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Hydration of Nafion and Dowex in liquid and vapor environment: Schroeder's paradox and microstructure

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Abstract

Functioning of ion-exchange resins and ionomers strongly depends the state of hydration (equilibrium water uptake), which strongly affects their performance. The relation between water activity and uptake by such polymers (isotherm) has usually been measured by equilibration with water vapor of known activity. However, at the point of saturation (pure water) hydration by liquid water and water vapor differ, i.e., depend on the mode of equilibration. This effect, known as Schroeder's paradox, leads to an ambiguity in determination of the chemical potential and calculating the solvent transport in such systems. In order to verify the general nature of this phenomenon, we carried out a systematic examination of the paradox in a wide range of water activities using solutions of a polyelectrolyte (polyvinylsulfonic acid salts) as an osmotic stressor. This allowed measuring hydration isotherms in parallel vapor- and liquid-equilibration modes for two solid polymer electrolytes: Dowex (a cross-linked resin) and Nafion (an ionomer). The results indicate that for the studied polymers Schroeder's paradox extends to the whole range of the examined water activities. Furthermore, the difference between the isotherms could be related to the polymer microstructure, however, it suggested that a correction due to the difference between the surface and bulk microstructure is necessary for Nafion.

Keywords: Hydration; Nafion; Dowex

1. Introduction

Solid polymer electrolytes (SPE) are polymeric materials, in which highly polar ionizable groups are covalently attached to an organic polymer matrix, most often hydrophobic in nature. The symbiotic structure of SPE prevents dissolution of ions in polar environments making SPE one of the best materials for ion-selective barriers in electro-membrane applications, fuel cells etc., as well as other applications such as packaging or adhesives [1–3]. SPE may be roughly divided to two groups of materials: chemically cross-linked ion-exchange resins [1] and ionomers, in which dissolution in polar solvents (most often water) is prevented by the hydrophobicity of their matrix [2,3].

The properties and functioning of SPE are known to depend largely on the degree of swelling, i.e., the amount of solvent taken up by the polymer [1–4]. For this reason, measurements of sorption isotherms constitute an essential part of studies on resins and ionomers. Two main techniques have been employed to measure solvent sorption. In the first one, the isopiestic method, the material is exposed to a solvent vapor of known activity, e.g., by placing it over a salt solution, which avoids the need to remove residues of the solution stuck to the sample surface. Most of the available sorption data, covering the whole range of solvent activities, were obtained with this method. However, sorption at the point of saturation has more often been measured simply by immersion in a pure solvent. Thermodynamically both methods were believed to give identical results, since the solution, vapor and sample are all in

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equilibrium. Nevertheless, it has been found that there is a discrepancy between the results from the isopiestic and immersion methods at otherwise identical conditions [5–8]. This phenomenon is known as Schroeder's paradox.

Many early works tried to explain it by experimental failures such as non-uniform temperature in the saturated vapor and liquid phases [8,9], lack of saturation in the vapor phase [10], or slow mass transfer in vapor [8,9,11]. However, more recent works seem to adopt the view (supported by experiments) that the effect is real and truly thermodynamic [8,12,13]. Recently, Choi and Datta [14,15] assumed that in the case of vapor-equilibration the water–vapor interface at the sample boundary is curved and thus exerts an extra Laplace pressure on the aqueous phase confined in a quasi-porous structure formed by the hydrophobic matrix. Their calculations showed reasonable quantitative agreement with experiments for water/Nafion system. This picture was further elaborated by Elfring and Struchtrup in their analysis of stability of water in Nafion [16]. Weber and Newman [17,18] proposed a phenomenological model of water-swollen Nafion, which involved somewhat non-thermodynamic reasoning to include the effect of the external boundary on the structure of water-swollen Nafion. Yet, while considering water transport, they assumed capillary pressure to be a part of the chemical potential, which makes this model fairly similar to Choi and Datta's. An entirely different explanation was proposed by Vallieres et al. [19] who presumed that the paradox is a result of the non-monotonous variation of the free energy with composition. Using the Flory–Rehner model of gels they demonstrated that there might be two local minima of free energy, one presumably corresponding to vapor-equilibration and the other – to liquid-equilibration. It may be argued, however, that "falling" into a particular minimum should depend on the swelling history. For instance, a sample pre-swollen in water should not go to the vapor-equilibrated state when transferred to vapor or vice versa, which disagrees with experimental observations.

All suggested explanations were tested only for the data obtained at saturation conditions, i.e. water activity equal to 1, since to date the point of saturation has been the only one, for which both vapor- and liquid-equilibration data existed. The main purpose of this study was to examine Schroeder's paradox experimentally in a systematic way in a wide range of water activities. For that purpose, parallel water sorption isotherms of two representative SPE materials were measured in vapor- and liquid-equilibration modes. Two common SPE polymers, Nafion (a sulfonate ionomer with perfluorinated backbone) and Dowex (a cross-linked polystyrene sulfonate resin), were chosen to represent ionomers and covalently cross-linked resins, respectively. The central idea was that the liquid would be an osmotic bath containing a solute (osmotic stressor) that could significantly reduce the water activity in solution, but would not enter the sample to affect polymer–water interactions. This "osmotic stress" approach in combination with microstructural characterization has been used to study biological systems [20], surfactant multilayers [21] and clay dispersions [22]. Apart from shedding light on the nature of this long-standing paradox, the data may help to remove ambiguity related to expressing solvent chemical potential in transport models in such systems, in particular, water management in fuel cells [23]. We will also show that such data could provide new and independent insight into the structure of these polymer materials at different degrees of hydration.

