Chapter 33
Hydrocarbon membranes

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1 INTRODUCTION

As already pointed out in **Perfluorinated membranes**, Volume 3, hydrocarbon based polymers containing acid functional groups, such as sulfonated phenol-formaldehyde resins or sulfonated polystyrene, were the first membrane materials tested in polymer electrolyte membrane (PEM) fuel cells, preceding even the perfluorosulfonic polymers, in particular Nafion, which have become the materials of choice because of their superior chemical and morphological stability.

Subsequently, the availability of oxidation resistant high-performance polyarylenes brought nonfluorinated polymers back into focus. The initial motivation was essentially to mimic the properties of Nafion with low-cost alternatives, but it became increasingly clear that the distinct chemical and microstructural properties of this class of polymers gives rise to certain characteristic limitations but also new perspectives.

The actual situation is characterized by a variety of approaches (for review type articles see Ref. [1]) centered around different thermostable polymer backbones. The poor reproducibility of sample preparation and characterization, however, make it difficult to compare results reported by different laboratories. This is not surprising considering the fact that many membrane properties strongly depend on the polymer microstructure, which is itself sensitive to the molecular weight of the polymer, the presence of impurities, the membrane forming process (kind of solvent, evaporation rate, etc.), membrane thickness, and to a large extent, membrane pretreatment. In addition, there is no commonly agreed upon methodology for membrane characterization.

Therefore, after a brief identification of the properties relevant for the application of membranes in PEM fuel cells and an introduction to the preparation of sulfonated polyarylene membranes, only the properties of plain sulfonated poly ether ketones and Nafion® are compared. Both membrane materials may be considered typical representatives of partially sulfonated polyarylene main chain polymers and poly(perfluoro) sulfonic acid polymers, respectively. The reasonable reproducibility and completeness of the available data renders a direct comparison and discussion of the characteristic differences possible. With the background of the semi-quantitative concepts developed during this discussion, other more recent approaches are introduced subsequently. These comprise the modification of poly ether ketones by acid/base blending and/or cross-linking, acid membranes based on poly benzimidazoles (PBI), polyimides, and polyphosphazene backbones.

While the proton conductivity of all these membranes is associated with the presence of water, recent approaches are based on employing heterocycles (e.g., imidazole) as the proton solvents. These are particularly interesting for PEM fuel cells operating at higher temperature and in low humidity environments, as discussed in Section 8.

2 MEMBRANE PROPERTIES RELEVANT FOR PEM FUEL CELL APPLICATIONS

The function of a PEM in a fuel cell is to separate effectively the anode and cathode gases and to conduct protons, under a variety of operating conditions and over the entire life time of the fuel cell. The first implies chemical and

Handbook of Fuel Cells – Fundamentals, Technology and Applications, Edited by Wolf Vielstich, Hubert A. Gasteiger, Arnold Lamm.
Volume 3: *Fuel Cell Technology and Applications*. ISBN: 0-471-49926-9.

morphological stability and low gas permeability as indispensable requirements. The second requirement is high proton conductivity which is closely related to the degree of hydration for most membrane types. Since fuel cells are open systems with different sinks and sources for water, the chemical state and transport properties of water and protonic charge carriers have to be known and to fall within defined ranges. These depend on the actual operating conditions such as temperature, choice of fuel, gas humidification and gas flow, properties of the membrane/electrode interfaces, transport within the gas diffusion electrode, and electrical current drained from the fuel cell. The relevant membrane properties can then be sufficiently described by: (i) the relation between water concentration and water activity (hydration isotherms and swelling in liquid water); (ii) the dependence of the proton conductivity, water diffusion coefficient, electroosmotic drag of water, and water permeability on the water concentration; and (iii) the elastic properties of the membrane. These parameters determine the water concentration profiles and the dependent properties (such as the overall proton conductivity) for given boundary conditions. For direct methanol fuel cell (DMFC) applications, these parameters have to be considered for the relevant range of water/methanol ratios.

