



# Water and phosphoric acid uptake of poly [2,5-benzimidazole] (ABPBI) membranes prepared by low and high temperature casting

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## ABSTRACT

Phosphoric acid-doped membranes based in poly[2,5-benzimidazole] (ABPBI) were obtained by a new low temperature casting procedure and by the classical high temperature casting from methanesulfonic acid. These membranes, which can be suitable for application in direct methanol proton exchange membrane (PEM) fuel cells, were studied in relation with their phosphoric acid doping level by measuring the free and bonded acid. The water isotherms were also determined for the low and high temperature casted ABPBI membranes. Both, acid and water sorption properties, were compared with those determined in poly [2-2'-(*m*-fenylene)-5-5' bibenzimidazole] (PBI) membranes. The water sorption of the ABPBI membranes over the range of all water activity is described by the modified BET equation, commonly known as Guggenheim–Anderson–de Boer (GAB) and a two-parameters empirical isotherm. The acid uptake behaviour of the membranes prepared by low and high temperature casting are related with differences in their supramolecular structure.

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## 1. Introduction

Hydrogen fed proton exchange membrane (PEM) fuel cells and direct methanol PEM fuel cells (DMPEM) fed with liquid methanol use Nafion<sup>®</sup>, a perfluorosulfonated ionomer, as electrolyte membrane [1], and a number of Nafion<sup>®</sup> composites have been proposed as electrolytes for these type of fuel cells [2–7]. Due to the dehydration that occurs at temperatures above 100 °C and the high permeability of methanol through Nafion<sup>®</sup>, that significantly lowers the electrochemical efficiency of DMPEM fuel cells, a number of alternative ionomeric materials are being investigated [8]. Among these materials are sulfonated polyarylene sulfones [9,10], polyphosphazene [11], poly [2-2'-(*m*-fenylene)-5-5' bibenzimidazole] (PBI, Celazole<sup>®</sup>) [12], poly [2,5-benzimidazole] (ABPBI) [13], and composite materials of these polymers with inorganic fillers [14–16].

Polybenzimidazoles are among the most promising materials for DMPEM and high temperature PEM fuel cells. Commercial PBI (Celazole<sup>®</sup>) is a neutral polymer that becomes an acceptable Grotthuss proton conductor by acid doping, commonly with H<sub>3</sub>PO<sub>4</sub>. The interest in this membrane polymer is based on its high oxidative and thermal stability [17] and low methanol crossover [18]. The properties of PBI membranes relevant to its use in fuel cells, such as

proton conductivity, methanol crossover rate and water drag factor, have been extensively studied during the last decade and Li et al. [19] have recently reviewed their properties as isolated membranes and in fuel cell tests.

The proton conductivity of PBI has been reported to exceed the operative range of mobile and stationary applications (0.05 S cm<sup>-1</sup>) only above 150 °C [20,21]. To improve the PBI performance, higher levels of acid doping are need with a detrimental effect on the membrane mechanical properties [19,22]. In order to overcome this problem the inclusion of inorganic fillers and heteropolyacids, as reviewed recently by Carollo et al. [22], or new *in situ* doping during casting techniques [23] have been proposed.

Other approaches are the sulfonation of the polybenzimidazole [24–26] and the chemical modification of the monomer unit of the polybenzimidazole polymers [13,22,27–30]. One of the simplest polymerization processes to obtain a modified PBI was described by Asensio and Gómez-Romero [27], who synthesized ABPBI (see Fig. 1). A similar procedure was adopted by Carollo et al. [22] to developed different kinds of PBI-based polymers with different number and interspacing of the N–H groups in the monomer unit.

Fig. 1 shows the chemical structure of poly [2-2'-(*m*-fenylene)-5-5' bibenzimidazole] (PBI) and poly [2,5-benzimidazole], the polymeric membranes studied in the present work. Both polymers can be used in fuel cells at high temperature under non-humidification conditions, but the monomer for PBI is expensive and its mechanical strength of the polymer is low in the doped state. On the contrary, ABPBI can be prepared at low costs and

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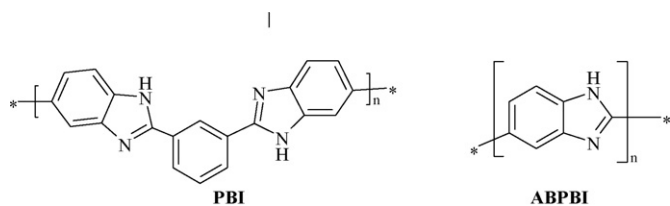


Fig. 1. Structure of PBI and ABPBI.

