

# Water Vapor Sorption Thermodynamics of the Nafion Ionomer Membrane

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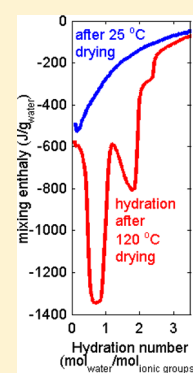
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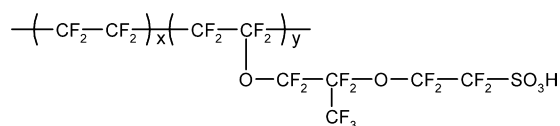
**S** Supporting Information

**ABSTRACT:** The water interactions of polymer electrolyte membranes are of significant interest when these materials are used in, for example, fuel cells. We have therefore studied the sorption thermodynamics of Nafion with a sorption calorimeter that simultaneously measures the sorption isotherm and the mixing (sorption) enthalpy. This unique method is suitable for investigating the sorption thermodynamics of ionic polymers. The measurements were made at 25 °C on a series of samples dried at different temperatures from 25 to 120 °C. The sorption isotherms indicate that the samples dried at 120 °C lost about 0.8 more water molecules per sulfonic group during the drying than did the samples dried at 25 °C, and this result was verified gravimetrically. The mixing enthalpies showed several peaks or plateaus for the samples dried at 60–120 °C. This behavior was seen up to about 2 water molecules per sulfonic group. As these peaks were not directly related to any feature in the sorption isotherm, they probably have their origin in a secondary process, such as a reorganization of the polymer.

**INTRODUCTION**

**Polymer Electrolyte Membranes.** Polymer electrolyte membrane fuel cells (PEMFC) have the potential to generate both power and heat with high efficiency and minimum pollution for transportation, residential, industrial, and aerospace applications. Most commonly, these devices are fueled by hydrogen and use oxygen (air) as oxidant. The function of a PEMFC is critically linked to the thin polymer electrolyte membrane (PEM) that separates the anode and the cathode and transports the electrochemically generated protons from the former to the latter electrode. The membrane must also form an effective barrier against the fuel and be electrically insulating to force the electrons through an outer electrical circuit to provide power, before they are returned to the cathode to be joined with the oxygen and the protons.

State-of-the-art PEMs currently include perfluorosulfonic acid membranes such as Nafion (Figure 1) and are generally composed of a hydrophobic backbone functionalized with highly acidic and hydrophilic acid groups.<sup>1</sup> There are several varieties of Nafion; Nafion 115 has an equivalent weight of 1100 (molar mass of dry polymer per sulfonic group) and a



**Figure 1.** Chemical structure of the perfluorosulfonic polymer Nafion.

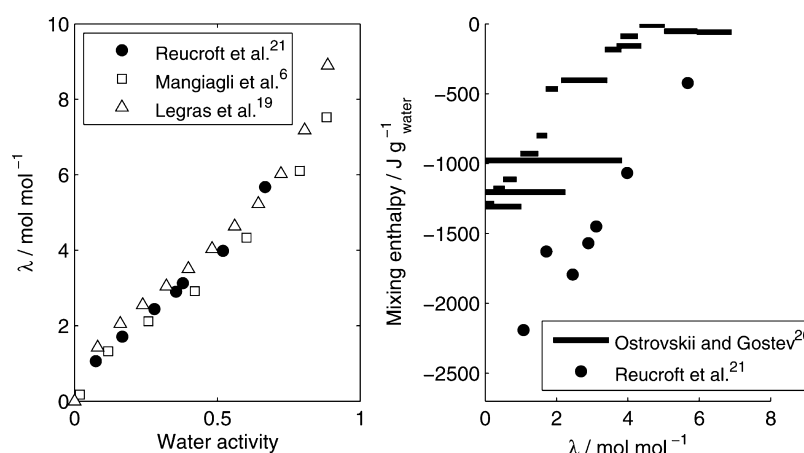
thickness of 0.005 in. (approximately 130  $\mu\text{m}$ ). There is no universally accepted detailed model of the morphology of Nafion, but it is generally accepted that hydrated PEMs are characteristically phase separated into a percolating network of nanopores containing water and a hydrophobic polymer-rich phase domain.<sup>2,3</sup> The water in the nanopores dissociates the acid units and functions as the proton solvent to facilitate the transport of the acidic protons. Thus, membranes based on sulfonated polymers rely critically on water for proton conductivity. Efforts are currently made to further improve the properties of perfluorosulfonic acid PEMs for use in different PEMFC applications, especially at temperatures above 90 °C. The approaches include shortening the side chains and increasing the acidic content of the ionomers, as well as increasing the crystallinity and using various mechanical reinforcements.<sup>4</sup>

As already mentioned, a critical factor for the performance of a PEM is its water content. At very low hydration levels the percolation of the water filled nanopores is not developed in the membranes, and both water and protons are bound to the sulfonic groups. Consequently, the proton transport will be limited. As the hydration level increases, the water molecules will eventually form a percolating network of water filled nanopores in which the protons can be transported. However, if the humidity of the membrane in a PEMFC is increased

**Received:** September 7, 2012

**Revised:** May 16, 2013

**Published:** June 18, 2013



**Figure 2.** Review of sorption isotherms and mixing enthalpies measured on Nafion 117. (a, Left) sorption isotherms from refs 6, 19, and 21. (b, Right) mixing enthalpies from refs 21 and 26. Both were measured as mean values over certain  $\lambda$ -intervals, but ref 21 reported each mean value at one  $\lambda$ , and their results are therefore shown with markers.

beyond a certain level, liquid water is likely to condense out on the cathode side to cause so-called “cathode flooding”. This leads to restricted oxygen diffusion to the cathode and the PEMFC performance will be severely reduced. Flooding at the cathode occurs because water is produced at the cathode and because water is actively transported to the cathode by the protons as they cross the membrane (electro-osmotic drag).<sup>5</sup> The difference in water content between the two sides of the membrane can be reduced by back-diffusion, humidification on the anode side, and/or dehydration on the cathode side. The last two options should be avoided if possible as they add to the cost of a PEMFC and also reduce its efficiency. However, relying only on back-diffusion is not trivial. Membranes with a high concentration of sulfonic groups allow a more rapid back-diffusion of water from the cathode to the anode, but they also exhibit a higher propensity to dehydrate.<sup>5</sup> It is thus a complex task to find optimal membrane materials for a PEMFC application. The mechanical properties of the membrane will also deteriorate if the membrane swells excessively. There is thus an optimum moisture content of a PEM in a fuel cell, and one of the main problems with designing a PEMFC is to balance the humidity in the PEM at the optimal level. If the membrane has poor water balance characteristics, the consequences are poor dimensional stability, chemical degradation, etc., which are detrimental to the overall cell performance.