3 PARTIALLY SULFONATED POLYARYLENE MAIN CHAIN POLYMERS

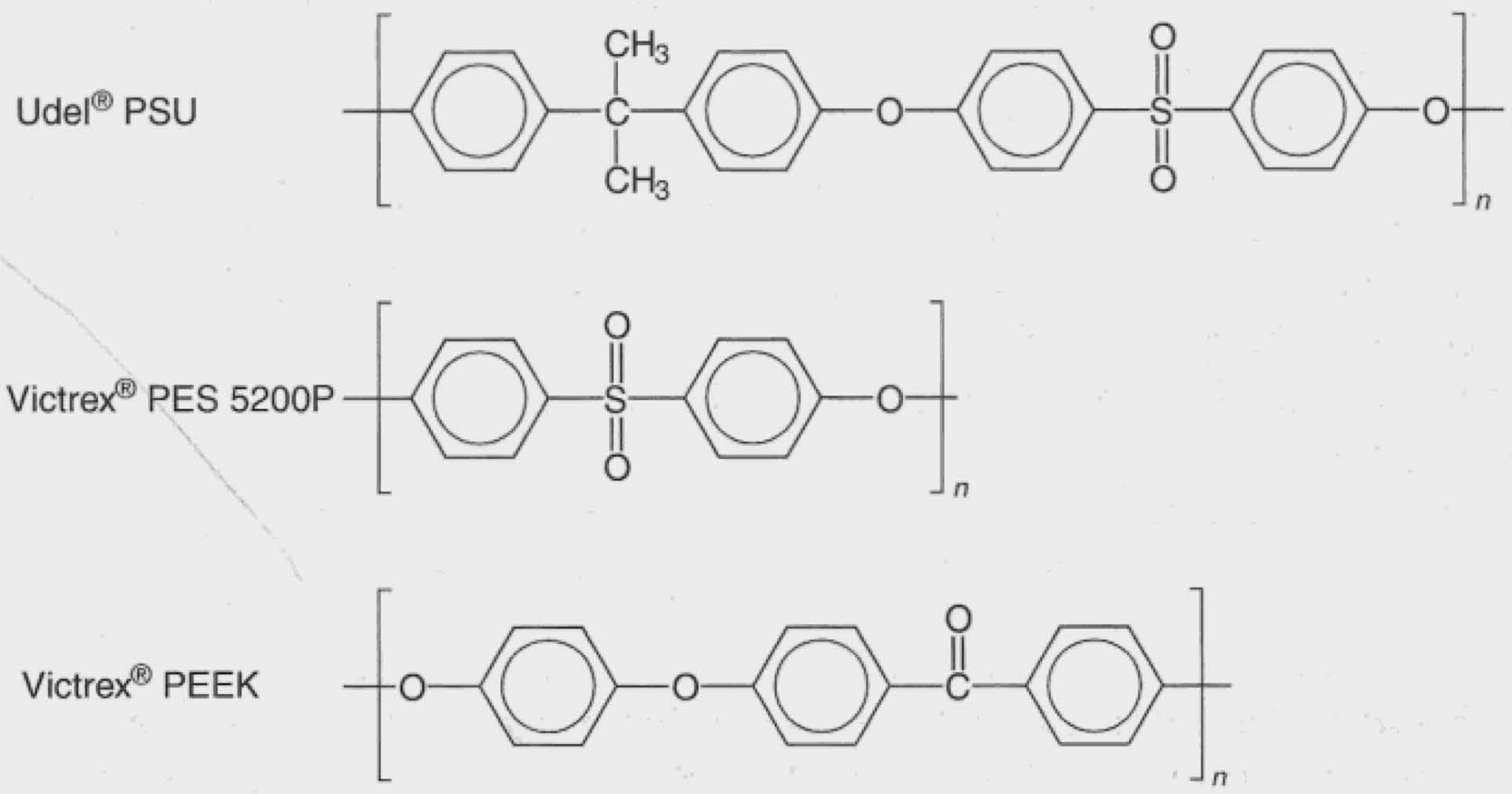
The use of polyarylenes, in particular the different poly(arylene)-etherketones, instead of perfluorinated polymer backbones was mainly motivated by cost and stability considerations. Stability screening tests under oxidizing and reducing conditions at various temperatures had revealed remarkable durabilities (as indicated by minor weight losses) for several types of these polymers.[2] Although the chosen conditions were significantly different from those in a PEM fuel cell, the results were frequently taken as guide lines for the selection of the polymer backbone.

3.1 Membrane preparation

Some of the high performance polymers are commercially available, such as the different poly ether sulfones (e.g., Udel® poly arylene sulfone (PSU), Victrex® poly arylene ether sulfone (PES)) and one variety of poly ether ketones (Victrex® poly arylene ether ether ketone (PEEK)).

While some laboratories are using such products for polymer-analogue sulfonations, others rely on their own polymerization processes, such as the reductive coupling of aryl chlorides[3] or straight Friedel–Crafts polymerization especially for the different poly ether ketones, which are no longer commercially available (such as polyarylene ether ether ketone ketone (PEEKK) (Hostatec®), polyarylene ether ketone ether ketone ketone (PEKEKK) (Ultrapec®), polyarylene ether ketone (PEK) (Victrex®)).

Most polyarylenes allow direct electrophilic sulfonation (e.g., by concentrated sulfuric acid (H_2SO_4/SO_3),[4] chlorosulfonic acid[5] or more softly with its trimethylsilylester)[6] in the electron rich parts of the polymer backbones, e.g., the bisphenol part of Udel® PSU. The electron deficient parts of the polyarylenes (e.g., the diarylsulfon part of Udel® PSU) may be sulfonated by metalorganic deprotonation and subsequent reaction with electrophiles.[7] For the latter preparation procedure it is claimed that the resulting sulfonic acid function is more stable against hydrolytic attack. Especially for the poly ether sulfones the reactions may be carried out in homogeneous solutions (e.g., of dichloroethane), but owing to the low solubility of poly ether ketones, sulfonation is generally commenced in the solid state and continued in solution (e.g., of N-methyl-2-pyrrolidone (NMP)) of low sulfonated intermediates. The final degree of sulfonation is commonly controlled



by reaction temperature and time.[8] Since the weight of the polymer repeat units vary, the degree of sulfonation should be expressed as equivalent weight (in $\mathrm{g\,eq^{-1}}$) or ion exchange capacity (in $\mathrm{meq\,g^{-1}}$) of the dry polymer rather than percent sulfonation. For polyarylenes equivalent weights around $700\,\mathrm{g\,eq^{-1}}$ ($1.4\,\mathrm{meq\,g^{-1}}$) correspond to the same volumetric concentration of fixed acidic sites as in Nafion 117.