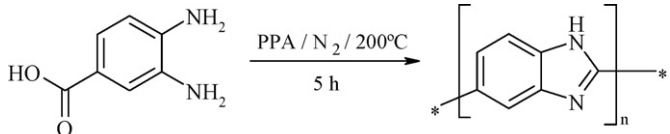
membranes can be casted from different acid solvents, with the possibility of creating a supramolecular structure with improved water and phosphoric acid uptakes and good mechanical strength as compared to PBI.

The aim of this work is to describe the determination of phosphoric acid and water uptakes of PBI and ABPBI membranes synthesized in this work as a part of a more comprehensive study of the properties for application in DMPEM fuel cells.

## 2. Experimental

PBI powder (Goodfellow) was dissolved in N,N-dimethylacetamide (DMAc) at 70 °C under stirring. 5 wt% PBI solution in DMAc was poured in a glass mold and placed in a vacuum furnace at 80 °C for 4 h to cast a membrane of thickness ranging from 50 μm to 150 μm. The resulting membrane was immersed in 68.8 wt% H<sub>3</sub>PO<sub>4</sub> (10.64 M) for at least 72 h prior to use in order to protonate the imidazole ring.

ABPBI was prepared by condensation of 3,4-diaminobenzoic acid (DABA) monomer in polyphosphoric acid (PPA) following the procedure reported by Gómez-Romero and coworkers [13] as indicated in the scheme below.



The resulting polymer was condensed in water, grinded, and washed with water. Then it was immersed in 10 wt% NaOH aqueous solution for 20 h while stirring to eliminate remaining polyphosphoric acid and then washed until neutral pH was attained. Finally it was dried at 90 °C.

High temperature casting ABPBI (HT-ABPBI) membranes were made by pouring 5 wt% solution of ABPBI in pure methanesulfonic acid on a glass plate kept at about 200 °C over a heating plate inside a ventilated hood. After several hours the solvent was eliminated and the plate was immersed in water to remove the membrane.

For ABPBI low temperature casting membrane preparation, a solution of 1 wt% ABPBI in formic acid was poured in a Teflon mold and the formic acid was evaporated overnight in a ventilated hood at room temperature. The membrane was easily removed from the mold. Finally all the ABPBI membranes were doped in 10.64 M H<sub>3</sub>PO<sub>4</sub> for 72 h to protonate the imidazole ring.

The molecular weight of polybenzimidazole polymers was estimated by viscosity measurements of solutions in concentrated H<sub>2</sub>SO<sub>4</sub> (96%). The intrinsic viscosity,  $[\eta]$ , is defined as:

$$[\eta] = \lim_{c \rightarrow 0} \left( \frac{\ln t/t_0}{c} \right) \quad (1)$$

where  $c$  is polymer concentration in the sulfuric acid solution, in g dl<sup>-1</sup>,  $t$  is the flow time of the polymer solution of concentration  $c$ , and  $t_0$  is the flow time of 96 wt% H<sub>2</sub>SO<sub>4</sub>.

A Cannon–Fenske 150 viscosimeter was employed in the viscosity measurements. Polymer solutions of concentrations 3 g dm<sup>-3</sup>,

4 g dm<sup>-3</sup> and 5 g dm<sup>-3</sup> were prepared and left several days until complete dissolution.

The value of the extrapolated intrinsic viscosity at 30 °C was 2.35 dl g<sup>-1</sup> for ABPBI, and was used to estimate the polymer molecular weight,  $M_w$ , resorting to the Mark–Houwink equation [31],

$$[\eta] = KD_p^a \quad (2)$$

where  $D_p$  is the degree of polymerization and the constants  $K$  and  $a$  for ABPBI are  $8.7 \times 10^{-3}$  and 1.10, respectively [27]. The average molecular weight of the polymer can be calculated from the known molecular weight of the monomer unit ( $M_m = 116 \text{ g mol}^{-1}$ ), using the relationship  $D_p = M_w/M_m$ . The resulting polymer molecular weight,  $M_p = 18,800 \text{ g mol}^{-1}$ , was 20% lower to that reported by Asensio et al. [32] and approximately half to that reported by Carollo et al. [22]. However, the degree of polymerization was high enough for casting membranes with good mechanical stability.

The value of the extrapolated intrinsic viscosity at 30 °C was 0.482 dl g<sup>-1</sup> for PBI, and was used to estimate the polymer molecular weight,  $M_p$ , resorting to the Mark–Houwink–Sakurada equation [33],

$$[\eta] = K_1 M_p^\alpha \quad (3)$$

where the constants  $K_1$  and  $\alpha$  for PBI are  $1.94 \times 10^{-4}$  and 0.791, respectively [33]. The result,  $M_p = 19,600 \text{ g mol}^{-1}$ , is somewhat lower to that reported by He et al. [33].

