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Cation-conducting ionomers made by ion exchange of sulfonated poly-ether-ether-ketone: Hydration, mechanical and thermal properties and ionic conductivity

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ABSTRACT

The hydration in liquid water of various thermally treated SPEEK membranes was determined and confronted with data in saturated water vapor. Significant differences, which correspond to the so-called Schroder paradox, are observed only in un-crosslinked ionomers with $IEC > 2$ eq/kg.

After cation exchange in electrolyte solutions (2 and 0.1 mol/L), the hydration and density of the ionomers was determined and confronted with a physical model. There is no clear correlation with cation properties, such as ionic radius or Robinson–Stokes hydration numbers.

The ionic conductivity ranges from 3 mS/cm for K, NH_4 and Mg-exchanged membranes to 0.6 mS/cm for Ca and Zn. Although the latter might be related to ionic cross-linking by the divalent cations, the relatively high conductivity of Mg ions might be useful for electrochemical applications.

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1. Introduction

Ionic conducting polymers (also called ionomers) are a fascinating class of materials with many highly rewarding applications, including energy and environment [1–8]. Ionomers can be classified into two main families: (1) in dry ionomers above their glass transition temperature, the ionic transport is supported by the macromolecular chains and is a highly activated process with rather elevated activation energy [9–13]; (2) in hydrated ionomers, the ionic motion occurs in hydrated nanometric channels, decoupled from the polymer backbone, and the activation energy is low, when the hydration is sufficient [14–20]. Hydrated ionomers are actually nanocomposite solids and are the topic of this work.

The water uptake of hydrated ionic-conducting polymers is a decisive parameter for many of their technologically important properties, foremost mechanical behavior and ionic conductivity, and hydration is a double-edged sword [7,21,22]. On the one hand, given the conduction mechanism, hydration is important for high ionic conductivity [23,24]; we have discussed the relation between hydration and proton mobility in hydrated acidic ionomers, such as Nafion and Sulfonated Aromatic Polymers (SAP) [22,25–29]. On the other hand, hydration reduces the Van der Waals interactions between macromolecular chains, due to the high dielectric constant of water, and degrades the elastic properties of the ionomer, leading at high water activity to the phenomenon called "swelling", which is very detrimental for the durability of ionomers [30,31] and their application in electrochemical energy technologies.

Sulfonated aromatic polymers are promising materials in terms of reducing cost and improving environmental viability of ion-conducting membranes, because they do not need expensive and environmentally problematic fluorine-containing monomers [32–36]. The most investigated SAP is sulfonated poly-ether-ether-ketone (SPEEK [37–45]) that is also a model material, given that many properties have already been reported in the literature [46].

In principle, ionic exchange with mono- and bivalent cations is a way to obtain cation-conducting SAP [47], but relatively little has been reported about their properties [48–50]. The exchange of cations in polymeric ion exchange resins and the influence of cross-linking on ion exchange have been discussed long time ago by Gregor, based on Gibbs–Donnan equilibria [51–53]. Beyond ion exchange, some excess electrolyte is sorbed in the polymer matrix; the amount of sorbed electrolyte is related to that of the external electrolytic solution by the sorption coefficient [48,54]: the quantity of sorbed electrolyte is negligible when the external solution is diluted, but it can reach significant amounts when the external solution is concentrated. Geise et al. reported NaCl sorption on sulfonated poly-arylene-ether-sulfone [48] and found that for an external solution concentration of 1 mol/L about 0.1 mol/L NaCl was sorbed; this result is in agreement with data on sulfonated polymeric ion exchange resins reported by Gregor [54].

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In polymers without ionic groups, all ions sorbed by the polymer are presumably mobile; in a cation exchange polymer, such as SPEEK, the sulfonate anions are fixed on the polymer backbone and only the counter-cations are mobile. For measuring the "true" membrane conductivity, one must first remove excess sorbed electrolyte. The cation mobility can presumably be enhanced by the presence of a large quantity of water [20]; in a simple physical picture, water reduces the possible association of cations and sulfonate anions, fixed on the channels walls, giving uncharged and immobile ion pairs.

Although the principles of ion exchange and electrolyte sorption are known for a long time, several important questions remain open, including (1) What is the influence of cation exchange on the hydration of ionomer membranes? (2) What are the chemomechanical consequences of ionic exchange: does the cationic volume modify the swelling behavior of membranes? (3) What is the influence of the counter-osmotic pressure on hydration, when membranes are immersed in concentrated electrolyte solutions instead of pure water? (4) Can the water uptake be rationalized and predicted based on properties of the ionomer, elastic modulus and free volume, and of the exchange cations, such as ion radius and mass? and, finally (5) What is the ionic conductivity of such cation-exchanged hydrated ionomers?

In this work, we study the influence of cation exchange and salt sorption on the water uptake and ionic conductivity of SPEEK, taken as a model material. Different cases are treated: (1) immersion into 2 M electrolyte solutions: both ion exchange and electrolyte sorption occur; (2) immersion into 0.1 M electrolyte solution: cations are exchanged, but electrolyte sorption is negligible; (3) immersion of cation-exchanged membranes into pure water.

We have recently presented a simple physical model allowing the description of experimental water uptake isotherms of hydrated acidic polymers and the prediction of hydration properties [55]. The model assumes elastic behavior of the ionomers and a linear dependence between the volume of the internal electrolytic solution and the thermodynamic osmotic pressure of water; it neglects electrostatic and interfacial energy terms that are difficult to estimate. The calculated data are in more than decent agreement with the experiment for various ionomers (including Nafion and SAP), which behave in good approximation like elastic solids in a large range of water activities ($0 < a(H_2O) < 0.95$) [55].