Polymers sulfonated in this way generally show statistical sulfonation for each type of site, while polymerization of sulfonated and unsulfonated monomers allows one to build up polymers with defined sulfonation patterns, e.g., with a statistical[8a] or ordered (see Section 5) distribution of sulfonated and unsulfonated segments.

Membranes are commonly prepared by casting solutions of the sulfonated polymer in highly polar aprotic solvents such as NMP or dimethylformamide (DMF) on a glass substrate and subsequent solvent evaporation either in vacuum or a flow of dry gas. The film forming conditions are generally poorly reported, but they seem to have a non-negligible effect on the properties of the final product.

3.2 Comparison between sulfonated poly ether ketone and Nafion membranes

3.2.1 Chemical and microstructural features

Sulfonated polymers naturally combine, in one macromolecule, the high hydrophobicity of the backbone with the high hydrophilicity of the sulfonic acid functional groups. In the presence of water, this gives rise to some hydrophobic/hydrophilic nano-separation. The sulfonic acid functional groups aggregate to form a hydrophilic domain, which is hydrated in the presence of water. While the connected hydrophilic domain is responsible for the transport of protons and water, the hydrophobic domain provides the polymer with morphological stability and prevents the polymer from dissolving in water.

As a result of the smaller hydrophilic/hydrophobic difference (the backbone is less hydrophobic, and the sulfonic acid functional group is less acidic and therefore also less polar) and the smaller flexibility of the polymer backbone, the separation into hydrophilic and a hydrophobic domains is expected to be less pronounced for sulfonated poly ether ketones compared to Nafion. This is directly confirmed by the results of small angle X-ray scattering (SAXS) experiments[9, 10] providing microstructural information on a nano scale indicating smaller characteristic separation lengths with a wider distribution and a larger internal interface between the hydrophobic and hydrophilic domains for hydrated sulfonated poly ether ketones compared to Nafion. The SAXS data and water self-diffusion coefficients obtained by pulsed-field-gradient (PFG)-NMR have been used to parameterize in a consistent manner a simple model for the microstructure, which is based on a cubic hydrophilic channel system in a hydrophobic matrix. In this way, estimates of channel diameter, channel separation, degree of branching, and the number of dead-end channels were obtained for both type of polymers.[9] As schematically illustrated in Figure 1, the water filled channels in sulfonated polyarylene ether ether ketone ketone (S-PEEKK) are narrower compared to those in Nafion. They are less separated and more branched with more dead-end "pockets". All these features correspond to the larger hydrophilic/hydrophobic interface and, therefore, also to a larger average separation of neighboring sulfonic acid functional groups. Recent high-resolution SAXS data and the evolution of characteristic spacings with the water/polymer ratio revealed structural features even on the subnanoscale.[11] According to this study, the microstructure of Nafion® may be represented by an arrangement of low-dimensional polymeric objects with the spaces between filled with water. But on the basis of SAXS data alone the controversy between this model and the frequently assumed model of a system of interconnected inverse micelles[12] will hardly be resolved.

3.2.2 Hydration behavior

The hydration behavior at low water activities is quite similar for both types of polymers. As can be seen from Figure 2, a little water is absorbed at low water activities (slightly more for poly ether ketones compared to Nafion®), and only close to the dew point of water does the degree of hydration increase significantly, i.e., most of the water is only loosely bound. At 100% humidity Nafion® actually takes up significantly more water than sulfonated poly-ether ketones (14 compared to 11 water per sulfonic function) which is due to the more polar character of the sulfonic acid function of Nafion®. Interestingly, the water up-take in liquid water, i.e., at the same water activity, may be significantly higher, suggesting that in this environment water in the membrane may be present as an extended second phase.[13, 14] While at low water activities the hydration isotherms are virtually independent of the sample pre-treatment, only slightly dependent on temperature and quite similar for all sulfonated poly ether ketones, the amount of absorbed liquid water may vary dramatically. The increasing swelling with increasing temperature (Figure 3) is generally irreversible to some extent thus allowing a certain control of the maximum water uptake at room temperature by appropriate preconditioning. While exaggerated swelling in liquid water begins at temperatures above 130 °C for Nafion®, this temperature is significantly lower for sulfonated poly ether