For acid doping level measurements, PBI and ABPBI membrane samples previously doped in 10.64 M aqueous H<sub>3</sub>PO<sub>4</sub> were equilibrated at 25 °C by keeping the membranes in the vapor phase of 10.64 M aqueous H<sub>3</sub>PO<sub>4</sub> in capped and sealed (parafilm) polypropylene flasks thermostated, and were weighted periodically until a constant weight was obtained. Each membrane sample was then immersed in 0.1 M KCl at 25 °C and the initial pH of the solution was measured with a 682 titroprocessor (Metrohm) using a combined pH glass electrode (Metrohm 6-0204-100) with N<sub>2</sub> bubbling. The evolution of the pH was monitored as a function of time until a final pH value was reached. The difference between the final and initial pH allowed us to calculate the free acid content (not bonded to the imidazole group) in the membrane. The solution with the membrane inside was then titrated drop by drop with 0.1 M NaOH enabling enough time to neutralize the membrane bonded acid. The total titration time was about 4 h.

Finally, the membrane sample was removed from the titration vessel, washed with water and dried at 130 °C for 12 h.

The total H<sub>3</sub>PO<sub>4</sub> uptake was calculated from the volume of NaOH solution added between each of the two step pH jumps, corresponding to the equilibria:



The degree of acid doping,  $\lambda_a$ , i.e., the moles of acid per imidazole ring, was calculated as:

$$\lambda_a = \frac{VcM_m}{w_o} \quad (6)$$

where  $V$  (in cm<sup>3</sup>) is the averaged volume of NaOH solution added for the neutralization of the second proton,  $c$  (in mol cm<sup>-3</sup>) is the NaOH concentration,  $w_o$  (in grams) is the dry membrane weight,  $M_m = 116 \text{ g mol}^{-1}$  for ABPBI, corresponding to the molecular weight of the monomer unit; and  $M_m = 142 \text{ g mol}^{-1}$  for PBI, considering that 284 g mol<sup>-1</sup> is the molecular weight of the monomer unit and there are two imidazole ring in each monomer unit of PBI.

The free acid content, expressed as a fraction of total H<sub>3</sub>PO<sub>4</sub> inside the membrane is calculated as:

$$\lambda_f = \frac{V(c - c_f)}{Vc} \quad (7)$$

$$c_f = 10^{pH_i - pH_f} \quad (8)$$

where  $pH_i$  is the initial pH value and  $pH_f$  is the final pH value reached after the membrane sample immersion in the 0.1 M KCl solution.

The water uptake of PBI and ABPBI doped membranes were measured in the relative humidity range from 0.15 to 1. The membrane samples were first equilibrated in vapor phase with  $H_3PO_4$  10.64 M in capped and sealed (parafilm) polypropylene flasks thermostated at 30 °C and weighted daily until a constant weight was obtained. Then they were maintained in isopiestic equilibrium, suspended over saturated salt solutions, in capped and sealed vessels thermostated at 30 °C, and weighted twice a day until constant weight was attained. In order to obtain the dry weight of membrane samples, they were washed several hours in boiling water until neutral pH to remove all the doping acid and finally dried at 130 °C until constant weight was attained (approximately 6 h).

The water content in doped membranes was expressed by means of two hydration numbers defined as  $\lambda_{wa}$  and  $\lambda_w$ , the first being the number of water molecules per molecule of acid, and the second the number of water molecules per imidazol ring. Thus, the acid based hydration number was calculated as,

$$\lambda_{wa} = \frac{w_w M_a}{w_a M_w} \quad (9)$$

where  $M_w = 18.016 \text{ g mol}^{-1}$ , and  $M_a = 98.00 \text{ g mol}^{-1}$  are water and acid molecular weight, respectively; and  $w_w$  and  $w_a$  are the mass of water and acid in the membrane, respectively, calculated as:

$$w_w = w - w_o - w_a \quad (10)$$

$$w_a = VcM_a \quad (11)$$

being  $w$  the doped membrane mass. The dry polymer based water content,  $\lambda_w$ , was calculated as:

$$\lambda_w = \frac{w_w M_m}{w_o M_w} \quad (12)$$

where the symbols have the same meaning as before and  $M_m$  corresponds to the molecular weight of the monomer unit per imidazol ring ( $142 \text{ g mol}^{-1}$  for PBI and  $116 \text{ g mol}^{-1}$  for ABPBI).