**PEM–Water Interactions.** The interaction between water and a solid material such as Nafion is complex, and a difference should be made between two cases: when the water interacts with the solid in its vapor state (sorption) and when the water is in its liquid state (immersion). The latter process is termed immersion as it is in this case only relevant to let the solid go from a certain moisture state to full saturation. Because of sorption hysteresis, it is in practice not possible to dose liquid water directly to a solid and get a homogeneous equilibrium moisture state. If a small amount of liquid water is placed in contact with the surface of a solid, the surface will initially be saturated, and as the water later redistributes within the sample, the surface will experience desorption while in the inner parts water will be absorbed. Sorption hysteresis will then prevent a homogeneous moisture distribution. Because of this phenomenon, the interaction between water and solids is studied by immersion measurements or, preferably, by vapor sorption

measurements in which the relative humidity surrounding the sample is changed and the sample mass, the heat produced, or other properties are studied.

The moisture state of a solid can be characterized either through the amount of water in the system, typically the moisture content  $c$  ( $\text{g}_{\text{water}} \text{g}_{\text{dry solid}}^{-1}$ ), or through the state of the water. For the latter we here use the water activity  $a_w$ , which at equilibrium at low temperatures and pressures can be taken to be equal to the relative humidity  $\phi$ . For PEM materials it is also relevant to describe the absorbed amount in relation to the number of hydrophilic sites and this is usually called the hydration number  $\lambda$ .<sup>6</sup> For Nafion the hydration number is the number of water molecules per sulfonic group in units of  $\text{mol}_{\text{H}_2\text{O}} \text{mol}_{\text{SO}_3\text{H}}^{-1}$ . Nafion 115 and 117 contain 0.91 mmol of  $\text{SO}_3\text{H}$  per g of dry polymer, so the conversion from moisture content  $c$  to hydration number  $\lambda$  for Nafion 115 and 117 is

$$\lambda = 61c \quad (1)$$

The factor 61 is the inverse of the product of  $0.91 \times 10^{-3}$  and 18 (the molar mass of water).

The interaction between water and Nafion (and other PEM materials) have been intensively studied. The main methods have been measurements of (references given are recent examples) water uptake as a function of water activity (sorption isotherms),<sup>6</sup> water loss at elevated temperatures (TGA),<sup>7</sup> freezable water (DSC),<sup>8</sup> melting temperature of water (DSC),<sup>9</sup> infrared spectroscopy (FTIR),<sup>10</sup> and NMR cryoporosimetry.<sup>11</sup> A large body of information has also been accumulated by molecular dynamics simulations.<sup>10,12–15</sup>

The sorption isotherm (the hydration number as a function of the water activity) of Nafion has been measured in several studies, see for example refs 6 and 16–25. The results of these studies agree rather well considering that different methods of pretreatment and measurement methods were used. We give three recent examples of measurements on Nafion 117 at 20–30 °C in Figure 2a.

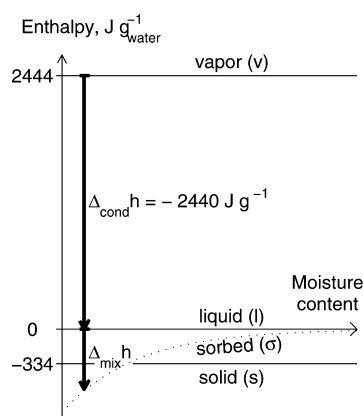
**Sorption Thermodynamics.** After reviewing the literature on the thermodynamics of the water–Nafion system (Supporting Information), we found that the subject is not trivial as different authors use different definitions and nomenclature. We will therefore give a short overview of sorption thermodynamic measurement techniques and nomenclature.

What is most often measured is the enthalpy associated with the transfer of one unit mass of water vapor to a sample; this enthalpy we call the sorption enthalpy  $\Delta_{\text{sorp}}h$  ( $\text{J g}_{\text{water}}^{-1}$ ) and it is the sum of the condensation enthalpy and a mixing enthalpy:<sup>27</sup>

$$\Delta_{\text{sorp}}h = \Delta_{\text{cond}}h + \Delta_{\text{mix}}h \quad (2)$$

The sorption enthalpy and the mixing enthalpy are properties of the moisture state (water activity, moisture content) at which the sorption/mixing takes place, whereas the condensation enthalpy is constant at isothermal conditions. Note that mixing/sorption enthalpies expressed in units of  $\text{J g}_{\text{material}}^{-1}$  are also found in the literature; usually as results from immersion experiments (not discussed further here).

The mixing enthalpy is the enthalpy of interaction between liquid water and the solid. As discussed above, it is difficult to realize this process in practice, but the mixing enthalpy can be evaluated by subtracting the condensation enthalpy from a measured sorption enthalpy, as shown in Figure 3. In the



**Figure 3.** Nomenclature of sorption thermodynamics. The heat produced when water vapor is sorbed by a solid is the sorption enthalpy (the dashed line), which is dependent on the moisture content. The sorption enthalpy is the sum of the condensation enthalpy and a mixing enthalpy (shown by arrows for one moisture content). The dashed curve for sorbed water is typical of cellulosic materials.<sup>33,46</sup> Enthalpies of the three states of water are schematically shown by solid horizontal lines (the enthalpy of the vapor is for 25 °C, and the enthalpy of ice is taken at 0 °C).

following we will discuss sorption thermodynamics in terms of mixing enthalpies; they can be seen as “excess enthalpies” indicating how much more heat that a sorption process produces than when the same mass of water vapor condenses. Note also that we use the thermodynamic sign convention that states that processes are seen from the viewpoint of the system; i.e., if heat is lost by the system to the surroundings (heat is produced), the enthalpy is negative. Enthalpies of sorption and condensation are therefore always negative; enthalpies of mixing are negative except in cases where driven by entropy effects (see ref 28 for an example of this).