However, the assumption of elastic behavior must be checked at even higher water activities and especially in the presence of liquid water, where measured water uptake data are sometimes significantly different from those observed in saturated water vapor (at $a(H_2O)=1$). This still not completely understood inconsistency, called "Schroder paradox" [24,56–61], has been attributed to various kinetic effects, such as sluggish conformational changes and relaxation of the ionomer [58], and also thermodynamic reasons (existence of a Laplace pressure due to interface curvature of the aqueous domains [61]). The study of the acidic form of SPEEK is a necessary first step before investigating the effects of cation exchange in aqueous solution.

The physical model will then be extended to the case of cation exchange, as done in the original work by Gregor et al. on cation exchange resins [54,62,63], including also the effect of excess electrolyte sorption. The extended model will then be used to rationalize the experimental results on cation sorption.

2. Experimental

2.1. Preparation of SPEEK membranes

Sulfonated poly-ether-ether-ketone (SPEEK) with 3 degrees of sulfonation (DS = 0.6, 0.7 or 0.9) was prepared by reaction of PEEK with concentrated sulfuric acid as reported elsewhere [64,65]. Membranes were cast using a home-made doctor-blade type apparatus and dimethylsulfoxide (DMSO) or dimethylacetamide (DMAc) as casting solvent. Thermal treatments were then applied to the membranes: those at 160 °C in the presence of DMSO lead to a certain degree of cross-linking, depending on the treatment time. Those at 120 °C or any treatment in the presence of DMAc do not induce any cross-linking, but might change the free volume to some extent [66–68].

2.2. Characterization of SPEEK membranes (acidic form)

The ionic exchange capacity (*IEC* in eq/kg) of SPEEK membranes in acidic form was determined by acid–base titration with potentiometric equivalence point detection according to a procedure reported previously [69]. The degree of cross-linking (DXL) was calculated measuring the ionic exchange capacity before and after the treatment [67].

The hydration in liquid water was studied by immersion of small pieces of SPEEK membranes with precise dimensions (measured with a micrometer) during 72 h in a closed Teflon vessel at 25 ± 1 °C. After equilibration, the excess of water was quickly wiped off and the membranes weighed rapidly in a closed vessel (m_{wet}). The samples were then dried for 72 h over P_2O_5 and weighed again (m_{dry}). The mass difference is related to the water uptake *WU*:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{1}$$

The hydration number (λ) is defined and can be calculated as follows:

$$\lambda = \frac{n(H_2O)}{n(SO_3M)} = \frac{WU}{IEC\ M(H_2O)} \tag{2}$$

where $M(H_2O)$ is the molar mass of water.

The density of dry SPEEK samples in acidic and cationic forms was determined from their mass and their dimensions, measured with a micrometer.

Mechanical stress–strain tensile tests were performed on SPEEK membranes in "dry" and "swollen" state at room temperature using an Adamel-Lhomargy DY30 traction machine and ionomer samples with 25 mm length and 5 mm width. The constant crosshead speed was 5 mm/min. Particular attention was devoted to the macroscopic homogeneity of membranes made by casting and only apparently homogeneous membranes were used for the mechanical tests. The clamping pressure, determined in a preliminary tensile stress–strain test, was about 40% of the elasticity limit.

2.3. Cation exchange procedure and water uptake measurements

Protons were exchanged against cations (Fig. 1) by immersion of small pieces of SPEEK membranes (*IEC* = 2.5 eq/kg) in a large quantity of electrolytic solution during 72 h in a closed Teflon vessel at 25 ± 1 °C. All chemicals were high purity and used as-received. In order to minimize as far as possible cation contamination, only high purity demineralized water (σ = 18 MΩ cm) was used and all experiments were performed in Teflon vessels. Two different solution concentrations, 2 M and 0.1 M, were studied in order to observe the effects of a counter-osmotic pressure and of electrolyte sorption on the water uptake.

1. *Cation exchange without electrolyte sorption*: We used a 0.1 M electrolytic solution containing HCl, LiCl, NaCl, KCl, NH_4Cl, $MgCl_2$, $CaCl_2$ or $ZnCl_2$. After equilibration, the excess of

electrolytic solution was quickly wiped off and the membranes weighed rapidly in a closed vessel (m_{wet}). The samples were then dried for 72 h over P_2O_5 and weighed again (m_{dry}). The mass difference is related to the hydration number (λ) and the water uptake *WU* according to Eqs. (1) and (2). The *IEC* is calculated taking into account the molar mass of the various cations.

2. *Cation exchange with concomitant electrolyte sorption*: We used a 2 M electrolytic solution containing HCl, LiCl, NaCl, KCl, NH_4Cl, $MgCl_2$, $CaCl_2$ or $ZnCl_2$. After equilibration, the excess of electrolytic solution was quickly wiped off and the membranes weighed rapidly in a closed vessel (m_{wet}). The samples were then dried for 72 h over P_2O_5 and weighed again (m_{dry}). Under these conditions, excess sorbed electrolyte does not appear in the result and the mass difference is again related to the hydration number and water uptake according to Eqs. (1) and (2).
3. *Immersion in pure water*: The cation-exchanged samples were also immersed in high purity water in order to check the influence of excess sorbed electrolyte on the water uptake data and the consistency of our results. For that purpose, samples were (i) immersed prior to drying (in that case the excess sorbed electrolyte from 2 M electrolyte is dissolved and not included in the dry weight, so that the determined *WU* is apparently larger) or (ii) after drying (in that case the sorbed electrolyte from 2 M electrolyte is present in the dry weight and the *WU* is apparently smaller). In the case of 0.1 M solutions, the results were similar, because no electrolyte sorption is observed. These experiments allow also checking the existence of Schroder paradox-type behavior in cation exchanged ionomers (see Section 4).

