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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, NH₄ 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 :

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (1)$$

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

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

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 ($\sigma=18$ M Ω 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

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