There are two commonly used methods to assess sorption enthalpies. The most direct one is a calorimetric step method in which the heat is measured when a relatively large change in water content is made on a specimen is made (often from different initial water contents to saturation). The measured heat  $Q$  (J) divided by the mass of water taken up  $m$  (g), often determined on parallel samples by other methods, gives a sorption enthalpy. This is the mean enthalpy change when the

sample absorbs water vapor, e.g., from moisture content  $c_1$  to moisture content  $c_2$ :

$$\Delta_{\text{sorp}}\bar{h}(c_1, c_2) = \frac{Q}{m} \quad (3)$$

The enthalpy is here a mean value of the enthalpy in the interval in which the measurement was made and as these intervals is typically quite wide (greater than one  $\lambda$ -unit in the case of PEMs) it is difficult to draw any detailed conclusions about, e.g., how the different water molecules (“layers”) are absorbed.

The second commonly used method is the calculation of sorption enthalpies by the van’t Hoff equation from sorption isotherms measured at different temperatures. Although this relation is thermodynamically valid, sorption isotherm data are often not good enough to permit the determination of precise sorption enthalpies. Similar problems with the van’t Hoff equation have been noted for the determination of other types of enthalpies, see for example the discussion in ref 29.

A third method is used in the present paper. In this method the hydration is a continuous process that takes place over about 1 day. During this time, the thermal powers of vaporization of water from a water source and the corresponding sorption on the sample are continuously and separately measured and can thus be compared on a second by second basis. This gives sorption enthalpies as a function of the moisture content:

$$\Delta_{\text{sorp}}h(c) = \frac{P}{q_m} \quad (4)$$

Here,  $P$  ( $\text{J s}^{-1}$  or W) is the thermal power (heat production rate) and  $q_m$  ( $\text{g s}^{-1}$ ) is the mass flow rate (mass change rate). The enthalpy in eq 3 is the mean enthalpy in a certain moisture content range, but the presently used method gives the sorption enthalpy as a function of the moisture content (eq 4) so that one can see details in the sorption enthalpies. Note that the enthalpy in eq 4 is calculated as the ratio of two rates, whereas the enthalpy in eq 3 is the ratio of two integrated properties (the present method is further discussed in the Methods section).

The enthalpy of mixing is the heat produced when a unit mass of water in the liquid state is absorbed by an infinite mass of an absorbent. This heat is often attributed to the change of state of the water molecules that are absorbed, but it is actually the response of the whole system (consisting of the absorbent, the previously absorbed water, and the water that is absorbed) to the addition of more water. This is most clearly seen in systems where large conformational changes occur in the sorbent when water is taken up (see, for example, ref 28), but minor such effects are always present when water is taken up in the bulk of a system.

Only a few studies have been published with sorption enthalpy data of the Nafion–water system, and those studies that exist have been made either by calorimetric measurements using eq 3 or by using the van’t Hoff equation on sorption isotherm data. In Figure 2b we show the results of Ostrovskii and Gostev<sup>26</sup> and Reucroft et al.<sup>21</sup> that both made calorimetric studies by stepwise increasing the humidity level of their samples. Ostrovskii and Gostev incrementally added water vapor by crushing glass bulbs with known amounts of water in a vacuum system connected to the calorimeter. They thus knew both the heat produced and the moisture content increase.

Reucroft et al. used a flow microcalorimeter and measured the heat released when the relative humidity of the flowing nitrogen gas was increased. To get the sorption enthalpies, they combined the calorimetric data with a separately measured sorption isotherm. The data of Ostrovskii and Gostev and Reucroft et al. agree fairly well considering that there were several factors that differed between their measurements; for example, the sample pretreatment and the measurement temperature. We also found other results in the literature,<sup>23,30,31</sup> but these either were of doubtful quality or could not be interpreted in terms of mixing enthalpies (see Supporting Information).

**Importance of PEM–Water Interactions.** It is not possible to overemphasize the importance of solid–water interactions in the case of polymer materials for fuel cells, where the water management at low water activities is essential. However, due to practical difficulties only few measurements of sorption thermodynamics have been made. With our sorption calorimeter we can completely map the thermodynamics of such processes. This is significant as it will enable a fundamental thermodynamic understanding of the hydration of ionomers, something that is essential for their function in fuel cells. The aim of the present paper is to present the used technique and measurements of the sorption enthalpy of water vapor on Nafion dried at different temperatures.

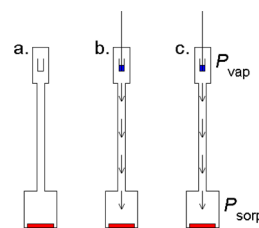
## MATERIAL

Nafion 115 (SigmaAldrich) was cut into 5 mm wide strips and converted to acid form by a standard procedure:<sup>32</sup> boiling in 3% H<sub>2</sub>O<sub>2</sub>, boiling in deionized water, boiling in 0.5 M H<sub>2</sub>SO<sub>4</sub>, and finally boiling in deionized water (the duration of each step was 1 h). Samples were then stored in deionized water until the measurements. New samples were used for each sorption calorimetric measurement; for the gravimetric experiment one sample was used for each experiment consisting of one drying at 25 °C and a subsequent drying at 120 °C.