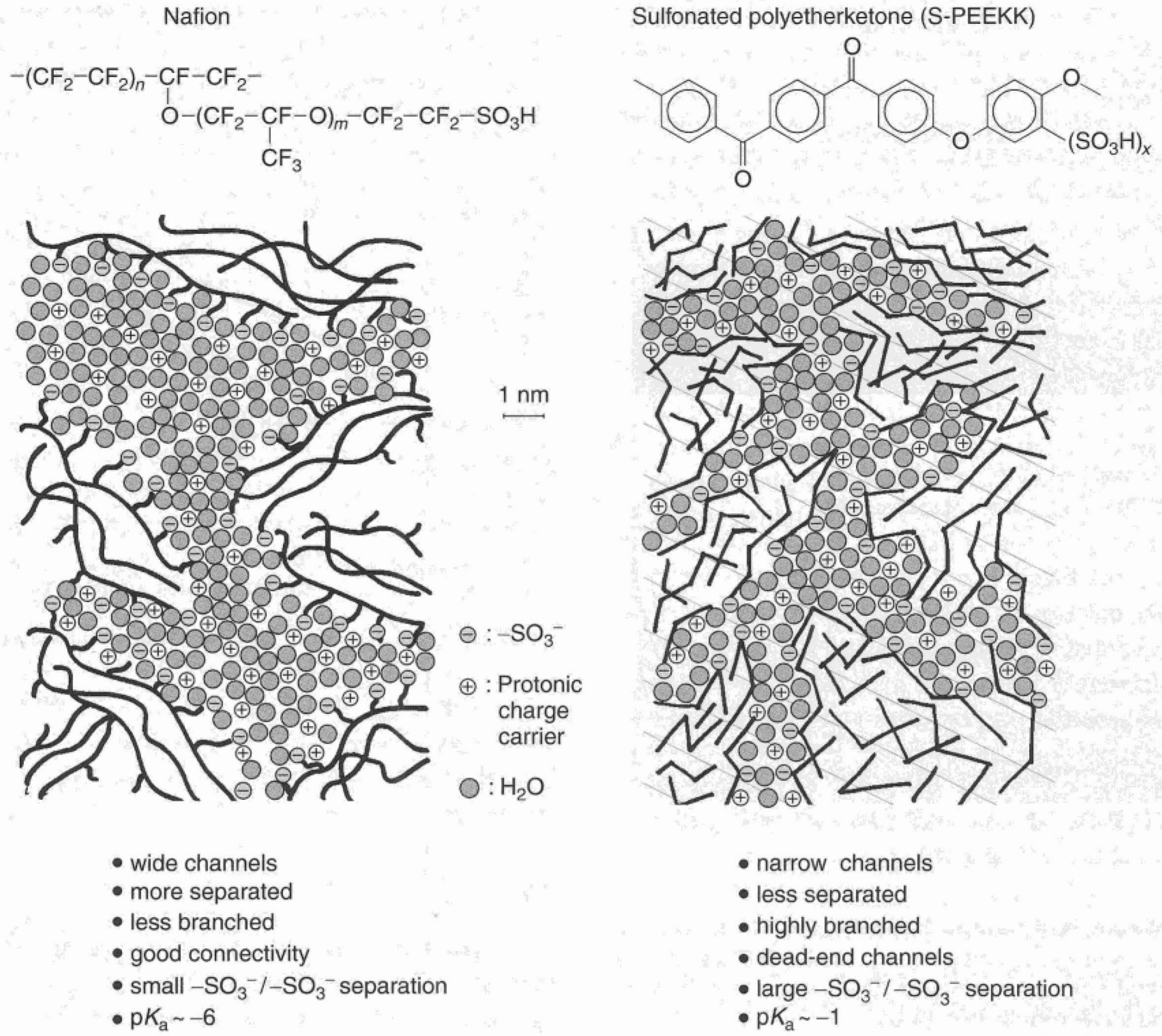


Figure 1. Schematic illustration of the microstructures of Nafion 117® and a sulfonated poly-ether ketone.[10]

ketones, which is most likely a consequence of the less developed hydrophobic domain, its lower hydrophobicity (see above) and the absence of any detectable crystallinity which has been shown to have a positive effect on the suppression of swelling in Nafion® type membranes.[14a] It is a general observation that swelling increases with increasing degree of sulfonation (Figure 3).

3.2.3 *Proton and water transport*

Since the transport of protons and water takes place in the hydrated hydrophilic domain, the corresponding transport coefficients may be understood qualitatively on the basis of the available microstructural data and the chemistry of the two types of systems. In Section 3.2.3.1 proton conductivity, comprising formation and mobility of protonic charge carriers, and water diffusion are discussed together, while electroosmotic drag and water permeation are treated in Section 3.2.3.2.

Proton conductivity and water diffusion

In heterogeneous systems transport coefficients are dependent on the length scale under consideration as discussed in the following sections.

