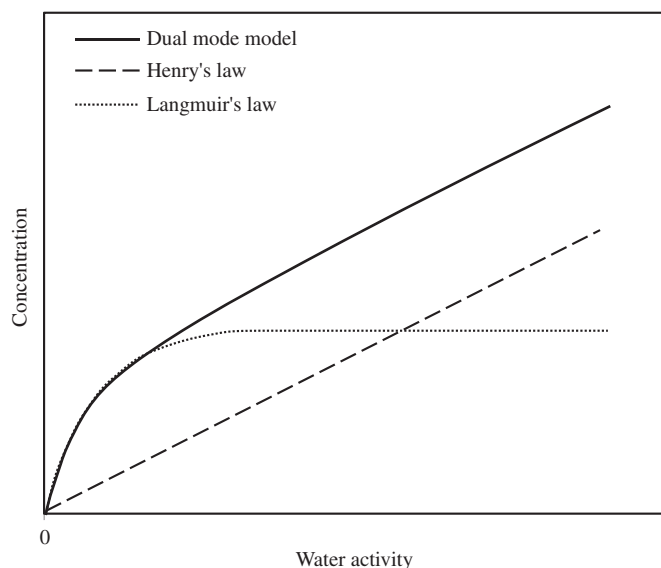


**Fig. 1.** Type 1 sorption isotherm in glassy polymers: dual mode isotherm which is the combination of Langmuir and Henry isotherms.

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]:

$$C = C_H + C_L = k_H a_w + \frac{A_L b_L a_w}{1 + b_L a_w} \tag{1}$$

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