2. Experimental

2.1. Materials

Nafion 117 membrane (H form) and Dowex 50WX4-50 resin (Na form, 100–200 mesh) were purchased from Aldrich. The Nafion polymer is an ionomer composed of polytetrafluoroethylene backbone with perfluorinated pendant side chains terminated by a sulfonate ionic group (one side chain per about 6.5 tetrafluoroethylene units). The Nafion membrane has thickness of 175 μm and nominal equivalent weight of 1100 g/mol (ion-exchange capacity 0.91 meq/g), as was verified by titration. It was cleaned and pretreated in a standard way [24,25] as follows: it was first boiled in 70% nitric acid for 5 h, followed by rinsing in deionized (18 MΩ) water, and finally, boiled in deionized water for 3 h. In order to convert the H form to Na or Li ionic forms, the membrane was neutralized in a 1 M solution of NaOH or LiOH, respectively, and thoroughly washed with deionized water to remove excess electrolyte. The Dowex 50WX4-50 is a sulfonated copolymer of styrene with 4% divinylbenzene with nominal cation-exchange capacity of 5 meq/g, as was verified by titration. Purchased Dowex resin was washed in a large excess of 1 M NaOH to ensure complete conversion of the resin to Na form, followed by thorough repeated rinsing with deionized water. Necessary amounts of Li form were prepared by repeated equilibration in excess of 1 M LiOH followed by thorough rinsing.

Poly(vinylsulfonic acid) (PVS, sodium salt) as 25% (wt) solution in water with nominal average $M_w \sim 2000$ Da used as an osmotic stressor was purchased from Aldrich. The characterization using matrix-assisted laser adsorption/ionization time of flight (MALDI-TOF) mass spectrometry in both positive and negative modes suggested that this polymer has a wide molecular weight distribution with average molecular weights somewhat smaller than nominal, the latter possibly being a common MALDI-TOF artifact. Most PVS appears to have molecular weight above 800 Da with virtually no oligomers below 300 Da. It was then expected that partitioning of PVS to the samples would be insignificant due to its relatively large size and charge. Infrared (FTIR) spectra obtained in the attenuated total reflection mode using the spectrum of water as background displayed only two significant bands in the fingerprint region assigned to the symmetric (1035 cm^{-1}) and asymmetric (1182 cm^{-1}) stretching of the S=O bond of the sulfonic group. Ion chromatography and elemental analysis showed small amounts of inorganic ions (mostly sulfate) not exceeding 1% of the PVS amount. These results indicate that the PVS solution contained a fairly pure mixture of vinylsulfonate oligomers (3–20 monomer units) with a wide molecular weight distribution possibly containing some minor impurities and/or decomposition products. (The details of the above characterizations of PVS are presented in the Supplementary data.)

In experiments with Na forms of polymers the PVS solution was used as received. For experiments with polymers in Li form, it was first converted to H form by passing through a column packed with stoichiometric excess of a cation-exchange resin in H form followed by elution with deionized water. The collected fractions with the highest conductivity were combined and neutralized with LiOH to pH 7. Absence of sodium (<0.1% mol) was verified using atomic absorption.

The salts used for maintaining enclosed atmosphere of fixed water activity were chosen based on the data from Ref. [26] and were chemical grade K_2SO_4 (saturated solution produces water activity of $a = 0.97$ at 30 °C), KCl (0.83), K_2CO_3 (0.43) and $MgCl_2$ (0.32) purchased from Frutarom, KNO_3 (0.91), NaCl (0.75), $Mg(NO_3)_2$ (0.51), and LiCl (0.11) obtained from Sigma, BioLab, and Romical. P_2O_5 used to dry the samples was purchased from Fluka.

2.2. Experimental approach

The goal of this work was to construct hydration isotherms by equilibrating a SPE in a series of solutions of an osmotic stressor in a range of water activities and compare with standard vapor-equilibration. To aid interpretation of the results the osmotic stressor had to be

- highly soluble in water to cover the widest possible range of water activities yet to remain fluid, i.e., not to form a solid gel that may impose uncontrolled stresses on a swollen sample;
- strongly excluded from the sample in order not to interfere with polymer–water interactions, which may be achieved using large or negatively charged water-soluble polymers.

The criteria of large size and high solubility, as well as those of large negative charge and high gelation concentration are in effect contradictory, yet it was found that commercially available sodium poly(vinyl sulfonate) with nominal $M_w \sim 2000$ Da offers a fair compromise and forms highly concentrated solutions that remain fluid down to water activities $a \approx 0.5$. Furthermore, using the more hydrated Li form of this polymer it was possible to reduce this limit to $a \approx 0.3$. Apparently, the small and non-uniform molecular weight of PVS allowed good solubility and fluidity of solutions and prevented gelation at high concentrations. Still, the size and negative charge of the PVS oligomers could be sufficient for good exclusion hence minimal uptake by the negatively charged polymers.

The hydration isotherms in SPE has been conventionally determined by *weight* gain [1,6,7,12,26–30]. This approach was obviously unsuitable here due to formidable difficulties of wiping off the excess of a viscous solution from the sample surface before weighing. We therefore chose to use dimensional or *volume* changes, i.e., *swelling* of the sample. Accurate conversion of such data to water uptake depends on the volume additivity, i.e., variation of the partial molar volume of water at different hydrations, and isotropy of swelling (these points are addressed below). On the other hand, it does not require removal of the sample from the equilibrating environment and may be used for liquid- as well as for vapor-equilibrated samples.