## METHODS

**Drying Procedure.** Each specimen was dried under vacuum at one of six temperatures (25, 40, 60, 80, 100, or 120 °C) for 24 ± 2 h before being charged into the sorption calorimeter. The sample sizes ranged from 65.42 to 99.24 mg, except for one sample at 100 °C with a mass of 172.66 mg. The charging of a specimen into the calorimetric ampule took about 10 s and was made in a box with a relative humidity of less than 10%.

**Sorption Calorimetry.** In this study we have used a sorption calorimeter at 25 °C in which the transfer of vapor to the sample is by diffusion.<sup>33–35</sup> In the instrument, two microcalorimeters (a double twin microcalorimeter)<sup>34</sup> simultaneously and separately measure the heat production rate (thermal power) of the vaporization of water from a vapor source and of the absorption of the same vapor in a sample. Figure 4 gives a schematic description of a measurement. At each time during a measurement, the thermal power of vaporization  $P_{\text{vap}}$  (W) and the thermal power of sorption  $P_{\text{sorp}}$  (W) are measured. We count both of these as positive for exothermal processes, so  $P_{\text{sorp}}$  is positive and  $P_{\text{vap}}$  is negative. From these two thermal powers it is possible to evaluate a triplet of information: water activity  $a_w$  (1), moisture content  $c$  (g<sub>water</sub> g<sub>dry sample</sub><sup>−1</sup>), and enthalpy of mixing  $\Delta_{\text{mix}}h$  (J g<sub>water</sub><sup>−1</sup>):<sup>35</sup>



**Figure 4.** Schematic description of the calorimetric sorption vessel and a measurement. (a) The sorption vessel is charged with a dry sample in the lower part. (b) A measurement is started by the injection of water to the cup in the top part of the vessel. Water vaporizes and diffuses through the tube down to the sample. (c) The thermal power of vaporization  $P_{\text{vap}}$  and the thermal power of sorption  $P_{\text{sorp}}$  are simultaneously and separately measured by the double twin microcalorimeter used. From the measured thermal powers as a function of time it is possible to calculate both the mixing enthalpy and the moisture content as a function of the water activity of the sample.<sup>35</sup>

$$a_w(t) = 1 + \frac{P_{\text{vap}}(t)}{P_{\text{max}}} \quad (5)$$

$$c(t) = c_0 - \frac{1}{m_0} \int_{\tau=0}^t \frac{P_{\text{vap}}(\tau)}{\Delta_{\text{vap}}h} d\tau \quad (6)$$

$$\Delta_{\text{mix}}h(t) = \Delta_{\text{vap}}h \frac{P_{\text{sorp}}(t) + P_{\text{vap}}(t)}{P_{\text{vap}}(t)} \quad (7)$$

Here,  $P_{\text{max}}$  (W) is the maximal thermal power of vaporization in the device, i.e., when a measurement is made with a drying agent that keeps the water activity at zero in the sample position;  $c_0$  (g<sub>water</sub> g<sub>dry sample</sub><sup>−1</sup>) is the initial moisture content of the sample;  $m_0$  (g) is the dry mass of the sample; and  $\Delta_{\text{vap}}h$  (J g<sup>−1</sup>) is the vaporization enthalpy of water. For an ionomer the moisture content can be recalculated to the hydration number by eq 1.

Equations 5–7 are based on Ficks law of diffusion (eq 5), a mass balance (eq 6), and a heat balance (eq 7). The method is thus only based on a few fundamental physical principles and can in this respect be regarded as robust. The only major problem in the interpretation of results from the method is the question of whether the results are equilibrium results or not; in other words, the results we present are true results in the sense that we correctly follow water activity, hydration number, and mixing enthalpy during a hydration process, but the results may not in all respects be equilibrium results. This is further discussed below.

The method has been tested on several systems with good results. For microcrystalline cellulose and a carboxymethylated cellulose the sorption isotherms agreed closely with isotherms measured by equilibration over saturated salt solutions, and for microcrystalline cellulose and bentonite clay a good agreement was found with mixing enthalpies evaluated from heat of immersion measurements.<sup>33</sup>

The present sorption calorimetric technique is distinctly different from other sorption techniques, where the relative humidity is set with water or saturated salt solutions or programmed to different relative humidities in sorption balances. In those techniques the approach to equilibrium at each humidity level can be monitored and used as a measure of how near equilibrium conditions a sample is. In the sorption calorimeter the moisture state of the sample is slowly scanned



from an initial level (usually the dry state) to higher levels. The rate of diffusion is controlled by the difference in water activity between the water source and the sample and the size of the tube through which the diffusion takes place (cf. Figure 4). The rate of change of water activity (scanning) is thus controlled by the sample. When the sample has taken up water to increase its water activity, the rate of diffusion will decrease to accommodate the change of the vapor pressure difference between the top and bottom. As there is a distance of about 10 cm between the water source and the sample, there is a time lag between the vaporization of a water molecule and its sorption, and between an event taking place in the sample and the (natural) adjustment of the rate of vaporization from the water source. The time constant of this process is about 4 min and will give some blurring of discrete features of the sorption isotherm or the sorption enthalpy; however, as a full measurement is 0.5–2 days long, this can usually be neglected.

Of the three parameters measured (water activity, hydration number, mixing enthalpy), the water activity is the parameter that is most easily disturbed by kinetic effects (that give nonequilibrium states). As an example, if a salt hydrate is to be formed at a certain water activity (thermodynamically), internal diffusion resistance in the sample or the fact that the process is solvent mediated (proceeds through reactions in the liquid phase) may make the measured water activity pass above the equilibrium value before the process occurs. However, when sorption does take place, it does so with a certain mass gain and the corresponding sorption/mixing enthalpy. The measured hydration numbers and mixing enthalpies are therefore more robust than the water activity and should be seen as our main measurables. It should be noted that a similar situation often exists in other types of sorption measurements: water uptake is easily measured by a balance, but whether the corresponding (equilibrium) water activity has been reached is often more difficult to know. A check of whether a measurement with our sorption calorimetric technique is done close to equilibrium conditions or not can be made by making measurements with samples of different sizes, as one will then get different rates of sorption (the sorption rate is inversely proportional to the sample size). If sorption events take place at lower water activities for larger samples, this indicates a nonequilibrium situation.