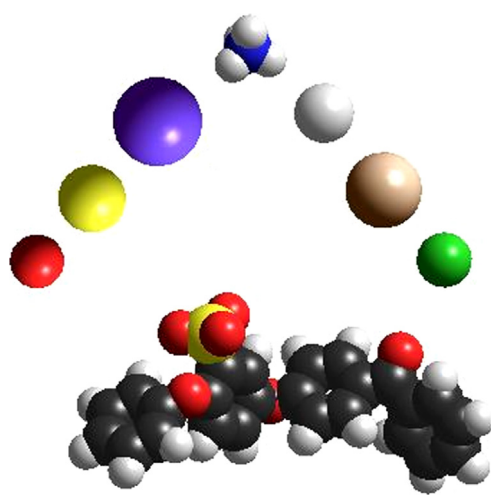

Fig. 1. Geometrically optimized repeat unit of SPEEK (PEEK–SO_3^-) and non-hydrated cations (from left to right: Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Zn^{2+}).

2.4. Thermogravimetric and ionic conductivity measurements

The thermal stability of SPEEK in acidic and sodium forms was studied by high resolution thermogravimetric analysis (TGA Q500, TA Instruments) between 30 and 500 °C using a platinum sample holder with a heating rate of 3 K/min under air flux (60 ml/min).

The ionic conductivity of the ionomers was measured after immersion in water at 25 °C during 24 h so that excess sorbed electrolyte was removed. The fully humidified samples were then fitted into a gas-tight Swagelok cell with two stainless steel electrodes, closed with reproducible force to ensure a constant contact pressure on the membranes. The measurements were made by impedance spectroscopy (EG&G model 6310) between 10^{-1} and 10^5 Hz with 20 mV amplitude. The through-plane resistance was determined at the intersection of the impedance arc with the real axis and the conductivity calculated using the membrane thickness and electrode area (0.19 cm^2).

3. Results

3.1. SPEEK (acidic form)

Table 1 shows hydration numbers in liquid water for various SPEEK samples together with their thermal treatment conditions. Calculated values were obtained using the physical model outlined in Section 4. The first 6 rows correspond to samples treated at 120 °C in DMSO or in DMAc at any temperature, where no cross-linking is observed [66]. The next 5 samples (rows 7–11) are heated at 160 °C in the presence of a small quantity of DMSO inside the membrane so that the macromolecular chains are cross-linked [27,67,68,70]. The last two lines correspond to uncross-linked SPEEK samples with high *IEC*: they show a very large water uptake, much higher than in the other cases. Here, an inconsistency between hydration in liquid water and water vapor is evident ("Schroder paradox", see Fig. 2). Tensile stress–strain tests of "dry" and swollen slightly cross-linked (*DXL*=0.19) SPEEK membranes are shown in Fig. 3. The elastic modulus is 1200 MPa in the dry and 200 MPa in the swollen state (Table 2).

Table 1
Experimental and calculated water uptake *WU* of various thermally treated SPEEK ionomers in liquid water at 25 °C for 72 h, including the type of treatment, the ionic exchange capacity *IEC*, the degree of cross-linking and the two parameters used for modeling.

Row	Thermal treatment (solvent, *T* (°C), *t* (h))	*IEC* (eq/kg)	Degree of cross-linking	Deformation parameter (L mol^{-1} bar^{-1})	Free volume parameter (L/mol)	λ Experiment	λ Model
1	DMSO 120, 64	1.79	0	1.5×10^{-4}	0.13	8	8
2	DMSO 120, 64	2.04	0	1.5×10^{-4}	0.13	10	8.2
3	DMSO 120, 168	1.79	0	1.5×10^{-4}	0.13	7	8
4	DMAc 120, 168	1.79	0	1.5×10^{-4}	0.07	5	5.1
5	DMAc 160, 64	1.79	0	1.5×10^{-4}	0.07	5.4	5.1
6	DMAc, 120, 64 +160, 64	1.79	0	1.5×10^{-4}	0.07	5.2	5.1
7	DMSO 160, 64	1.50	0.16	7.5×10^{-5}	0.11	5.2	6.5
8	DMSO 160, 64	1.96	0.22	7.5×10^{-5}	0.11	6.2	6.6
9	DMSO, 120, 64+160, 64	1.33	0.26	7.5×10^{-5}	0.07	3.6	4.4
10	DMSO, 120, 64+160, 64	1.54	0.24	7.5×10^{-5}	0.07	3.8	4.5
11	DMSO, 120, 64+160, 64	1.9	0.24	7.5×10^{-5}	0.07	5	4.6
12	DMSO 120, 168	2.5	0	1.5×10^{-4}	0.13	17	8.4
13	DMSO 120, 64	2.5	0	1.5×10^{-4}	0.13	33	8.4

The dry density of the acidic form of SPEEK is 1.34 ± 0.08 kg/L (average of 8 samples). The dry volume can be calculated using the molar mass of an ionomer repeat unit ($M(RU)=360$ g/mol): $V(SPEEK)=0.275$ L/mol.