2.3. Water uptake measurements

Swelling of Nafion 117 membrane and Dowex 50W-4 resin was determined from the dimensional changes of small square pieces of Nafion and beads of Dowex. The dimensions of the samples in different conditions were measured from digital images taken through the bottom of a standard 96-well microplate containing 30–60 samples, one sample in a well, using an inverted optical microscope (TS 100, Nicon) equipped with a digital camera (Nicon Coolpix 5400). The microscope was equipped with a heating stage (MATS-TMS, Tokai Hit) and a transparent plastic cover to maintain the samples at the desired constant temperature (30 °C) during photographing. The diameter of the objective (×4) was much larger than the size of the samples, therefore the sample dimensions were not distorted when the wells were filled with solutions, which was also verified by photographing small metal balls (0.8 mm). Sample dimensions were determined from images using a computer program ImageJ.

The experimental setup is schematically shown in Fig. 1. In all experiments (vapor- and liquid-equilibration) samples in Na or Li forms placed in a 96-well microplate were first dried in an evacuated desiccator over P_2O_5 at 30 °C for two weeks to

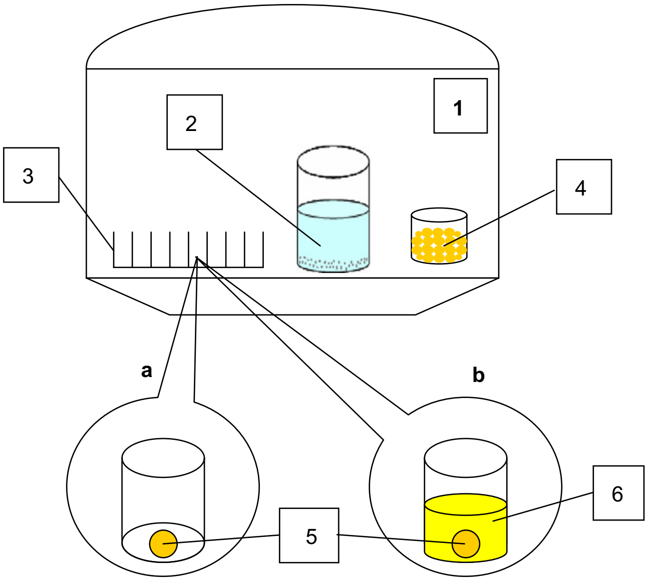

Fig. 1. A schematic drawing of the experimental setup: 1 – an evacuated desiccator, 2 – a saturated salt solution with excess salt to control humidity, 3 – a 96-well microplate, 4 – a cup containing a large sample (Dowex or Nafion) or a PVS solution for weighing, 5 – a small piece of polymer (Dowex or Nafion), 6 – PVS solution. The expanded views at the bottom show the content of a well in plate (3) in (a) vapor- and (b) liquid-equilibration.

ensure the same thermal history and determine their dry dimensions. Afterwards, the same samples in the microplate were equilibrated at different activities created by appropriate saturated salt solutions containing excess salt inside an evacuated and thermostated (30 °C) desiccator. For vapor (isopiestic) equilibration, samples were exposed directly to a vapor atmosphere of a desired water activity (relative humidity). In liquid-equilibration the wells (each containing a sample) were filled with a solution of, respectively, Na or Li forms of PVS and exposed to the same atmosphere. Since at the end of the latter experiments the PVS solution attained equilibrium with the vapor atmosphere, the water activity in the liquid solution as well as in Nafion or Dowex samples was equal to that in the vapor. The water uptake at the point of saturation was measured using pure water to create the atmosphere or to fill the wells. Once the equilibrium was ensured, the vessel was opened, equilibrated microplate was quickly (within a few seconds) closed with a lid, sealed with Parafilm and placed on the heating stage and covered with a transparent cover (stage and cover pre-stabilized at 30 °C) for photographing.

Equilibrium was ensured by weighing daily a larger sample of Nafion or a few grams of Dowex beads (in the isopiestic experiments) or a PVS solution (in the liquid-equilibration experiments) in a small beaker placed in the same desiccator together with the open 96-well plate containing the samples (Fig. 1). For isopiestic measurements this also allowed parallel measurements of the isotherm using the weight gain of the larger sample to verify the consistency with dimensional changes and available literature data. The time required to open the desiccator and weigh the larger sample (the desiccator being closed during the weighing), was usually below one minute, after which the equilibration conditions were quickly restored. Since this time was negligible compared to the equilibration times (4 days in vapor and 7–31 days in liquid), the equilibration was presumably negligibly disturbed by this examination. The agreement of the measured isopiestic isotherms with the published ones (see below) apparently confirms that the error associated with the whole procedure was reasonably low.

Water uptake was expressed as the number of H_2O molecules taken up by per SO_3 group (λ) and calculated using the following formula:

$$\lambda = \left[\left(A/A_{\mathrm{dry}}\right)^{3/2} - 1\right]\frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{p}} M_{\mathrm{w}} Q_{\mathrm{p}}} \qquad (1)$$

where A and A_{dry} are the projected (photographed) areas of the same sample in hydrated and dry states calculated from the images, ρ_{w} and ρ_{p} are the densities of water and dry polymer, M_{w} the molar weight of water, and Q_{p} is the molar content of SO_3 group per unit weight of dry polymer (ion-exchange capacity).

Eq. (1) assumes volume additivity and isotropic swelling of the swollen polymer. The data on partial molar volume of water suggest that volume additivity is a fair approximation for the most practically important range of moderate and large hydration for Dowex. Nafion additivity was verified by buoyancy tests kindly performed and communicated to the authors by Dr. Peter van der Heijden at the Groupe Polymeres Conducteurs Ioniques, CEA-Grenoble, using a balance for weighing suspended samples. In these experiments, immediately after a suspended sample of dry Nafion had been immersed in water, the balance reading changed insignificantly in the course of swelling. This indicates that when the volume of the sample increased, the gain in the weight of the samples due to sorption of water was nearly exactly balanced by the increasing buoyancy (Archimedes) force all the way from dry state to full hydration. This means that the partial molar volume of water in swollen Nafion remains approximately equal to that in solution meaning volume additivity. A similar conclusion is reached by analyzing the density of Nafion as a function of hydration reported by Morris and Sun [24].