1. *Transport on a molecular scale (<1 nm).* On scales smaller than the size of the channels, the diffusion of water and protonic charge carriers is reminiscent of the situation in aqueous solutions of acids.[14–16] This is indicated by similar activation enthalpies of the transport coefficients for membranes at degrees of hydration where $\lambda > 3$ for Nafion® and $\lambda > 5$ for sulfonated poly ether ketones, i.e., for relatively high water activities corresponding to loosely bound water of hydration (see above). Similar to dilute aqueous solutions of acids, the mobility of protonic defects ($D_\sigma = \sigma RT/(F^2 c_{H^+})$) is somewhat higher than the water diffusion coefficient in fully hydrated membranes (Figure 4). This is characteristic for the presence of structural diffusion, i.e., proton mobility involving intermolecular

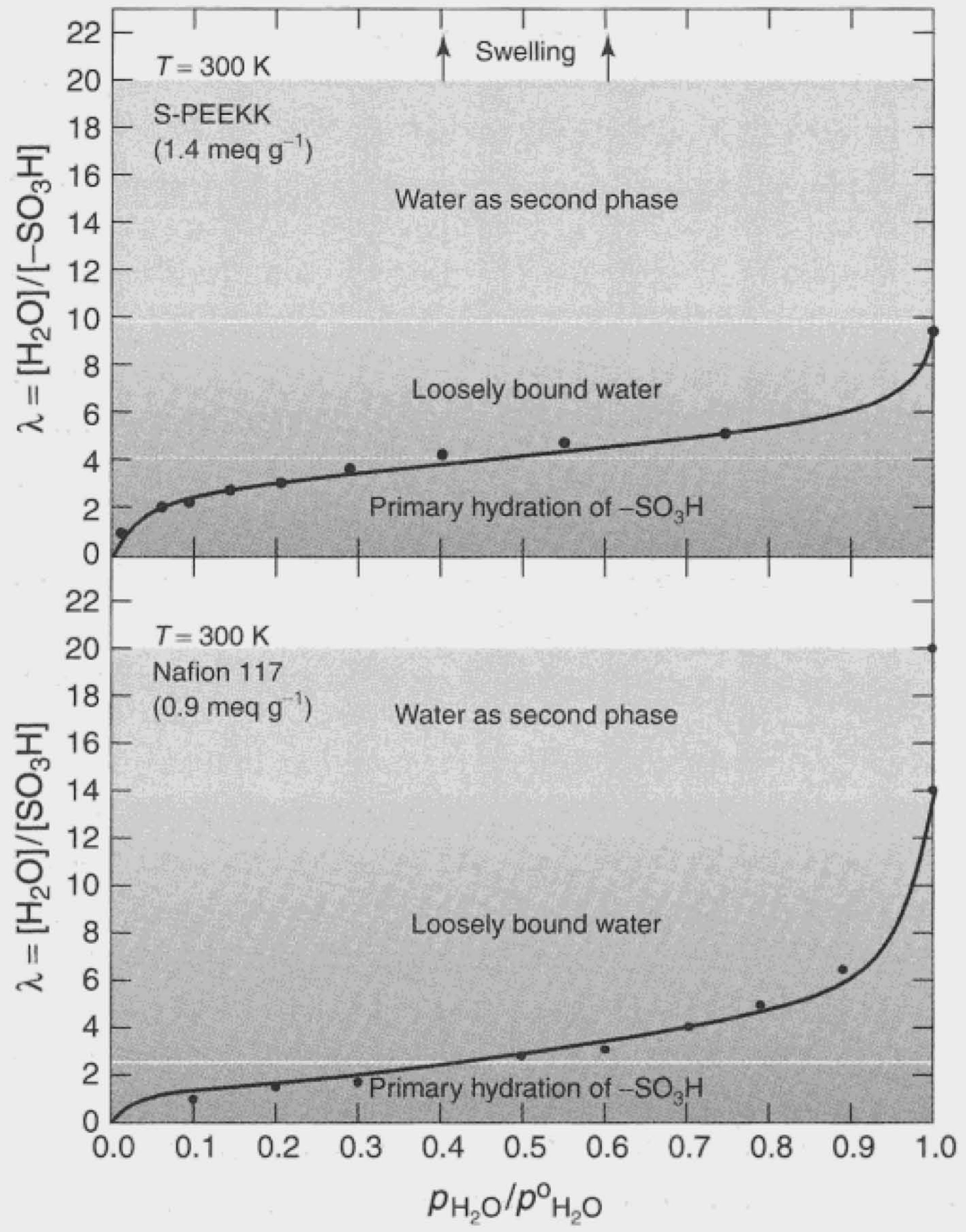


Figure 2. Hydration isotherms for Nafion® and a sulfonated poly ether ketone at room temperature after standardization in 1 M HNO_3 for 1 h and repeated washing in distilled water at the same temperature (data taken from Ref. [14]).