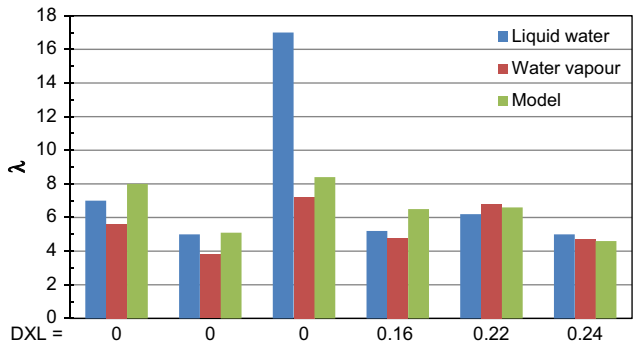

Fig. 2. Hydration numbers (λ) in liquid water and water vapor ($a(H_2O)=0.95$) for SPEEK with various degrees of cross-linking (DXL) and ionic exchange capacities (IEC in eq/kg^{1}).

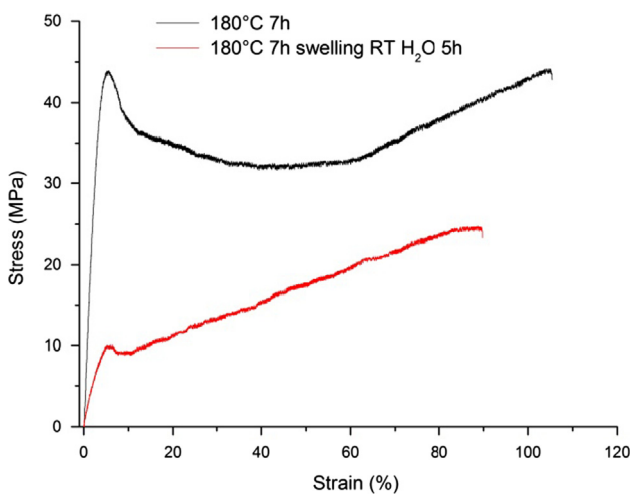

Fig. 3. Typical tensile stress–strain tests of a partially cross-linked SPEEK membrane ($DXL=0.19$) in "dry" and wet states.

Table 2
Mechanical properties of cross-linked SPEEK membranes (see Fig. 2) in dry and wet conditions: elastic modulus E, tensile strength σ_{Max} and elongation at break ε_{Break}.

Conditions	E (MPa)	σ_{Max} (MPa)	ε_{Break} (%)
"Dry"	1270 ± 20	43 ± 1	103 ± 3
Swollen	280 ± 60	10 ± 1	100 ± 10

3.2. Cation-exchanged SPEEK

Table 3 reports the molar mass $M(cation)$ and molar volume in the dry state $V(cation)$ of the investigated exchange cations (see also Fig. 1) and experimental and calculated dry densities of cation-exchanged SPEEK. The dry density of cation-exchanged SPEEK ρ_{calc} can be calculated using the equation:

$$\rho_{calc} = \frac{M(RU)+M(cation)}{V(SPEEK)+V(cation)} \quad (3)$$

$M(RU)$ is the mass of the repeat unit (360 g/mol). There is a decent agreement between experimental and calculated dry densities in Table 3; the experimental values for monovalent cations show however a large uncertainty.

The ionic conductivity of cation-exchanged ionomers stable in water is also reported in Table 3; the ionomers containing Li and Na dissolve in water and are not stated. These values were checked over 4 months with good reproducibility.

Table 4 shows the water uptake of SPEEK samples immersed in 2 M electrolyte solutions together with calculated values according to the physical model outlined in the discussion section. The water uptake "without sorbed electrolyte" was calculated using a dry weight obtained after dissolution of sorbed electrolyte; WU is consistently higher than the water uptake "with sorbed electrolyte". In the latter case, sorbed electrolyte is present in the dry weight and dissolved during the water uptake experiment so that the measured WU appears lower. This difference is decently reproduced by the model data.

Table 5 shows the water uptake observed when samples cation-exchanged in 2 M electrolytic solution are subsequently immersed in pure water. The samples containing H, Li and Na dissolve in pure water and are not reported in the table. On the right side in Table 6, the water uptake is obtained after previous elimination of sorbed electrolyte (the dry weight does not include

Table 4
Experimental and calculated water uptake WU of SPEEK ionomers ($IEC=2.5$ eq/kg) exchanged in 2 M MCl solutions at 25 °C for 72 h. n_0 is the calculated hydration number. The only two constants used for modeling are: $a=1.5\times10^{-4}$ L mol^{-1} bar^{-1}, $b=0.13$ L/mol (see Eq. (7)).

Cation	n_0	Without excess electrolyte		With excess electrolyte	
		WU_{exp} ($\pm5\%$)	WU_{model} (%)	WU_{exp} ($\pm5\%$)	WU_{model} (%)
H	8.4	45	42	48	41
Li	8.2	47	41	39	39
Na	8.1	46	39	30	36
K	7.9	34	36	26	34
NH_4	7.8	36	37	23	35
Mg	7.6	51	39	30	35
Ca	7.5	37	37	22	33
Zn	7.6	54	38	34	33

Table 3
Molar mass and dry molar volume (from Ref. [73]) of studied cations; n is the Robinson–Stokes hydration number of cations according to Ref. [72] and u_{ion} the cation mobility at infinite dilution in water at 20 °C (from reference [88]). The experimental (average of 4 values) and calculated dry densities ρ of cation-exchanged SPEEK and the ionic conductivity σ at 25 °C in water are also reported.