Dowex beads are spherically symmetric hence they were expected to swell isotropically, however, swelling of Nafion is likely to be somewhat anisotropic. Using about 0.5 × 6 cm strips of Nafion cut from a membrane in the longitudinal (extrusion) and transversal directions first dried over P_2O_5 and then equilibrated in a water vapor of different activities, we could not find significant differences in relative variation of their length in the two lateral directions. We did not attempt measuring variation of thickness with hydration. Morris and Sun [24] reported a quite large (40%) difference for dimensional changes in lateral and thickness directions using several membranes stacked together. However, Elliott et al. [31] could not observe such anisotropy within the precision of their optical technique (about 20%). We therefore assumed isotropic swelling for all experiments. Since the purpose of this study was to compare different isotherms, given fairly symmetric shape of the samples (Fig. 2), the consistent use of the above simplifying assumptions was unlikely to affect any of the conclusions.

3. Results

3.1. Dowex resin

First, the optical measurements were compared with our own and published weight gain data in isopiestic (vapor) mode. The results for Na and Li forms of Dowex are shown in Fig. 3. Admittedly, the literature data were obtained at

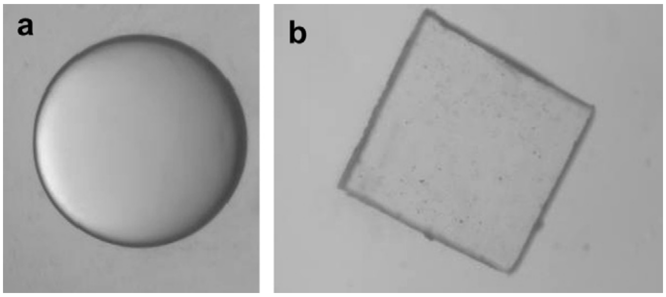

Fig. 2. Typical images: (a) a Dowex 50W-4 bead of about 0.7 mm diameter; (b) a piece of Nafion 117 membrane about 0.7 × 0.7 mm.

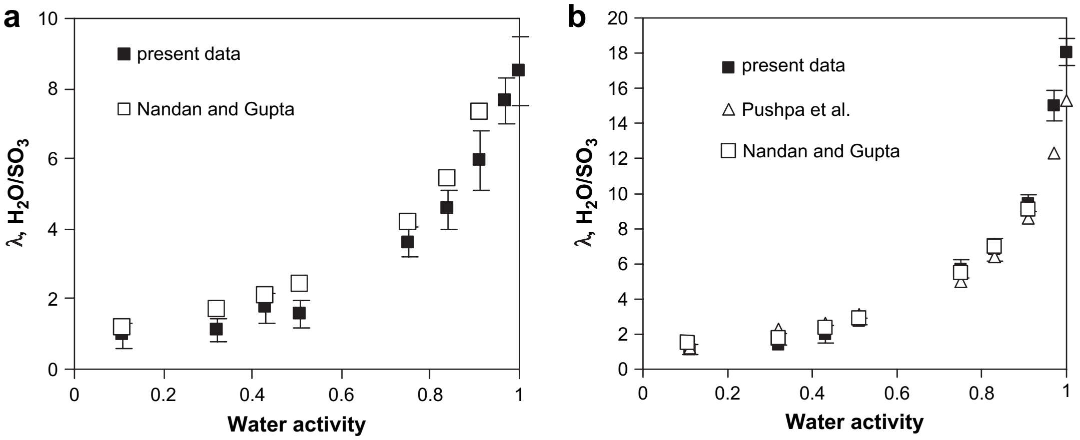

Fig. 3. Isopiestic isotherms of Dowex 50W-4 at 30 °C calculated from dimensional changes as obtained in this study compared to the data by Nandan and Gupta [27] and by Pushpa et al. (25 °C) [29]: (a) Na form and (b) Li form.

a slightly lower temperature (25 °C) than in our experiments. However, swelling of Dowex weakly depends on temperature [32,33] and a 5 °C difference was not significant. The reasonable agreement between these results suggests that optical method as well as the assumptions of volume additivity and isotropy of swelling were fairly adequate.

It was then possible to compare vapor- and liquid-equilibrated isotherms for these forms of Dowex. The results are shown in Fig. 4. Again, each point shows the average of 30–60 individual samples and the error bars correspond to the 95% confidence level based on the *t*-test. Note that the low activity range ($a < 0.5$ for Na form and $a < 0.3$ for Li form) was inaccessible for liquid-equilibration since the poly(vinyl sulfonate) solution solidified at these conditions. It is clear, however, that the vapor-equilibrated data very significantly differ from the liquid-equilibrated ones in the whole measured range of water activities.

It is to be noted that in this case, as well as in the case of Nafion below, the conclusion should not change, if, opposite to our assumption (see Section 2.1), substantial invasion of PVS or ionic impurities occurred in liquid-equilibration. It is well known that invasion of a salt into a solid polyelectrolyte usually causes a *decrease* in swelling compared to an ideal, non-invading, osmotic stressor, due to screened repulsion between fixed charged groups. If the osmotic stressor (PVS) behaves non-ideally, i.e., noticeably partitions into the samples, our results actually *underestimate* the difference between the polymer hydration in the liquid- and vapor-equilibration modes.

3.2. Nafion 117 membrane

As for Dowex, the isopiestic water sorption curves of Nafion obtained from the volume changes of the membranes samples were first compared with sorption data available in the literature for identical polymers. It can be seen in Fig. 5 that dimensional swelling agrees fairly well with the data by other authors obtained by the weighing method. Some discrepancies clearly exist; still they are commensurable with the scatter of the earlier published data (cf. Fig. 4b). The optical technique was then considered to be adequate for subsequent work.