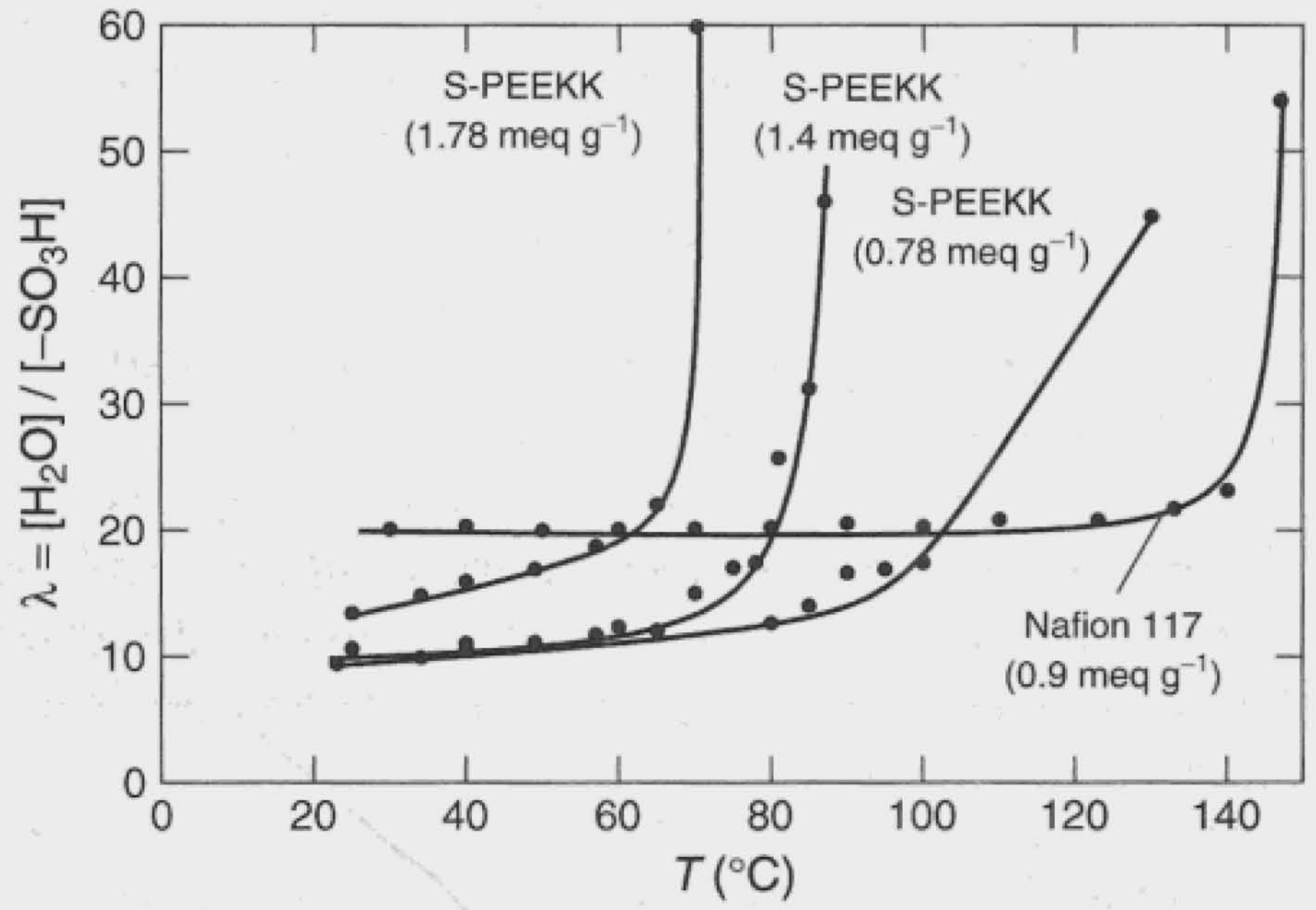


Figure 3. Swelling of sulfonated poly ether ketones of different degrees of sulfonation in liquid water (membranes were initially dry).[10]