Cation	$M_{(cation)}$ (g/mol)	$V_{(cation)}$ (mL/mol)	n	$u_{ion}\times10^4$ (cm^2/Vs)	ρ_{exp} (g/mL)	ρ_{model} (g/mL)	σ (mS/cm)
H	1	≈0	8	32.4	1.34 ± 0.08	1.34	20 ± 3
Li	7	0.90	7.1	3.4	1.4 ± 0.3	1.36	–
Na	23	2.30	3.5	4.6	1.5 ± 0.2	1.41	–
K	39.1	7.07	1.9	6.6	1.5 ± 0.3	1.44	2.7 ± 1.0
NH_4	18	8.18	–	6.7	1.39 ± 0.06	1.36	2.3 ± 0.2
Mg	24.3	0.87	6.9	5.5	1.45 ± 0.04	1.38	2.9 ± 1.2
Ca	40	2.76	6	5.3	1.39 ± 0.08	1.40	0.6 ± 0.3
Zn	65.4	0.87	–	4.8	1.46 ± 0.09	1.46	0.6 ± 0.4

Table 5
Experimental and calculated water uptake *WU* of SPEEK ionomers (*IEC*=2.5 meq/kg) exchanged in 2 M electrolyte and then immersed in pure water at 25 °C for 72 h after cation exchange. n_0 is the calculated hydration number. The two parameters used for modeling all experiments are $a=6\times10^{-4}$ L mol^{-1} bar^{-1} and $b=0.2$ L/mol (see Eq. (3)).

Cation M	n_0	Without excess electrolyte		With excess electrolyte	
		WU_{exp} (± 5%)	WU_{model} (%)	WU_{exp} (± 5%)	WU_{model} (%)
K	13.9	66	78	46	58
NH_4	13.8	72	72	64	63
Mg	12.8	74	66	70	57
Ca	12.7	65	67	40	54
Zn	12.8	58	71	52	52

Table 6
Water uptake of SPEEK ionomers (*IEC*=2.5 eq/kg) cation-exchanged in 0.1 M MCl solution at 25 °C for 72 h and then immersed in pure water at 25 °C for 72 h. n_0 is the calculated hydration number. The two constants used for the modeling are $a=6\times10^{-4}$ L mol^{-1} bar^{-1} and $b=0.2$ L/mol (see Eq. (3)).

M	n_0	WU_{model} (%)	**0.1 M MCl** WU_{exp} (± 5%)	**H_2O pure** WU_{exp} (± 5%)
K	13.9	61	43	82
NH_4	13.8	65	75	198
Mg	12.8	61	58	67
Ca	12.7	58	34	47
Zn	12.8	58	59	71

sorbed electrolyte); on the left side, the excess of sorbed electrolyte is dissolved during the water uptake experiment (the dry weight includes sorbed electrolyte) so that *WU* is apparently smaller. The trend is reproduced by the model.

Finally, Table 6 reports water uptake data after immersion in 0.1 M salt solution; dissolution is observed for H, Li and Na forms, which are therefore not reported. The other mono-valent K and NH_4 forms show also a very large water uptake. Here, the effect of an ionic cross-linking by divalent cations can be observed.

Fig. 4 shows thermogravimetric curves of SPEEK in acidic (a) and sodium form (b). The decomposition of sulfonic acid group and main chain are observed around 225 and 440 °C, respectively, whereas in the sodium form, all peaks are shifted to higher temperatures, indicating that the presence of cations stabilizes the polymer, probably by ion–dipol interactions ("ionic cross-links"). This is a reminder that salts are thermally more stable than the corresponding acids, e.g. acetates vs. acetic acid. The thermal stability is more than sufficient for any applications even at moderately elevated temperature. The thermogram of the sodium form is also more complicated with some small peaks indicating probably a distribution of local environments inside the polymer, such as different chain lengths etc., revealed by the presence of Na ions. This type of complicated thermogram was also reported recently in other cationic ionomers, for example in reference [71].

4. Discussion

The various water uptake data reported in Tables 1 and 4–6 are not easily rationalized. There appears to be no simple correlation with relevant physical properties of cations, such as the molar volume or reported cation hydration numbers from references [72,73]. For example, monovalent cations K and NH_4 show higher water uptake in water than divalent cations, although the Stokes–Robinson hydration numbers are much lower; Li and Mg have