The used procedure is described in ref 35. The calorimeter was calibrated with electrical heaters and the maximal output signal (about 750  $\mu$ W) was measured with drying agents (molecular sieves and phosphorus pentoxide). The Tian correction was applied to remove the effect of the thermal inertia of the calorimeter.<sup>36</sup> An initial correction<sup>35</sup> was made, but no diffusion time-lag correction was used (does not improve the result of this type of measurement appreciably).

A single measurement with the sorption microcalorimeter can give the following information (depending on the type of sample): (1) Shape of sorption isotherm. (2) Critical activity of hydrate formations. (3) Stoichiometry of hydrate formation. (4) Critical activity of deliquescence. (5) Solubility. (6) Activity of dilute solution as a function of concentration. (7) Enthalpies of hydrate formation. (8) Enthalpy of deliquescence. (9) Enthalpy of dilution as a function of concentration. It is also possible to calculate sorption entropy and osmotic pressure from the data. The present method is therefore possibly the closest one can come to a total characterization of the interaction between a solid and water (or other vapors). The method has been used for studies of interactions between water

and morphine sulfate,<sup>37</sup> phospholipids,<sup>28</sup> lysozyme,<sup>38</sup> *n*-octyl  $\beta$ -D-glucoside,<sup>39</sup> phospholipid-cholesterol bilayers,<sup>40</sup> and other systems.

It is not possible to give general data on the instrument alone (such as a response time), as it is the size and properties of the sample together with the geometry of the diffusion tube that determine, for example, how close to equilibrium conditions a measurement is made. For the present Nafion measurements made on samples with mass in the range 73–99 mg, the rate of sorption was such that the water activity increased from 0.00 to 0.25, 0.50, and 0.75 in 5, 8, and 15 h, respectively. Increasing the sample mass with a factor 2.6 did not change the results significantly, indicating that the measurements were made close to equilibrium (see the Discussion).

It should be noted that in the present instrument the rather high diffusion resistance of the diffusion tube is an important parameter as it governs the rate of vapor flow. This resistance is measured in a separate experiment and used as an evaluation parameter. In sorption measurements made in air with saturated salt solutions, the diffusion resistance influences the measurement in a negative way by giving long equilibration times. In the present method, the diffusion resistance is an inherent part of the method.

**Gravimetric Experiment.** To verify that the sorption isotherm results are correct, we used a balance based method to determine the difference in hydration number when the polymer was dried at 25 and 120  $^{\circ}$ C, respectively. This measurement was made by first determining the mass of an aluminum foil. A piece of approximately 1 g of wet polymer was then placed on the foil and the foil and polymer was dried in the vacuum dryer at 25  $^{\circ}$ C for  $24 \pm 2$  h. The foil and polymer was then taken out of the dryer and the foil was quickly folded around the polymer to prevent it from taking up water vapor from the air. The mass of foil and polymer was then determined, after which the sample and foil was dried at 120  $^{\circ}$ C for  $24 \pm 2$  h, and weighed a second time. The difference in hydration number was then determined by (cf. eq 1):

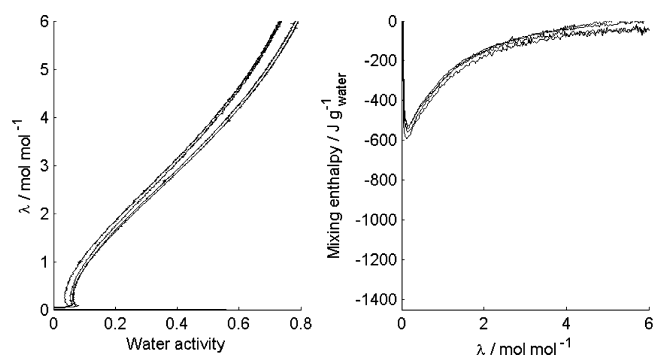
$$\lambda = 61 \cdot \frac{m_{25} - m_{120}}{m_{120} - m_F} \quad (8)$$

Here,  $m_{25}$  and  $m_{120}$  are the masses of foil and polymer after drying at the two temperatures and  $m_F$  is the mass of the foil. This measurement was made on eight polymer samples.

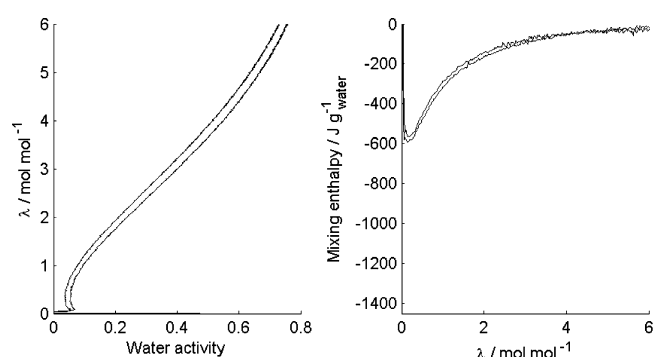
## RESULTS

Figures 5–10 show the sorption isotherms and the mixing enthalpies of Nafion 115 measured after drying at different temperatures. There were between two and five repetitions for each drying temperature; each line in the figures represents one measurement. Figure 11 compares one measurement from each drying temperature. Note that the  $\lambda$  scales in these figures are not strictly comparable as  $\lambda = 0$  is at the start of each measurement, but the samples dried at higher temperatures have lost more water during drying (see below). Therefore,  $\lambda = 0$  corresponds to a lower actual moisture content in these samples, compared to the samples dried at lower temperatures. In Figure 11 literature data for the mixing enthalpy of sulfuric acid–water has been added.