All the reagents analytical grade were used as received N,N-dimethylacetamide (Merck),  $H_3PO_4$  (Merck),  $H_2O_2$  (Merck),  $H_2SO_4$  (Baker Analyzed), NaOH (Merck), KCl (Merck), 3,4-diaminobenzoic acid, 97% (Aldrich), polyphosphoric acid 85% (Aldrich), methanesulfonic acid 99.5+% (Aldrich) and methanol (J.T.Baker). Water was deionized and passed through a Millipore filter.

The AFM images of the membranes were acquired under nitrogen atmosphere in tapping mode using a Multimode Nanoscope IIIa (Veeco), at a resonant frequency of 300 kHz. The parameters were carefully set to minimize the tip pressure on the membrane fibers. A commercial Si tip (MPP-11100-Veeco Probes) was used, with a nominal radius <10 nm and a nominal spring constant of  $40 \text{ N m}^{-1}$ . Very thin membranes were formed over a silicon chip having a flat surface by employing diluted solutions of the different polymers in order to minimize their deformation by interaction with the tip.

### 3. Results and discussion

#### 3.1. Phosphoric acid uptake

The degree of acid doping,  $\lambda_a$ , their free acid content,  $\lambda_f$ , and the acid based hydration number,  $\lambda_{wa}$ , of the membranes are summarized in Table 1. The results correspond to membranes doped in 10.64 M aqueous  $H_3PO_4$  and in isopiestic equilibrium with the same acid solution at 30 °C (water activity  $a_w \approx 0.32$ ).

The phosphoric acid uptake in ABPBI membranes is higher than in PBI ones, when compared per imidazol ring. On the other hand

**Table 1**

Doping degree ( $\lambda_a$ ), free acid content ( $\lambda_f$ ), and water content ( $\lambda_{wa}$ ) at 25 °C for PBI and ABPBI membranes doped in 10.64 M aqueous  $H_3PO_4$ .

Membrane	$\lambda_a$	$\lambda_f$	$\lambda_{wa}$
LT-ABPBI	3.5	0.098	0.95
HT-ABPBI	2.8 2.9 <sup>a</sup>	0.093	0.78
PBI	1.9 2.5 <sup>a</sup> 2.0 <sup>b</sup>	0.095	1.14 0.9 <sup>b</sup>

<sup>a</sup> Ref. [32].

<sup>b</sup> Ref. [34].

the acid uptake of low temperature cast ABPBI membranes (LT-ABPBI) is higher than the acid uptake of high temperature cast ABPBI (HT-ABPBI) membranes. The doping degree was compared with that reported for PBI and HT-ABPBI by Asensio et al. [32]. It can be observed from Table 1 that the agreement is rather good taking into account the differences in the degree of polymerization. Also, a good agreement is found with the phosphoric acid and water content for PBI membranes reported by Lobato et al. [34].

Only a small fraction of the total uptaken acid, about 10%, was not bonded to polymer imidazole groups in the PBI and ABPBI membranes.

The amount of water molecules per phosphoric acid molecule,  $\lambda_{wa}$ , are 0.78 and 0.95 for HT-ABPBI and LT-ABPBI, respectively, calculated from  $\lambda_a$  and the water moisture at the water activity of the doping solution ( $a_w = 0.32$ ). These values are slightly lower than those found for PBI (see Table 1), although the differences are not significant and could be linked to the higher acid doping observed for the ABPBI membranes as compared with PBI.

This excess of water linked with the doping acid in the case of LT-ABPBI membranes is probably related with the supramolecular packing of the ABPBI fibers during the casting process, which will be discussed in Section 3.3.

#### 3.2. Water uptake

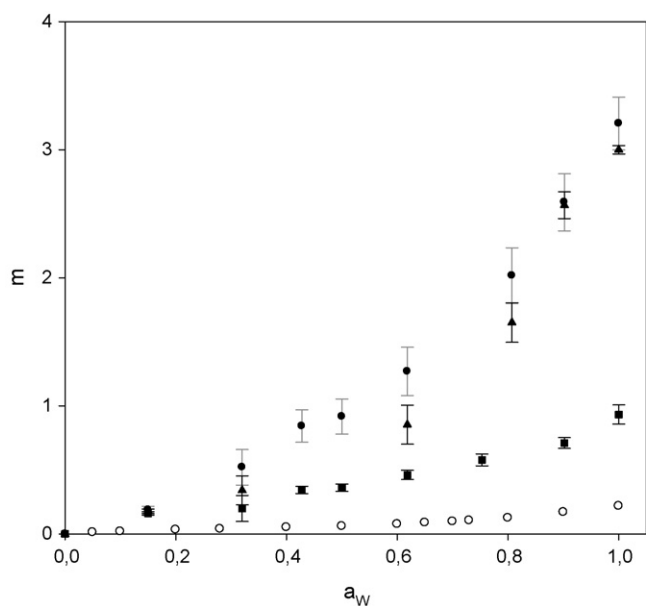
The water uptake of polymer membranes from vapor phase is of great importance, since water is involved in electrode reactions and in transport mechanism of species through the fuel cell.