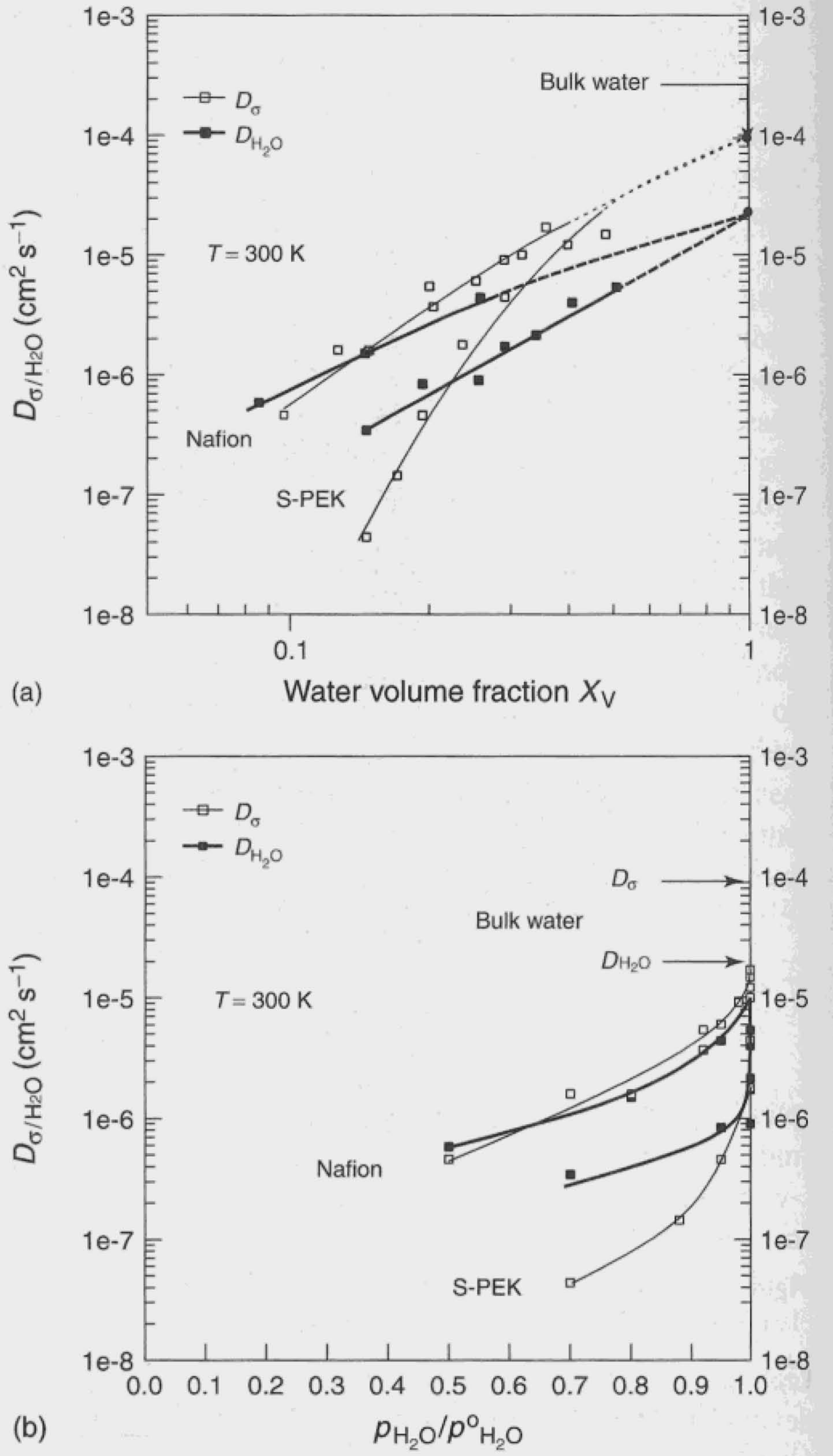


Figure 4. Proton mobility (D_σ) and water diffusion coefficient (D_{H_2O}) for Nafion® and a sulfonated poly ether ketone as a function (a) of the water volume fraction (data from Ref. [14]) and (b) from the water partial pressure (calculated using the data from Figure 2). D_σ has been calculated from conductivity data via the Nernst–Einstein relationship, assuming all protons to be dissociated (see text).

proton transfer and hydrogen bond breaking and forming processes.[16–18] Since this process is sensitive to the biasing of hydrogen bonds in the electric field of ionic charges,[19] this conduction mechanism breaks down with decreasing degree of hydration, and the remaining elementary process of proton conductance is simply the diffusion of hydrated protons (vehicle mechanism[16, 20]) as indicated by the proton mobility coinciding with the water diffusion coefficient (Figure 4). Only in the sulfonated poly ether ketones do the proton mobilities fall significantly below the water diffusion coefficient for very low water levels when assuming that all sulfonic acid sites are fully dissociated (Figure 4). In contrast to Nafion®, this assumption obviously does not hold for sulfonated poly ether ketones, which are only strong acids compared to the superacidity of Nafion® as estimated from empirical relations[9] and confirmed by quantum chemical calculations of the hydrated associated sulfonic acids.[21]

2. *Transport within a single channel (>1 nm).* Incomplete dissociation of acid sites does not fully explain the steep decrease of the proton conductivity with decreasing hydration of the polyarylenes,[13, 14] which is also observed at high temperatures where most fuel cells operate.[22] As opposed to aqueous solutions of acids, the charge of the anion ($-SO_3^-$) is fixed at the hydrophobic/hydrophilic interface of the polymer microstructure (Figure 1) forming space charge layers along these interfaces with the immobile sulfonate anions and the mobile protonic charge carriers in the hydrated hydrophilic domain being the mirror charges. The charge and potential distribution is obtained by solving the Poisson–Boltzmann equation with the dimensions of the hydrated channel and its dielectric constant being the dominant parameters. The potential distribution obtained by a two-dimensional numerical simulation of a model channel (Figure 5) shows significant gradients around the fixed sites. The potential barrier building up between fixed sites is shown to grow more with decreasing dielectric constant of the hydration water than with decreasing separation of fixed sites. The electrical field around the fixed sites is expected to localize even the dissociated protonic charge carriers within the vicinity of their anionic counter charge. This effect becomes apparent as an additional contribution to the activation enthalpy of proton conductivity with decreasing water level, i.e., with decreasing dielectric constant. The dielectric constant has in fact been measured by dielectric spectroscopy[23] and later calculated by a statistical mechanical model[24, 25] (see also **First principles modeling of sulfonic acid based ionomer membranes**, Volume 3). The latter revealed that the permittivity of water more slowly approaches the permittivity of bulk water with increasing distance from the fixed sites in the case of sulfonated poly-ether ketones suggesting stronger localization effects for this type of polymer. Based on the same physical scheme, proton mobilities and water diffusion coefficients were also calculated, assuming that transport prevails in the center of the channel.[26] The excellent agreement with experimental results seems to support this assumption.