Fig. 6 shows vapor- and liquid-equilibrated water sorption isotherms, obtained for the Na and Li forms of Nafion 117 (averages of many samples with error bars corresponding to 95% confidence level). It can be seen that liquid-immersed membrane samples take up several times more water than vapor-equilibrated ones for all examined water activities. Such a large difference is quite surprising and obviously

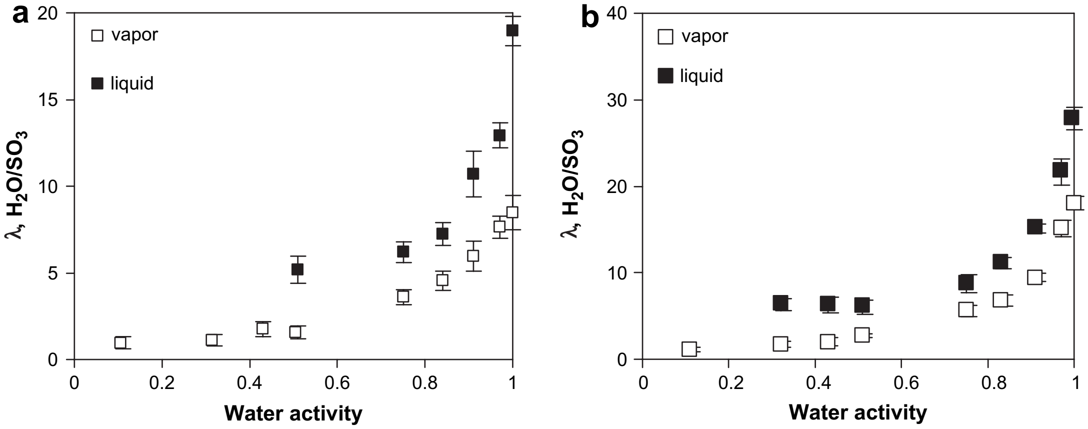

Fig. 4. Water uptake isotherms of Dowex 50W-4 at 30 °C based on dimensional changes in vapor- and liquid-equilibration modes: (a) Na form and (b) Li form.

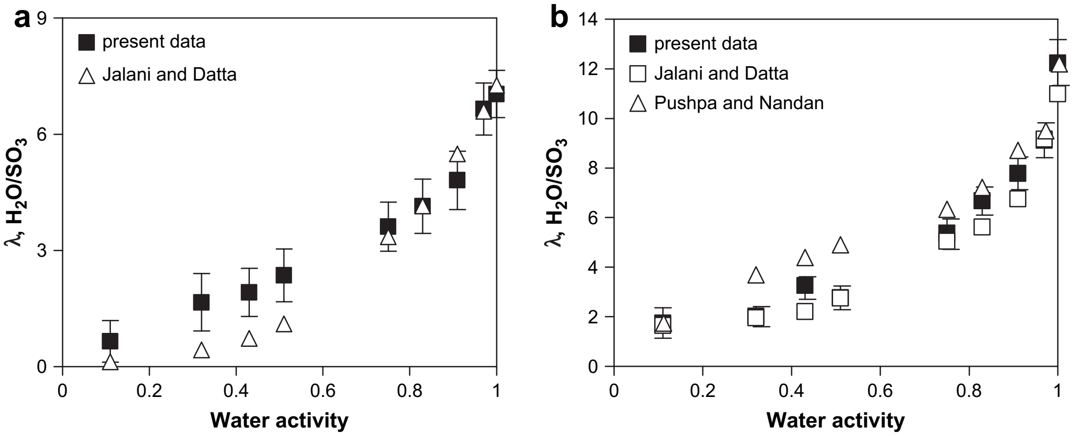

Fig. 5. Isopiestic isotherms of Nafion 117 membrane at 30 °C calculated from dimensional changes as obtained in this study compared to the data by Jalani and Datta (30 °C) [34] and by Pushpa et al. (25 °C) [29]: (a) Na form and (b) Li form.

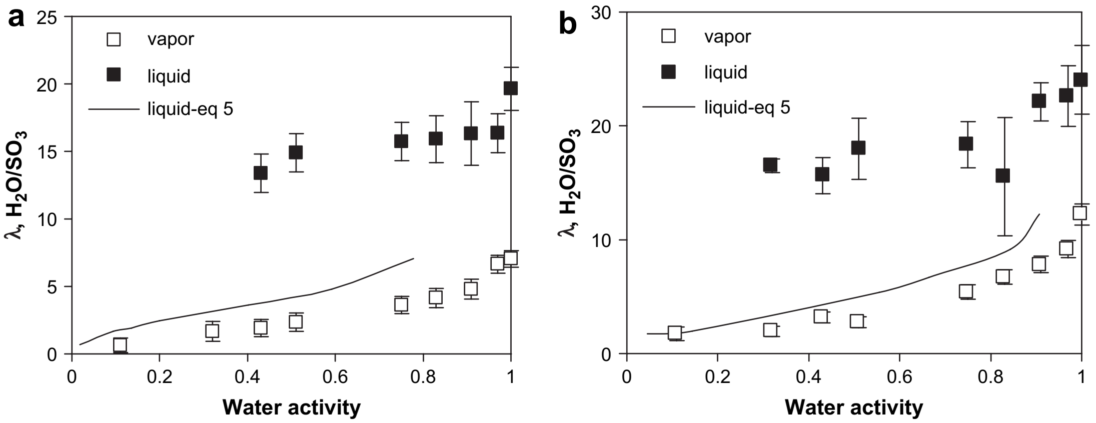

Fig. 6. Water uptake isotherms of Nafion 117 membrane at 30 °C based on dimensional changes in vapor- and liquid-equilibration modes: (a) Na form; (b) Li form. The solid line is calculated from the vapor-equilibrated isotherm using Eq. (5) and structural data.

cannot be explained by experimental artifacts. Since we made all possible effort to ensure the samples are in true equilibrium at the timescale of many days, the results suggest that for both materials one has to look for a thermodynamic explanation of this difference. In the following discussion we will try to address this point and its possible relation to the microstructure of hydrated SPE materials.