The water uptake of PBI and ABPBI (LT and HT casting) doped membranes from vapor phase at 30 °C, expressed as  $\lambda_w$  (Eq. (12)), and  $m = w_w/w_o$  (the mass, in grams, of water uptaken per gram of dry membrane), are summarized in Table 2 at different water activities. The water sorption isotherms for LT-ABPBI and HT-ABPBI membranes, shown in Fig. 2, have the form of type III in the Brunauer classification [35], while they seem to be type II-like for PBI membranes. Type II isotherm is a characteristic of strong physical adsorption followed by multilayer absorption, while type III isotherm suggests the presence of a hydrophobic surface exhibiting weak interactions with water. In terms of the the BET equation,

**Table 2**

Water uptake for PBI and ABPBI doped membranes at 30 °C expressed as  $\lambda_w$  and  $m$  (in parenthesis).

Water activity	PBI	HT-ABPBI	LT-ABPBI
0.15	1.26 (0.159)	1.14 (0.176)	1.21 (0.188)
0.32	2.19 (0.278)	2.19 (0.340)	3.35 (0.520)
0.43	2.71 (0.344)	–	5.43 (0.842)
0.50	2.84 (0.360)	–	5.90 (0.916)
0.62	3.63 (0.461)	5.50 (0.853)	8.18 (1.27)
0.75	4.56 (0.578)	–	–
0.81	–	10.64 (1.65)	13.00 (2.02)
0.90	5.60 (0.710)	16.54 (2.57)	20.01 (3.11)
1.00	7.36 (0.932)	19.33 (3.00)	20.65 (3.20)



**Fig. 2.** Experimental water sorption isotherms for PBI and ABPBI doped membranes at 30 °C: (■) PBI ( $\lambda_a = 1.9$ ); (▲) HT-ABPBI ( $\lambda_a = 2.8$ ); (●) LT-ABPBI ( $\lambda_a = 3.5$ ); (○) Nafion at 20 °C [35]. Error bars correspond to averaging on several samples.

a high values of the adsorption energy or the interaction parameter,  $c$ , lead to type II isotherms. When the adsorption heat is lower than the liquifaction heat,  $c < 1$ , and the isotherms have no inflection and become type III.

Also observed was that at water activity higher than 0.2 the water uptake by ABPBI membranes is higher than that of PBI membranes, while LT-ABPBI membranes showed higher water uptake than HT-ABPBI membranes, which is also consistent with the higher acid doping level observed in LT-ABPBI membranes.