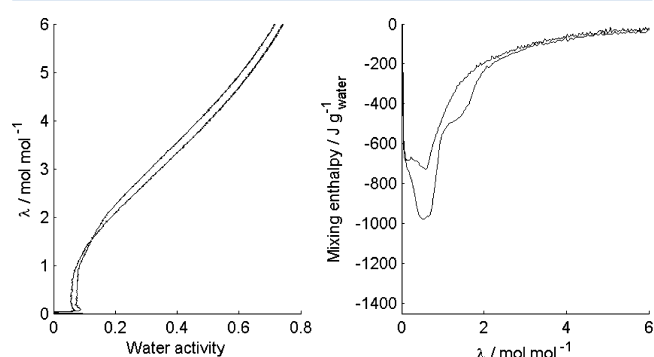
In Figure 12 the measured hydration number at a water activity of 0.2 is plotted for all measurements. It is seen that drying at higher temperatures results in a higher hydration number (more water vapor taken up), most probably because more water had been lost during the preceding drying. The



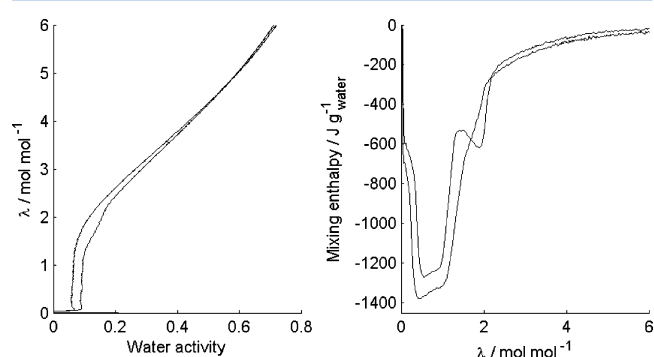
**Figure 5.** Sorption isotherms and mixing enthalpies of samples dried at 25 °C.



**Figure 6.** Sorption isotherms and mixing enthalpies of samples dried at 40 °C.

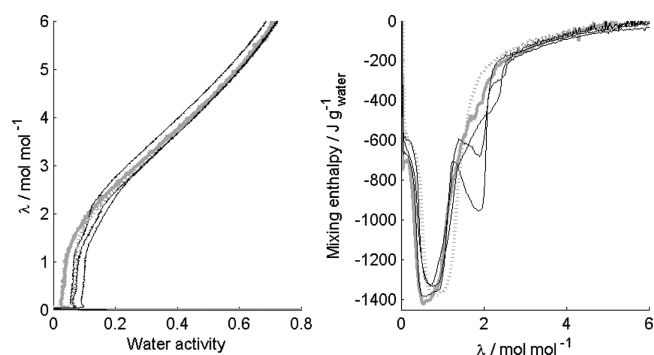


**Figure 7.** Sorption isotherms and mixing enthalpies of samples dried at 60 °C.

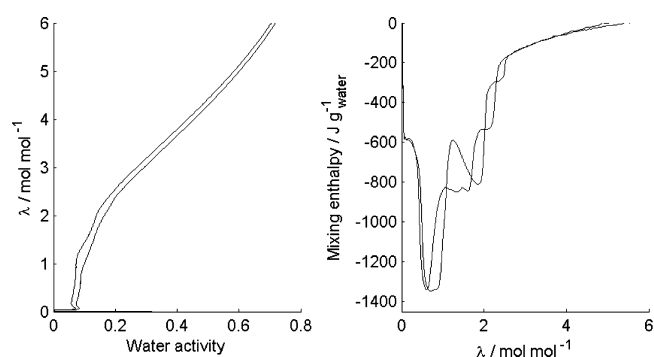


**Figure 8.** Sorption isotherms and mixing enthalpies of samples dried at 80 °C.

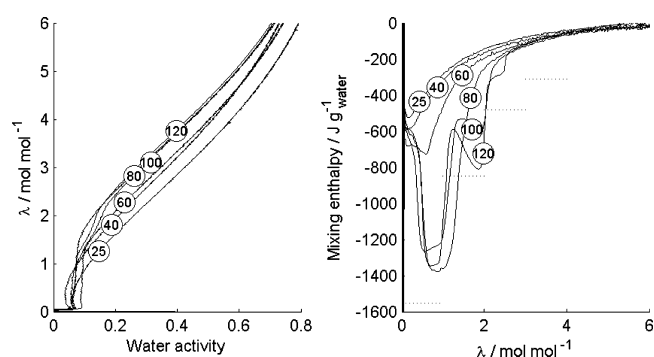
difference between the mean hydration numbers at  $a_w = 0.2$  for samples dried at 25 and 120 °C is about 0.8.



**Figure 9.** Sorption isotherms and mixing enthalpies of samples dried at 100 °C. The gray dashed curve is for a specimen with a mass of 65.42 mg and the continuous gray curve is for a sample of 172.66 mg, 2.6 times as high mass as the lighter sample.



**Figure 10.** Sorption isotherms and mixing enthalpies of samples dried at 120 °C.



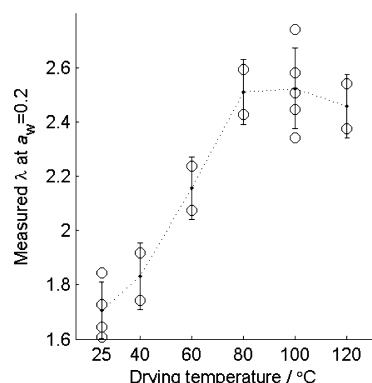
**Figure 11.** Selected sorption isotherms and mixing enthalpies of samples dried at different temperatures. (The temperatures in °C are given in the figures.) The dotted lines are the corresponding mixing enthalpy of sulfuric acid (each line represents the mean value between the hydration numbers at its end points).<sup>47</sup>

The gravimetric determinations of the difference in hydration number between drying at 25 and 120 °C gave  $1.0 \pm 0.1$  (standard deviation for eight samples). This is similar to the hydration number difference determined from the sorption isotherm measurements.

The integral of the enthalpy of mixing, the heat of mixing  $Q_{\text{mix}}$  ( $\text{J mol SO}_3\text{H}^{-1}$ ) is ( $M$  is the molar mass of water)

$$Q_{\text{mix}} = M \int_{\lambda=0}^{\lambda_{\text{end}}} \Delta_{\text{mix}} h \, d\lambda \quad (9)$$

We have calculated  $Q_{\text{mix}}$  from the start of each measurement to the arbitrarily chosen end point  $\lambda_{\text{end}} = 3$ . These values



**Figure 12.** Measured hydration number at water activity 0.2 as a function of drying temperature. The open circles are the measured values, the black dots are the mean values for each temperature, and the error bars are the standard deviation.