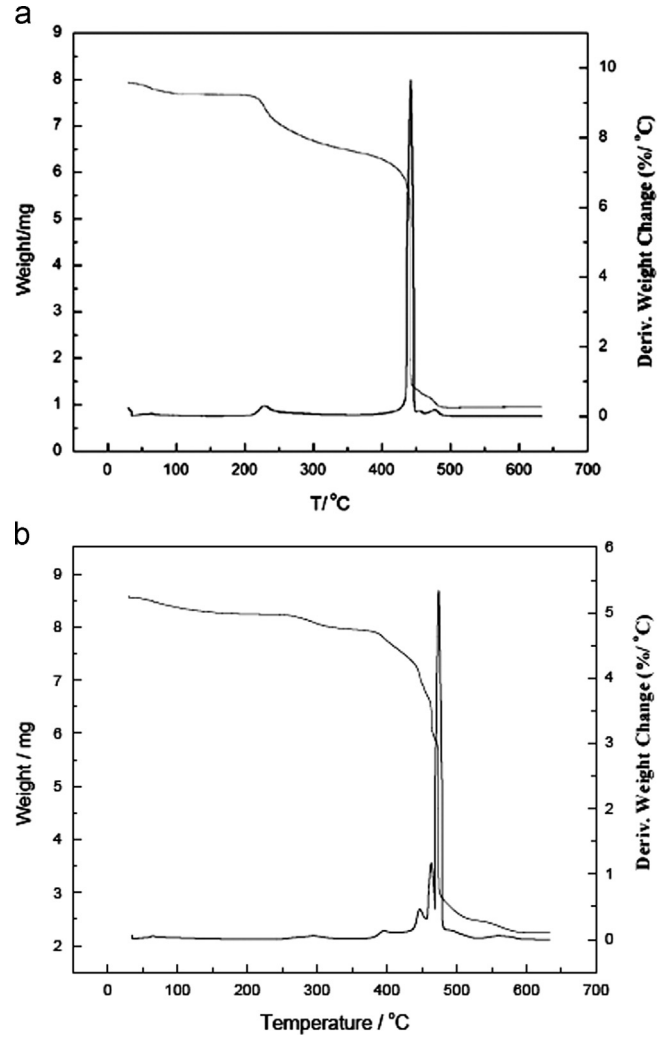

Fig. 4. Thermogravimetric analysis of SPEEK in acidic form (a) and sodium form (b).

similar dry radii, but the water uptake in water is very different (Tables 1 and 6). A tentative to analyze the data will be made using the physical model introduced for the interpretation of hydration isotherms of acidic ionomers [55].

4.1. Physical model of the ionomers

The equilibrium hydration of ionomers is governed by the Gibbs free energy of hydration, which can be written as the sum of various contributions:

$$\Delta G=\Delta G_{osmotic}+\Delta G_{elastic}+\Delta G_{interfacial}+\Delta G_{electrostatic} \quad (4)$$

The interfacial energy term $\Delta G_{interfacial}$ is due to the interfaces between hydrated domains and hydrophobic polymer; it also depends on the interface curvature of the domains. Generally, hydrated channels are assumed to have a spherical or cylindrical shape [61,74–76], but the exact shape distribution is unknown. The electrostatic energy term $\Delta G_{electrostatic}$ is related to the change of distance between cations and anions during hydration; it can only be obtained numerically [77]. Given that these two factors are difficult to assess, we use here a simplified model, considering only the osmotic contribution $\Delta G_{osmotic}$ due to the water and the elastic contribution $\Delta G_{elastic}$ due to the ionomer matrix.

The main assumptions of the physical model of hydration of ionomers are the following [55]. (1) The ionomer is considered as an elastic solid, characterized from a mechanical point of view by

its elastic modulus. (2) The system is ideal from a thermodynamic point of view: the activity coefficients are unity and the partial volumes are identical to the molar volumes. (3) The sulfonate anions are fixed on the macromolecular backbone and considered part of the ionomer matrix. (4) The cation exchange is quantitative and cations are inside the electrolytic solution.

During a water uptake or a cation exchange experiment, the electrolytic solution inside the elastic ionomer matrix is in contact with liquid water or an outer electrolyte solution. The thermodynamic osmotic pressure π of water can be written as [78]

$$\pi = \frac{RT}{V_0} \ln\left(\frac{x_{0,ext}}{x_{0,sol}}\right) \tag{5}$$

R is the gas constant and T the absolute temperature. $x_{0,ext}$ is the molar fraction of water in liquid water ($x_{0,ext}=1$) or in the outer electrolyte solution. $x_{0,sol}$ is the molar fraction of water in the electrolytic solution inside the hydrated ionomer. V_0 is the partial molar volume of water considered equal to its molar volume (0.018 L/mol). The volume of the inner electrolytic solution V_{el} can be written as

$$V_{el} = \sum_i n_i V_i = n_0 V_0 + n_1 V_1 + n_{sorp} V_{sorp} \tag{6}$$

n_0, V_0, n_1, V_1, and n_{sorp}, V_{sorp} are the mole numbers and molar volumes of water, compensating cations and sorbed electrolyte, respectively (see Table 3; the volume of the counter-ion is $V(Cl^-)=0.015$ L/mol). n_1 is directly available from the ionic exchange capacity (*IEC* in eq/kg) and the dry density of the ionomer (Table 3). If sorbed electrolyte is present, the volume of sorbed cations and chloride anions (V_{sorp}) has to be added to the sum in Eq. (6).

A linear relationship is postulated between V_{el} and the thermodynamic osmotic pressure π:

$$V_{el} = a\pi + b \tag{7}$$

This expression describes in a general way the elastic properties of a cross-linked polymer structure at moderate pressure [62,79]. A change of the hydration number n_0 changes V_{el} in Eq. (6), but also in Eq. (7) via a modification of the osmotic pressure π in Eq. (5).

The equilibrium hydration number $n_{0,eq}$ can be calculated by the simultaneous (numerical or graphical) solution of Eqs. (6) and (7). According to the definitions of molar quantities exclusively used in this work, $n_{0,eq}$ is directly equal to the hydration number or water uptake coefficient λ, defined in Eq. (2). The calculation of the water uptake *WU* is straightforward knowing the *IEC* of the ionomer, which can be calculated using the molar mass of the exchanged cation.