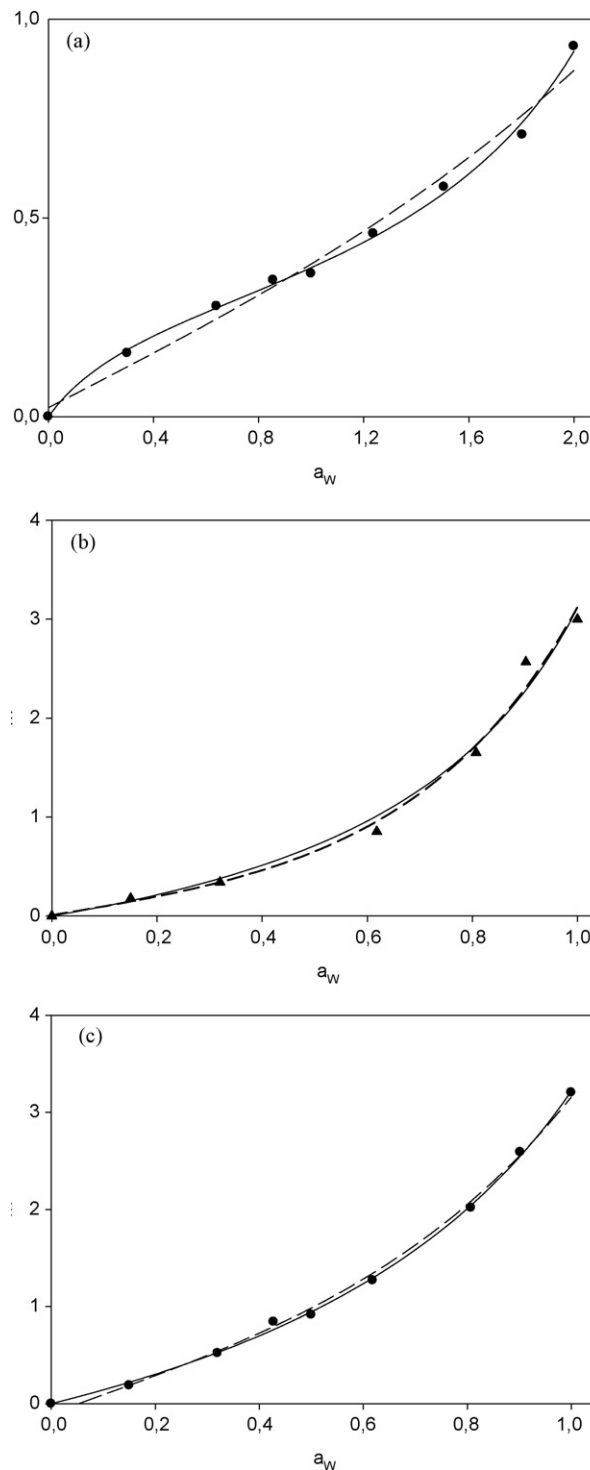
The water sorption of doped PBI and ABPBI membranes is much higher than the corresponding Nafion membranes in its protonated form, as shown in Fig. 2, where the results by Rivin et al. [36] are also plotted. Weng et al. [37] have shown that when equilibrated in 85%  $H_3PO_4$ , that is, at acid concentration close to that used for doping our ABPBI membranes, acid taken up by the Nafion membrane is about two moles per sulfonic acid group, and the water sorption of the Nafion/ $H_3PO_4$  membranes increases roughly by a factor of two as compared with Nafion. Because these measurements were performed at 125 °C, we did not compare them with our results in Fig. 2.

As expected by the form of the isotherms, the multilayer BET equation [38] only succeed to describe the water sorption data for  $a_w < 0.5$ , but fails at  $a_w > 0.5$ , as usually found in ionic conducting

**Table 3**  
Parameters of the GAB and Iglesias–Chirife isotherms.

Parameters GAB	PBI	HT-ABPBI	LT-ABPBI
$m_0$	$0.30 \pm 0.02$	$1.37 \pm 2.10$	$2.26 \pm 1.12$
$c$	$8.83 \pm 2.34$	$0.95 \pm 1.73$	$1.01 \pm 0.46$
$f$	$0.69 \pm 0.02$	$0.69 \pm 0.20$	$0.58 \pm 0.07$
$R^2$	0.99	0.98	0.99
$\sigma$	0.006	0.067	0.029
Parameters IC	PBI	HT-ABPBI	LT-ABPBI
$A$	$-0.45 \pm 0.05$	$-1.22 \pm 0.43$	$-0.15 \pm 0.03$
$B$	$1.10 \pm 0.06$	$3.05 \pm 0.45$	$2.01 \pm 0.04$
$m_{0.5}$	0.360	0.674 <sup>a</sup>	0.916
$R^2$	0.97	0.99	0.99
$\sigma$	0.014	0.063	0.040

<sup>a</sup>Fitted value.



**Fig. 3.** Comparison of experimental and calculated water sorption isotherms for (a) PBI ( $\lambda_a = 1.9$ ); (b) HT-ABPBI ( $\lambda_a = 2.8$ ); (c) LT-ABPBI ( $\lambda_a = 3.5$ ). Full line: GAB isotherm; dashed line: empirical isotherm.

membranes [39]. Therefore, we analyzed the data using two alternative isotherms.

Firstly, we analyzed the data with the modified BET equation, commonly known as Guggenheim–Anderson–de Boer (GAB) [40–42], which is a three-parameters isotherm expressed, in its linear form, by

$$\frac{a_w}{m(1 - fa_w)} = \frac{1}{fm_0c} - \frac{(c-1)}{m_0c} a_w \quad (13)$$

where  $m$  is the water moisture (dry basis),  $m_o$  is the mass (in grams) of water in the monolayer per gram of dry membrane,  $a_w$  is the water activity,  $c = \exp[(E_1 - E_L)/RT]$ , as in the BET isotherm, is related to the energy difference between the sorption energy of the first water layer ( $E_1$ ) and the heat of liquifaction of pure water ( $E_L$ ), while  $f = \exp[(E_2 - E_L)/RT]$ , is related to the energy difference between the subsequent water layers ( $E_2$ ) and the heat of liquifaction of pure water.