(collected in Table 1) show a marked difference between the samples dried at lower and higher temperatures.

**Table 1. Heats Measured per Sulfonic Group for Sorption up to  $\lambda = 3$  (Mean and Standard Deviation for Each Drying Temperature)**

drying temp (°C)	heat produced to $\lambda = 3$ (kJ mol <sub>SO<sub>3</sub>H</sub> <sup>-1</sup> )
25	-13 ± 1
40	-13 ± 1
60	-21 ± 4
80	-36 ± 4
100	-37 ± 3
120	-33 ± 3

## DISCUSSION

The sorption isotherms measured in the present study agree well with Nafion 117 isotherms given in the literature (Figure 2a) considering that different sample pretreatments and sorption methods have been used. Our enthalpy measurements also show good agreement with the less detailed results of Ostrovski and Gosev<sup>26</sup> and a qualitative agreement with the results of Reucroft et al.<sup>21</sup> In the latter study higher absolute enthalpies are reported.

The mixing enthalpy curves measured after drying at 80, 100, and 120 °C show several peaks and plateaus. There is first a plateau at about -600 J g<sup>-1</sup> in the approximate range  $0 < \lambda < 0.5$ . This enthalpy is similar to the initial enthalpy measured after drying at lower temperatures. There is then a peak (or possibly a plateau) at about -1400 J g<sup>-1</sup>, which indicates a very energetic event. This is followed by a return back toward about -200 J g<sup>-1</sup>, during which one or two more peaks/plateaus are seen in the approximate range  $1 < \lambda < 2$  (in some results the last plateau ends at about  $\lambda = 2.5$ ). The sorption process is thus complex and difficult to interpret, but the results indicate a two-step process below  $\lambda = 1$ , with the second step having a higher absolute enthalpy change than the first.

The calorimetrically determined sorption isotherms indicate that about 0.8 more waters per sulfonic group are taken up after drying at 120 °C compared to drying at 25 °C. This value is supported by the gravimetric measurement, which gave that 1.0 more water molecules per sulfonic acid were lost when the drying temperature was increased from 25 to 120 °C. There is

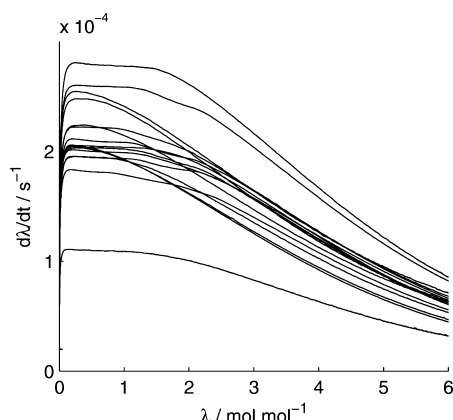
thus an interesting discrepancy here: about one more water is taken up after drying at the higher temperature, but the mixing enthalpy is influenced until two more waters have been taken up. This indicates that the events seen in the mixing enthalpy after drying at high temperature are nonequilibrium events (see below). It is known from studies by, for example, Alberti and co-workers<sup>41</sup> that hygrothermal treatment changes the material. There is also some evidence that water uptake after high temperature treatments proceeds in two steps: first the diffusion of water into the membrane, second a slow absorption that is probably related to mechanical relaxation of the membrane.<sup>41</sup>

Our mixing enthalpy results for samples dried at 80–120 °C are odd in that they show large exothermal events taking place after an initial period of low mixing enthalpy. This indicates that there are structural rearrangements taking place after a certain initial uptake of water. As no odd features are seen in the sorption isotherms (they are similar to previously reported isotherms), it is probable that the exothermal peaks are signs of internal events in the polymer. Although these events are possibly induced by the addition of more water, the exothermal peaks are not directly related to the sorption of water, but to restructuring events in the polymer and the already absorbed water. This may be related to the observation by Kusoglu et al. “that growth of water domains must be accompanied by secondary mechanisms at the meso- and/or nanoscales such as nanoscale reorganization and domain coalescence, [...] dilution of polymer aggregates, [...] and/or deformation and relaxation of the polymer backbone.”<sup>42</sup>

For the measurements on samples dried at 60 °C and higher, differences in the shape and timing of the mixing enthalpy curves were found for repeated measurements (Figures 7–10). However, as shown in Table 1, the integrals of the enthalpy curves were similar even if their shapes were different. The differences may be related to the above discussion of structural reorganization. A structural reorganization can be kinetically hindered and need a certain threshold to be exceeded to start. It can also be triggered by a random event and then spread through the material. This can explain why the exothermal peaks come at slightly different positions during different measurements.

Each of the measurements on samples of about 100 mg took about 24 h to make. As the flow rate in the sorption calorimeter is proportional to the difference in water activity between the vapor source and the sample, the flow rate will decrease during a measurement as the sample is humidified. This means that the highest flow rate is found in the beginning of a measurement when the equilibrium times are low.<sup>6</sup> This is seen in Figure 13, which shows the rate of change of the hydration number as a function of the hydration number during the measurements (the lowest curve is for the larger sample). The highest rates of sorption are about  $2 \times 10^{-4}$  s<sup>-1</sup>. It thus takes about 1.5 h for the hydration number to change one unit at the start of the measurement.