The values of the constants a and b in Eq. (7) depend upon the specific ionomer considered. As discussed in detail elsewhere [55] and following the treatment by Flory [79] and Gregor [77], the "deformation parameter" a is inversely proportional to the elastic modulus of the ionomer. Considering typical values of the elastic modulus of uncross-linked and cross-linked SPEEK (~600 MPa or ~1200 MPa, respectively, see [70] and Table 3), values of $a=1.5\times10^{-4}$ L mol^{-1} bar^{-1} or 7.5×10^{-5} L mol^{-1} bar^{-1} are used throughout this work for uncross-linked or cross-linked SPEEK. The "free volume parameter" b is related to the free volume of the ionomer V_{free}, which can be estimated from the Van der Waals volume using the Bondi equation [80] and group [81] or atomic contributions [82], so that $b=0.13$ L/mol is used for the calculations, except where otherwise noted. It is assumed that the cation exchange does not modify the parameters a and b; however, the presence of divalent cations might lead to so-called "ionic cross-linking" [83], which could rigidify the membrane. In that case, a low ionic conductivity should be also observed.

4.2. Hydration in liquid water of SPEEK in acidic form

Fig. 1 shows a comparison of water uptake data in liquid water and in water vapor ($a(H_2O)=0.95$) for various thermally treated samples. One notices a good agreement among data for ionomers with $IEC \leq 2$ eq/kg. The values calculated using the model are in good agreement with the experiments using the two values of deformation parameter for un-cross-linked or cross-linked SPEEK, respectively. This shows that the ionomers generally behave like elastic solids, even in liquid water, when the *IEC* is below 2 eq/kg and/or in the presence of cross-linking that stabilizes the chemomechanical properties of the ionomer. Concerning the free volume parameter, the annealing treatment performed at 120 °C before the cross-linking is assumed to reduce the free volume to some extent and the more the longer the thermal treatment is (rows 7–11 in Table 1) [84]. Accordingly, the free volume parameter was modified allowing a good description of the experiments. Furthermore, the solvent DMAc is known to strongly interact with sulfonic acid groups [43] so that a significant amount of solvent remains in the membrane, obstructing part of the free volume of the ionomer. Consequently, a small volume constant b is assumed for samples cast from DMAc (rows 4–6 in Table 1).

Summarizing the results, in all ionomers with $IEC \leq 2$ eq/kg, the assumption of elastic behavior is valid up to the highest water activity. This means also that the model can be used to predict the water uptake of such ionomers. The measured data in liquid water are consistent with data in water vapor; in other words, the so-called "Schröder paradox" [57] is not observed in ionomers with $IEC \leq 2$ eq/kg.

The two SPEEK samples having an $IEC=2.5$ eq/kg and no cross-links (rows 12–13 in Table 1) show instead a large discrepancy between water uptake in liquid water and in water vapor, reminiscent of the Schroder paradox. The experimental data are also strikingly higher than the calculated data. This indicates that the Schröder paradox might be related to ionomers that cannot be considered elastic anymore, but which deform plastically and irreversibly. In fact, the data can only be described assuming a very large deformation parameter: $a=6\times10^{-4}$ L mol^{-1} bar^{-1} (this would correspond to an elastic modulus of swollen SPEEK around 200 MPa). Indeed the mechanical tests performed on "dry" and "swollen" SPEEK are strikingly different and the elastic modulus of swollen samples (Table 2) is in reasonable accordance with this value.

Furthermore, a very large free volume parameter, $b=0.26$ L/mol (row 12) or $b=0.52$ L/mol (row 13) has also to be assumed in order to obtain water uptake coefficients of 17 and 30, which are in decent agreement with the experiment. These high values are decreasing with annealing time, which is reasonable, but they are higher than the dry volume of the ionomer and must be considered mere fitting parameters. One should mention that Freger has interpreted the Schroder paradox as a purely thermodynamic phenomenon [61] related to the interface curvature between hydrophilic and hydrophobic domains.

4.3. Cation-exchanged SPEEK: water uptake and ionic conductivity

All model data reported in Tables 4–6 were calculated using a unique set of parameters: $a=1.5\times10^{-4}$ L mol^{-1} bar^{-1} and $b=0.13$ L/mol, corresponding to uncross-linked SPEEK and DMSO as solvent, and without any fitting parameter.

The high solubility of H, Li and Na-exchanged membranes in pure water indicates an influence of the dry ionic radius of monovalent cations, which increases in the order $H^+ < Li^+ < Na^+ < K^+ < NH_4^+$ (Fig. 1). One notices that divalent cations have quite similar hydration numbers to monovalent cations, indicating that there is apparently

no strong influence of ionic cross-links between chains on the hydration behavior. This is consistent with the fact that Mg^{2+} ions show a quite high ionic conductivity inside the ionomer, comparable or even higher than K^+ and $NH_4{}^+$. However, the conductivity of Ca^{2+} and Zn^{2+} is much lower, which indicates some mobility reduction here, possible by ionic cross-link bridges as hypothesized in Ba-exchanged SPEEK [83].

During ion exchange in 2 M electrolytic solutions (Table 4), sorption of non-exchange electrolyte takes place inside the ionomer [85]. Gregor calculated the amount of excess salt as function of the molarity of the salt solution. Below 1 M, the excess is negligible; it is about 0.1 mol (with only negligible variations among cations) when a 2 M salt solution is used [54]. A comparable quantity of sorbed electrolyte was recently reported by Geise et al. for NaCl sorption in sulfonated ionomers [48]. We therefore assume a constant quantity of 0.1 mol sorbed electrolyte in all our model calculations. The volume of this sorbed electrolyte changes the electrolyte volume in Eq. (6) (see cation dry volumes in Table 3 [86]), but also in Eq. (7) through a change of the osmotic pressure in Eq. (5). The equilibrium hydration number can be calculated by solution of the modified system of equations. The mass change can then be calculated from the hydration number and the molar masses of water, exchange cations and sorbed electrolyte.