The GAB isotherm reduces to the BET one as  $f=1$ , but it predicts a finite sorption at  $a_w = 1$ , as observed in our PBI and ABPBI membranes, for  $f < 1$ . It is well known that the GAB isotherm, Eq. (13), has an extended range of applications as compared to the BET isotherm, but it fails at  $a_w > 0.7-0.8$  [40] in systems with infinite water moisture at  $a_w = 1$ , that is, for  $f > 1$ .

Secondly, we used the empirical two-parameter isotherm proposed by Iglesias and Chirife [43] to describe the sorption of water in high-sugar food:

$$\ln[m + (m^2 + m_{0.5})^{1/2}] = A + Ba_w a \quad (14)$$

where  $m_{0.5}$  represents the water sorption at  $a_w = 0.5$ , and  $A$  and  $B$  are empirical parameters. This expression was derived by considering that both, type III and low  $c$  BET parameter type II isotherms, have the shape of the arc  $\sin h$  function [43]. Eq. (14) becomes a two-parameter isotherm, provided that  $m_{0.5}$  is an experimental data. While its validity was restricted to  $0.1 < a_w < 0.8$  in fruits and related products [43], it was extended up to  $a_w = 0.9$  for the water sorption by polyaramide blend fabrics [44].

Fig. 3(a–c) shows the linear fit of the water sorption isotherms using GAB and the empirical Iglesias–Chirife isotherms represented by Eqs. (13) and (14), respectively. It can be observed that both equations describe reasonably well the experimental data for LT-ABPBI and HT-ABPBI membranes over the entire range of water activities, being the standard deviation of the fits almost equivalent. In the case of the PBI membranes the GAB isotherm is clearly better than the two-parameters empirical isotherm, which is expected because its type II shape.

The parameters of the GAB and Iglesias–Chirife isotherms for all the membranes are summarized in Table 3. It is remarkable that the validity of Eq. (14) for LT and HT-ABPBI membranes extends all over the water activity range in this work ( $0 < a_w < 1.0$ ) without any serious deterioration of its performance, as compared with results in other systems [43,44]. The  $f$  parameter in the GAB

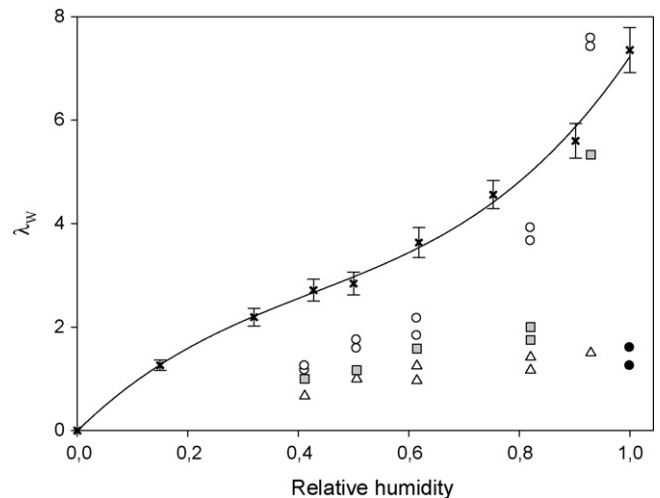


Fig. 4. Water uptake of PBI membranes: (x) PBI ( $\lambda_a = 1.9$ ); 30 °C (this work); ( $\Delta$ ) PBI ( $\lambda_a = 0.85$ ); ( $\blacksquare$ ) PBI ( $\lambda_a = 2.0$ ); ( $\circ$ ) PBI ( $\lambda_a = 2.85$ ), and ( $\bullet$ ) undoped PBI (Ref. [19], at 25 °C).

isotherm is lower than one, as expected for membranes exhibiting finite water sorption at  $a_w = 1$ , and has the same value for the PBI and HT-ABPBI membranes, while is smaller for LT-ABPBI. The high value of the  $c$  parameter in PBI is consistent with the shape of the isotherm.

The monolayer parameter,  $m_o$ , is proportional to the water uptake, which follows the order: LT-ABPBI > HT-ABPBI > PBI. The monolayer sorption for PBI is reached at low water activity ( $a_w \approx 0.35$ ), while for ABPBI membranes the monolayer is completed at water activities about 0.75–0.80. In Fig. 4, our results of water uptake on PBI membranes are compared with those reported by Li et al. [19] for different acid doping grades. It was found that the water uptake by the PBI membrane doped with 1.95 moles of acid per imidazole group (3.9 moles of acid per monomer unit) was higher than that reported by these authors for doping levels between 1.7 and 5.7 moles of acid per monomer unit in the range  $0.4 < a_w < 0.8$ . However, at  $a_w$  close to 0.9 the water uptake seems to follow the expected trend. The observed behaviour could be due to differences in membrane properties, such as polymer molecular weight and undoped membrane pre-treatment.