The sorption rate in the present method is governed by the sample that needs to readily absorb water vapor for the measurement to proceed at close to equilibrium conditions. For the present measurements, two observations indicate that the sorption measurements were close to equilibrium: (1) Samples of different sizes give similar results (Figure 9). (2) The sorption isotherms agree with the literature (compare Figure 2(left) with Figures 5–11). The literature also gives some evidence that the rate of vapor absorption of Nafion is rather



**Figure 13.** The rate of change of the hydration number during our measurements as a function of the hydration number.

high. Mangiagli and co-workers<sup>6</sup> measured water vapor uptake in Nafion membranes in a sorption balance and found that the samples had taken up about 90% of the equilibrium amount after about 10 min for a 20% to 25% RH step, after about 15 min for a 40% to 50% RH step, and after about 30 min for a 70% to 80% RH step, all at 30 °C. Note that external gas phase resistances can severely limit the mass uptake rate when samples are exposed over, for example, saturated salt solutions. Such studies can therefore report excessive equilibration times for a sample. Mangiagli et al.<sup>6</sup> used a sorption balance with a flow of humidified gas that limits the external resistance. We thus believe that our sorption measurements were made at close to equilibrium conditions, whereas it is possible that the state of the polymer was not at equilibrium (see Discussion above).

In the present measurements, drying at higher temperature gives a higher sorption. Such a behavior is typical of most materials: they will lose more water if dried at a higher temperature and will then also take up more water when rehydrated. However, it has been reported that Nafion has the opposite behavior: drying at higher temperatures decreases the amount of water taken up.<sup>24,41</sup> This has been attributed to temperature-induced changes in the material. It may be that we see the opposite result (higher uptake after drying at higher temperature) because we only study rehydration with water vapor up to a water activity of about 0.8, whereas the rehydrations in refs 24 and 41 were done by immersion in liquid water. A water activity of 0.8 corresponds to a hydration number of about 6 (Figures 2 and 11), whereas rehydration by immersion at 20 °C results in hydration numbers from 9 (after 120 °C drying)<sup>41</sup> to 17 (after 20 °C drying).<sup>41</sup> Possibly it is the hydration from a water activity of 0.8 to unity that is negatively influenced by increased drying temperature.

Sorption in Nafion and other ionomers is often discussed in terms of “hydration shells”, but we prefer the term “hydrates”, similarly to what is formed by many inorganic salts and organic molecules. As the formation of a hydrate is a constant enthalpy process, with different mixing enthalpies for each distinct hydrate, they should give plateaus (parts with constant enthalpy) in the mixing enthalpy diagrams. The plateaus shown in Figure 10 give some support to the fact that hydrates are formed in Nafion, but the hydrates seem to be more linked to the hydration number changing in steps of 0.5, rather than to the more common steps of 1.0, indicating that water molecules

are shared between two sulfonic groups. This merits further investigation.

Although the mixing enthalpy curves vary for the same drying procedure, it is interesting that so many details are seen in the results. With the used sorption calorimeter such “detailed” curves have only been seen for hydrate forming organic substances (theophylline<sup>33</sup> and morphine sulfate<sup>43</sup>) and amphiphilic systems.<sup>28,39,44</sup> For polymeric materials such as microcrystalline cellulose, wood, and silk, the mixing enthalpy curves are monotonously increasing toward zero enthalpy, similar to the dashed line in Figure 3. It is interesting to note that our enthalpy results after drying at 25 and 40 °C are quantitatively similar to the result on wood given in Figure 3, showing no distinct hydrates. Possibly the loss of the last water molecule disrupts the structure of the hydrated Nafion, necessitating a major restructuring when new hydration takes place.

The hydration of sulfuric acid gives an enthalpy similar to that for the hydration of Nafion dried at 80–120 °C, as is seen in Figure 11. Similar results are shown in the paper by Ostrovski and Gostev.<sup>26</sup> As the hydration of both sulfonic groups and sulfuric acid are very energetic events, the enthalpies of other processes (sorption-induced creep etc.) are probably negligible.

It is our experience that the used sorption calorimeter often averages the result so that details are less clearly seen (typically when too small samples are used; see below); the opposite (that details like steps and peaks that repeatedly appear in the results are artifacts) does not occur. We therefore believe that the details seen in the mixing enthalpy graphs mirror real events in the polymer, although not all such events may take place at equilibrium conditions.

The vapor flow rate in the sorption method used is calibrated by running a measurement with a drying agent (typically molecular sieves) and water. The difference in the vapor pressure potential is then at its maximum (the saturation vapor pressure). When a very hygroscopic material such as Nafion dried at 120 °C is measured, one would expect that it should act similarly to a drying agent at the start of the measurement and that one would get sorption isotherms that start at zero water activity. In ref 33 two examples are shown in which the sorption isotherms generated by the presently used sorption calorimeter starts at zero (microcrystalline cellulose and porous Vycor glass) and two in which this is not the case (acetone sorption on 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl and water vapor sorption on theophylline). However, in the latter two cases stoichiometric clathrates/hydrates are formed and such a process is known to take place at a certain “critical” activity, below which possibly very little vapor is taken up. For the present measurements we believe that one reason that the water activity at the start of the sorption process is higher than zero is that there are kinetic limitations at the start of the measurement, so that the measured water activity lags slightly behind the true one. An indication that this is the case is the one specimen (Figure 9) that had 2.6 times the mass of the lightest specimens (and then 2.6 times lower rate of sorption<sup>35</sup>) did show a lower starting water activity ( $a_w = 0.025$ ) than all the other specimens (most of which started at about  $a_w = 0.05$ ) even if the rest of the measurement was similar to the other measurements.

There are two possibilities to decrease the influence of the internal kinetics in the sorption calorimeter. First, as was mentioned above, one can use larger samples. In the sorption



calorimeter the length of a measurement of a certain material is proportional to the sample mass; twice the sample gives twice the time until a certain moisture state is reached, and then also half the rate of increase in moisture content. Second, one can decrease the sample thickness, for example, by making a powder or thin slices of the material. This will increase the rate of the rate limiting process if this is diffusion. However, this is not always the case as sorption processes in many materials can be of a non-Fickian nature.<sup>45</sup>

We conclude that studies of the sorption thermodynamic of water–Nafion and other water–PEM systems are important for an understanding of the water state in ionomer materials. The measurements presented show that the used sorption calorimeter gives more detailed thermodynamic information than any other previously used method.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Background material for literature review. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We thank Bengt Nilsson for performing the measurements.

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