We can observe a decent global agreement between experimental and calculated sets of values in Table 4; the model data reproduce the fact that the apparent water uptake in presence of excess electrolyte is below that without it. The overall agreement of the model data with the experiments indicates that in 2 M salt solutions, where $x_{0,ext} \approx 0.965$, the ionomers can still be described by an ideal elastic model.

However, when $x_{0,ext} > 0.998$ (in 0.1 M salt solution and in pure water), the mass change and density can be described only with a large value of the deformation parameter, equivalent to the one used for SPEEK in acidic form (see Tables 5 and 6). Some experimental facts, such as the dissolution of ionomers containing H^+, Li^+ and Na^+, can obviously not be interpreted in the framework of the model. Although some semi-quantitative correlations between experimental and model data can be found in Tables 4 and 5, some inconsistencies appear in the data. The model is outside its limits of applicability, because uncross-linked ionomers with a high *IEC* cannot be considered as elastic solids anymore in this range of water activity.

Furthermore, cations can interact directly with the macromolecule or with the primary hydration shell of sulfonate groups; similar interactions are postulated to be the origin of the Hofmeister series of ions that can modify for example the solubility of proteins in water [87]. Specific interactions between cations and the polymer, which are not considered in most approaches, might lead to unpredicted results.

One might also ask if the equilibration times are sufficient to assure an exchange of all acidic groups inside the ionomer. The penetration depths of various cations in the hydrated membranes can be estimated from their diffusion coefficients (D) in aqueous solutions using a simple $\sqrt{Dt}$ dependence. With diffusion coefficients calculated from the mobility values in Table 3, this gives a penetration distance of 100 μm (the membrane thickness) after in the order of 100 s. Even taking into account the imperfect connectivity and tortuosity of the ionomer, which reduces the diffusivity of cations, and assuming sluggish ion exchange kinetics, the used equilibration times of 72 h should therefore be fully sufficient.

The ionic conductivity of various cation-exchange SPEEK membranes is 1–2 orders of magnitude below that of SPEEK in acidic form (Table 3) [20]. This reflects the lower mobility of cations vs. protons in aqueous solutions. Using cation mobility data at infinite dilution u_i (Table 3) and taking the tortuosity τ and porosity ε of the ionomer as scaling parameters into account, we can write an equation for the ionic conductivity σ of the cation-exchanged membranes

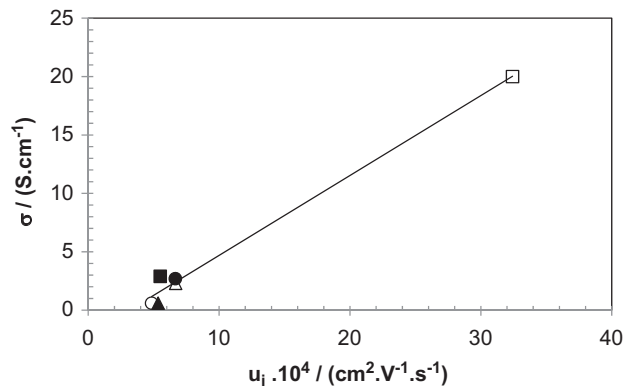

Fig. 5. Ionic conductivity of cation-exchanged SPEEK membranes as function of the cation mobility at infinite dilution in water at 25 °C from reference [88]. H^+ □, K^+ ●, NH_4^+ △, Mg^{2+} ■, Ca^{2+} ▲, Zn^{2+} ○.

$$\sigma = \frac{\varepsilon}{\tau} z_i e_0 u_i c_i \tag{8}$$

In this equation, z_i is the cation charge number, e_0 is the elementary charge, and c_i the exchange cation concentration. Assuming that the porosity and tortuosity of all ionomer samples is identical (and is not modified for example by ionic cross-linking), the cationic conductivity should therefore be proportional to the cation mobility. Fig. 5 shows a plot of the ionic conductivity of cation-exchanged SPEEK membranes vs. the cation mobility in aqueous solution, which shows indeed in good approximation a linear relation.

The very low ionic conductivity of Ca and Zn-exchanged membranes indicates some ionic cross-linking or specific interactions with the ionomer reducing the mobility of these cations. The high conductivity of Mg-exchanged samples is more surprising; such Mg-conducting membranes might be interesting for various electrochemical applications, such as rechargeable Mg batteries.

5. Conclusions

We have investigated the hydration and ionic conductivity of cation-exchanged SPEEK ionomers. The water uptake can be well described for ionomers with low *IEC* or in conditions where the water molar fraction is not above 0.97. In this range, the ionomers behave like elastic solids with constant deformation parameter (which is inversely proportional to the elastic modulus) and free volume parameter. The outlined physical model can be used to predict hydration properties of various membranes. Above this limit, the ionomer shows large irreversible plastic deformation and no correlation between the experimental data and physical properties of the ions could be revealed.

The ionic conductivity of cation-exchanged SPEEK ranges between $\sim 3 \times 10^{-3}$ S/cm for K, NH_4 and Mg and $\sim 6 \times 10^{-4}$ S/cm for Ca and Zn. The low mobility of Ca and Zn seems to indicate some ionic cross-linking, which reduces the cation mobility. The relatively high ionic conductivity of Mg is surprising and might be very interesting for electrochemical applications, such as rechargeable Mg batteries. The thermal stability of SPEEK in acidic and sodium form is fully sufficient even for moderate temperature applications.

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