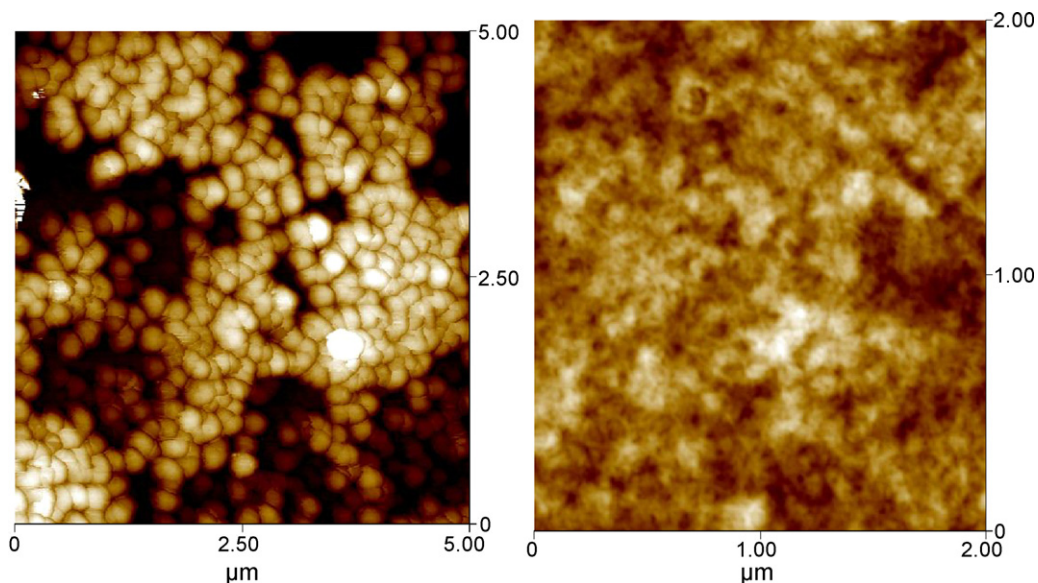


Fig. 5. AFM images of undoped HT-ABPBI (left) and LT-ABPBI (right) membranes prepared on a silicon surface with the standard casting mode.

### 3.3. Membrane morphology

The AFM images obtained in tapping mode for HT-ABPBI and LT-ABPBI membranes are shown in Fig. 5. It can be seen that the packing of the polymer chains is sensitive to the casting procedure. In the case of LT-ABPBI, the polymers chain aggregation yield to fibers around 25 nm in diameter, while aggregation in the HT-ABPBI seems to be more important, resulting in fibers around 200 nm in diameter. Probably the casting temperature has lower influence on the membrane morphology than the nature of the acid used for the casting. The magnitude of the electrostatic interactions between the protonated polymer chains and counterions during casting could lead to differences in the self-assembling capacity of the polymer. A detailed study of the effect of the casting chemistry and temperature on the membrane properties is out of the scope of this work, but will be addressed in a forthcoming study.

Independently of its origin, differences in morphology could explain the behaviour of the ABPBI membranes in relation to the uptake of water and phosphoric acid. The low temperature casting yields membranes with less compact structures, larger inter-fiber space and sorption surface, which enhance the sorption of acid (protonation) and the associated water.

### 4. Conclusions

The phosphoric acid and water uptakes were studied in ABPBI membranes prepared by casting and compared to the behaviour of PBI cast membranes. A new low temperature casting procedure was described to prepare ABPBI membranes yielding higher acid doping in relation to ABPBI and PBI membranes prepared by casting at high temperature, probably as a consequence of a less compact supramolecular packing, with a larger number of exposed sorption sites. It is uncertain the relationship between casting temperature and morphology since the nature of the acid used in the casting could account for the different packing of the polymer chains.

The LT-ABPBI membranes also exhibits higher water uptake than the PBI and HT-ABPBI membranes, as expected by its higher acid content. The sorption isotherms for the ABPBI membranes can be described by resorting to both, GAB and empirical two-parameters Iglesias-Chirife equations, all over the range of water activities. It is expected that the higher acid and water content in the ABPBI membranes, particularly in those prepared with the low temperature cast, yields higher electrical conductivity as compared to PBI, although it is not clear how it could affect the mechanical properties of the membranes. Both properties, fundamental for the application of these membranes in PEM fuel cells will be addressed in a forthcoming study.

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