3.3. Experimental errors

Measurements of swelling are known to be prone to errors, as discrepancies in the above literature data also show. The errors may apparently result from limited precision of the measurements, insufficiently accurate control of humidity and temperature and variability of the samples. Indeed, some scattering was always obtained at each measured point. Our analysis showed that the scatter was contributed mostly by the optical technique. Its relative standard deviation was independently estimated to be about 4% in terms of length, which will have to be improved in the future. The corresponding errors in the values of λ, calculated using Eq. (1) and standard error propagation relations were consistent with the overall scatter observed at different points. However, the uncertainty associated with this error was drastically reduced by using large sets of results, which allowed unequivocal conclusions regarding differences between relevant experimental isotherms. In fact in all cases the differences between vapor- and liquid-equilibration isotherms were statistically significant with a probability largely in excess of 99% based on the pairwise *t*-test.

4. Discussion

In the following we adopt the interpretation proposed by Choi and Datta [14,15] as part of their model, which assumes that the paradox originates from the extra Laplace pressure at the vapor–polymer interface, or, more specifically, at the *curved* interface between the external vapor and the aqueous microphase at the polymer surface exerted on the inner aqueous microphase. The situation is schematically shown in Fig. 7a, r representing the radius of the interface between vapor and "open" hydrated ionic clusters at surface. The extra Laplace pressure $\Delta p = 2\gamma/r$, where γ is the surface tension, will be negligible when the external medium is an aqueous solution (Fig. 7b), where the surface tension vanishes. This means that in a polymer *at identical hydration levels* λ, the

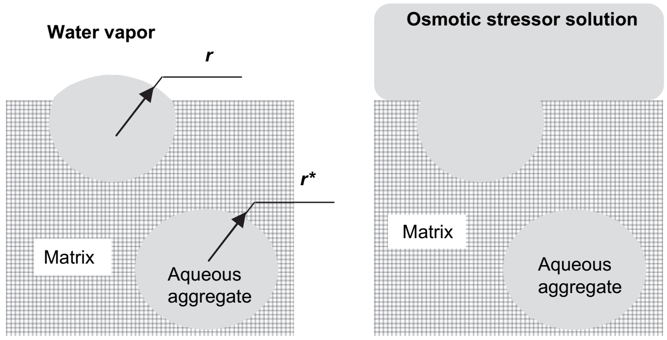

Fig. 7. Schematic view of the surface region of a hydrated solid polymer electrolyte in equilibrium with a vapor phase (a) and with a liquid phase (b).

chemical potential of water in the aqueous microphase will be larger in the case of vapor-equilibration by the amount given by the relation:

$$V_w \Delta p(\lambda) = RT \ln\frac{a_V(\lambda)}{a_L(\lambda)} = \frac{2V_w\gamma}{r(\lambda)}, \tag{2}$$

where V_m is the molar volume of water and Δp and r are taken at given λ and may be also related to the water activities $a_V(\lambda)$ and $a_L(\lambda)$, at which the given λ is attained in vapor- and liquid-equilibration modes, respectively. The last equality states that the Laplace pressure may be calculated using the Kelvin–Laplace equation [35] involving the interfacial tension γ and the λ-dependent average radius of curvature $r(\lambda)$ of the aqueous aggregates (ion-water clusters) at the polymer surface. The deviations of the surface tensions from that of pure water are fairly moderate even for very concentrated electrolyte solutions, about 15–20% [36]. In the subsequent analysis it was then fair to view the surface tension $\gamma \approx 70$ mN/m as approximately constant. The comparison of the two modes at the same hydration is particularly convenient, since osmotic and elastic parts of the chemical potential of water in the bulk state in a swollen SPE material are presumably identical then Eq. (2) may be written. This amounts to assuming that the equilibrium conformation of the bulk state, i.e., the one that minimizes the free energy at given λ should not depend on the mode, in which this state was obtained. Gebel [37] demonstrated using thorough SAXS data for hydrated solid Nafion and concentrated Nafion solutions that in a wide range of λ, where the two types of Nafion–water systems overlap, the Bragg spacing of ionic domains showed essentially the same dependence on λ, indicating that the microstructure of hydrated Nafion indeed insignificantly depends on the method of preparation for a given λ.

Choi and Datta further assumed in their model that the aqueous microphase forms what might be viewed as a pore structure approximated by an assembly of cylindrical “pores” [14,15]. Using the experimental observation that each group occupies a nearly constant surface area at the pore walls, thereby the total pore area is 210 m^2/cm^3 regardless of λ, the radius $r^*(\lambda)$ of the “pores” (Fig. 7a) could then be estimated as a function of λ. The radius $r(\lambda)$ was then calculated as the curvature of a meniscus formed inside the cylinder of radius r^* using the value of contact angle of water on Nafion matrix reported by Zawodzinski et al. [38]. This calculation obviously implies that $r(\lambda)$ should be bounded from below by the value of $r^*(\lambda)$ (the radius of a meniscus cannot be smaller than that of the capillary, in which it is formed), thereby $\Delta p^* = 2\gamma/r^*$ should be the upper estimate of the Laplace pressure Δp. (Note that the average curvatures may always be mathematically defined and experimentally determined, irrespective of whether the relevant interfaces are cylindrical, spherical or of any other regular or irregular shape, both connected or disconnected.)

The actual radius r^* is the radius of the interface between the hydrophobic matrix and aqueous microphase in the bulk of polymer (Fig. 7) hence Δp^* may be directly estimated as a function of λ from scattering experiments (SAXS or SANS) from the Bragg spacing of ionic aggregates assuming certain spatial arrangement, which is usually a cubic lattice, or some other data. On the other hand, the extent of Schroeder's paradox, i.e., the difference between a_V and a_L or $\Delta p = (RT/V_w)\ln(a_V/a_L)$ for a given λ, may serve as another independent approximate measure of r^* through the relation

$$r = \frac{2\gamma V_w}{RT}\left(\ln\frac{a_V}{a_L}\right)^{-1}. \tag{3}$$

One of our purposes was then to examine the relation between Δp and Δp^* or r and r^* for the two studied materials.

4.1. Analysis of isotherms for Dowex

In order to deduce $r(\lambda)$, the activities a_V and a_L had to be read from the isotherms at the same λ. To facilitate this analysis the experimental isopiestic isotherms of Dowex were fitted to the modified BET equation with three fitting parameters λ_0, c and k

$$\lambda = \lambda_0 \frac{cka}{(1 + cka - ka)(1 - ka)}. \tag{4}$$

This equation, also known as the GAB equation, successfully describes sorption of water vapor by ionic and other polar polymers [39,40]. It, however, failed to fit well liquid-equilibrated isotherms, in which case a good fit was obtained using Eq. (4) modified by addition of a constant fourth parameter. This treatment of the whole set of measured points served solely the purpose of interpolation and slightly smoothing the isotherm. The values of a_V and a_L could then be determined for any λ located between the lowest point of liquid-equilibrated isotherms and the highest point of the vapor-equilibrated one, from which r could be calculated using Eq. (3). Fig. 8 displays several such values of r for the Na and Li forms of Dowex as function of λ. It can be seen that the radius monotonously increases with the water content. The available λ range is much wider for the Li form, owing to the stronger hydration of this ion. Interestingly, the

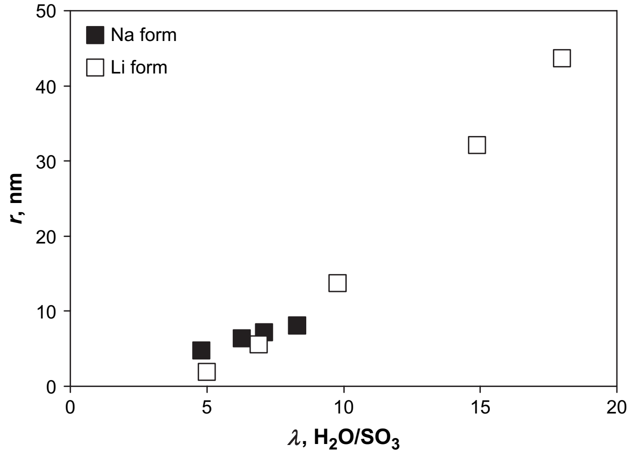

Fig. 8. The calculated radius of curvature r of the aqueous microphase at the surface of vapor-equilibrated Li and Na forms of Dowex 50X-4.

dependence of radius λ is fairly close for the two ionic forms suggesting that it is mostly the level of hydration rather than type of counter-ion that determines the microstructure of the aqueous phase.

The results in Fig. 8 may then be compared with the available information about the microscopic structure of ion-exchange resins. Although such data are quite scarce, it has been well known that copolymerization of styrene and divinylbenzene yields inhomogeneous networks due to the somewhat different reactivities of the two monomers and crosslinking-induced microscopic phase separation (microsyneresis) [41], thereby domains of low crosslinking alternates with highly cross-linked regions. Ikkai and Shibayama [42] investigated the microscopic structures of cation-exchange resins and their poly(styrene-*co*-divinylbenzene) precursors using small-angle neutron scattering (SANS). Their data indicate that the characteristic scale ξ of the intrinsic heterogeneities of the permanently cross-linked matrix similar to the one of the Dowex resin used in this work scale was about 7 nm for a fully swollen resin. It might be expected that the aggregates would tend to form in the least cross-linked domains and their size (r^*) would roughly be of the same order of magnitude as ξ, i.e., a few nanometers. Kim et al. [43] employed a technique based on quenching of a fluorescence dye to estimate the size of aqueous aggregates (“water pools”) in fully swollen resins. This size of a resin having the closest characteristics to the one used in this study was reported to be 8 nm. Comparison of these data with Fig. 8 and recalling that always $r > r^*$, indicates that Eq. (3) produces fairly sensible estimates and seems to support the main premise of the Choi and Datta model.

It must be noted that the calculations and results presented in Fig. 8 refer to the surface of microscopic aggregates located at the resin–vapor interface, whereas structural data were obtained for the bulk material. However approximate, the above agreement suggests that the two are probably not very different, which is reasonable, since the resin is highly and permanently cross-linked leaving very little freedom for structural rearrangements of aggregates and matrix in such resins. Their structure should then be topologically constrained and may then indeed bear some resemblance to a permanent pore structure implicitly assumed in the model of Choi and Datta. In contrast, ionomeric SPE materials allow much more freedom, therefore the two radii r and r^* do not necessarily refer to the regions with identical characteristics. This point will be further considered in the next section.

4.2. Analysis of isotherms for Nafion

Nafion has been perhaps the most studied ionomer and the literature abounds in high-quality structural data obtained by different techniques [31,37,44–48], therefore its microstructure is relatively well known in a wide range of λ and for a variety of ionic forms. This allows direct comparison with the isotherms measured in this study.

Unfortunately, the large difference between the isopiestic and liquid-equilibrated isotherms of Nafion does not allow to calculate $r(\lambda)$ directly, since the highest point of the former lies below the lowest point of the latter, both for the Li and Na ionic forms (Fig. 6). For that reason an opposite approach was undertaken, whereby we tried to predict the upper possible location of the liquid-equilibrated isotherm $a_L(\lambda)$, based on the vapor-equilibrated isotherm $a_V(\lambda)$ and the values of $r^*(\lambda)$ deduced from structural data using the relation

$$a_L^*(\lambda) = a_V(\lambda)\exp\left(-\frac{2V_w\gamma}{RTr^*(\lambda)}\right), \tag{5}$$

and compare it with the actually measured isotherm $a_L(\lambda)$.

The average size of the ionic clusters for the Li and the Na forms of Nafion was calculated from the data presented, respectively, by Gebel [37] and by Fujimura et al. [45] using the relations proposed by Gierke et al. [44] that assume the aggregates are spherical and arranged in a cubic lattice. The dependence thus deduced is shown in Fig. 9 and the predicted liquid-equilibrated isotherms may be seen in Fig. 6. Eq. (5)

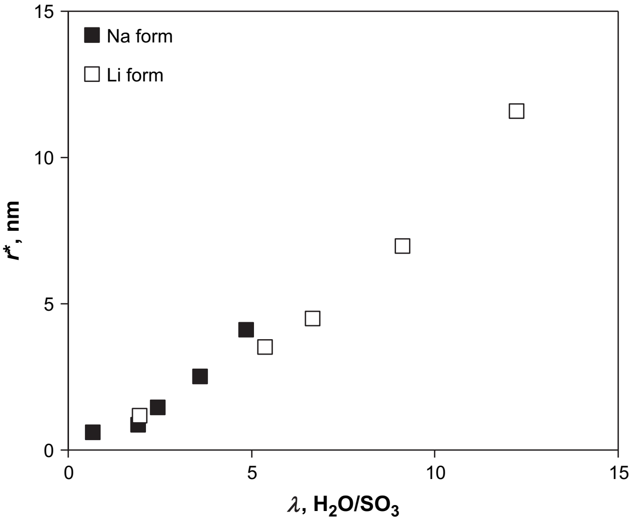

Fig. 9. The radius of aqueous aggregates (ionic clusters) vs. hydration for Li and Na forms of Nafion 117 estimated from scattering data by Gebel [37] and Fujimura et al. [45].

could only be used for the values of λ, for which $a_V(\lambda)$ were available, therefore the isotherm could only be calculated in a limited λ range. The λ ranges of a_L^* and a_L only partly overlap, yet it is clear that $a_L^*(\lambda)$ lies significantly lower than the actually measured isotherm $a_L(\lambda)$. Recalling that a_L^* is supposedly the upper estimate, we conclude that the main premise of the model of Choi and Datta, the close relation between r and r^*, is not satisfied for Nafion.

We arrived at a similar conclusion after trying to make calculations using the model of Choi and Datta and the reported values of the parameters for the H form of Nafion. The differences between the isopiestic isotherms hence relevant parameters of the H, Na and Li ionic forms of Nafion (see, e.g., [34]) are fairly minor compared to the difference between the two equilibration modes. Again, the model failed to predict the large difference between the measured vapor- and liquid-equilibrated isotherms.

Keeping the assumption that Eq. (1) correctly explains Schroeder's paradox for Nafion, the failure may only be explained by a distinct difference between r and r^*. A reason why r may be significantly smaller than r^* estimated from the structural data may be found, if we recall that the microstructure of SPE materials in the surface region and the bulk are not necessarily identical. In fact there have been strong indications in the literature that this is actually the case for Nafion. Based on contact angle measurements for vapor-exposed Nafion, Zawodzinski et al. [38] concluded that the ion-rich domains existing in the bulk of Nafion are covered by a thin fluoro-rich ''membrane'' at the surfaces. McLean et al. [49] reached the same conclusion based on AFM results that verified that the ion content at the outermost few angstroms of the Nafion surface exposed to vapor is substantially reduced compared to the concentration of ionic species just under the surface.

Such behavior is easily rationalized in view of the high surface tension associated with the aqueous ionic solution compared to the fluorinated matrix surface, which may lead to ''spreading'' of a thin ion-free layer over the polymer surface. The known microscopic thickness of this layer ($\sim$1 nm [49]) suggests that entropic factors would not allow complete absence of ionic groups and water molecules at the surface, still their content and size (r^*) should be much smaller than that in the bulk. A much larger Laplace pressure Δp^* may then be expected. The assumption about the role of the extra Laplace pressure made by Choi and Datta may still be valid, but the model will have to be modified to account for the different microstructure at the polymer surface.

5. Conclusions

The isopiestic (vapor-equilibrated) and liquid-equilibrated water sorption isotherms for Dowex and Nafion ion-exchange polymers were measured in a wide range of water activities using solutions of an osmotic stressor. It was observed, that the isopiestic water uptake differs from the liquid-equilibrated one for all studied materials. The differences between vapor- and liquid-equilibrated samples were smaller for the Dowex resin than for Nafion ion-exchange membrane, still it was significant in all cases. The obtained results confirm the occurrence of Schroeder's paradox in studied SPE in a range of water activities and not only at the saturation conditions, i.e. in the saturated water vapor or pure water. Testing of the Choi and Datta assumption about the existence of an extra Laplace pressure in the case of vapor-equilibration suggests that for ionomer materials here might be a need to account for substantial differences in the surface and bulk structures.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.11.054.

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