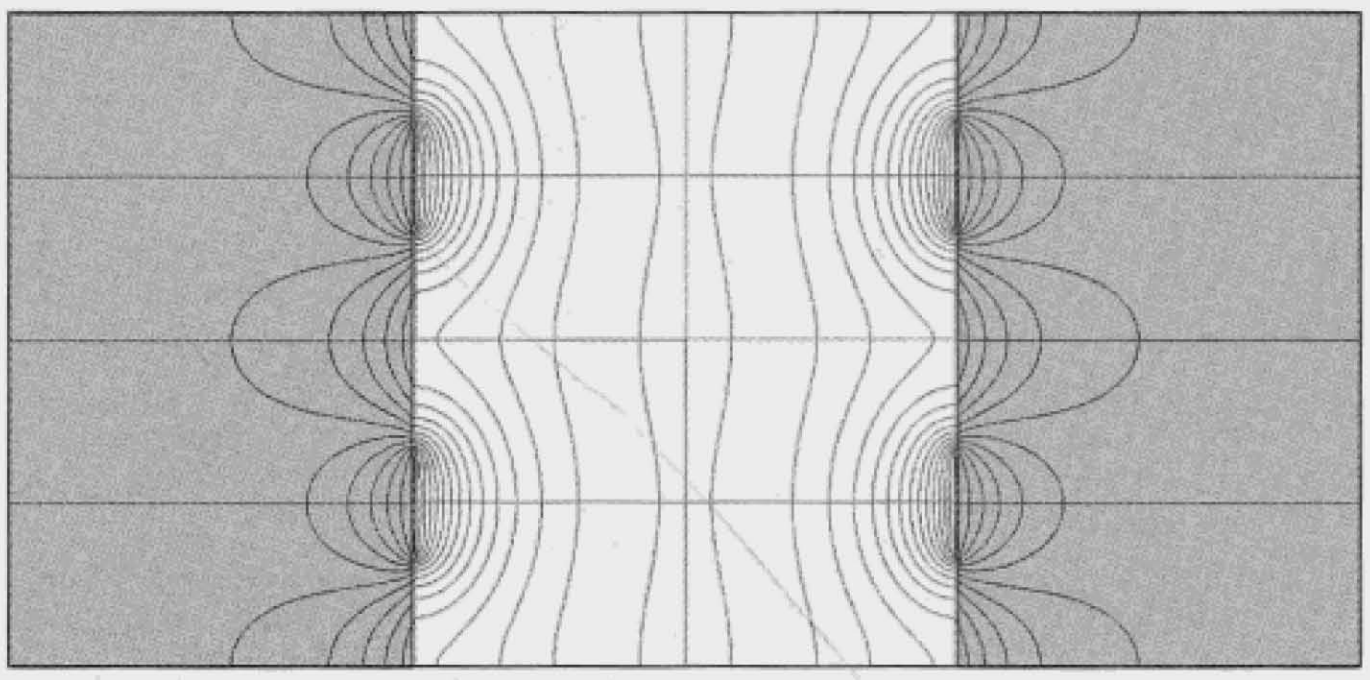


Figure 5. Potential distribution within a two-dimensional model channel as obtained by numerically solving the Poisson–Boltzmann equation for the following parameters: $-SO_3^-$ separation = 0.9 nm, channel width = 1.5 nm, ε(channel) = 80, ε(matrix) = 2[9] (parameters chosen close to these of Nafion®). The isopotentials are separated by 10 mV.

3. *Long range transport (>10 nm).* Such calculations were, however, restricted to single channels; i.e., long range percolation effects were omitted. At least for high water levels, i.e., in the range of low polymer/water interaction, water diffusion can be used as a probe for geometrical percolation within the hydrophilic domain. For Nafion® the water diffusion coefficient decreases with the water volume fraction with a slope close to unity, while the decrease in sulfonated poly ether ketones is steeper, as expected for the progressively less connected hydrophilic domains (Figure 4). Because of the close relation between the diffusion of water and protonic charge carriers, the latter is affected by percolation constraints in a similar way. But, because of the additional effects on smaller scales (see above), proton conductivity decreases more than water diffusion with decreasing water content.

Electroosmotic drag and water permeability

Proton conductivity and water diffusion are linearly related to the diagonal elements of the transport matrix for protons and water, but the electroosmotic drag coefficient K_{drag} describes the coupled transport of protons and water and is defined as the ratio of the off-diagonal elements (Onsager cross-coefficients $L_{12} = L_{21}$) and the proton transport coefficient (L_{11})

$$\begin{pmatrix} j_{\mathrm{H}^+} \\ j_{\mathrm{H_2O}} \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \nabla\mu_{\mathrm{H}^+} + F\nabla\phi \\ \nabla\mu_{\mathrm{H_2O}} \end{pmatrix}$$

$$K_{\mathrm{drag}} = \frac{F^2}{\sigma_{\mathrm{H}^+}} L_{12} = \frac{L_{12}}{L_{11}}$$

$$\sigma_{\mathrm{H}^+} = F^2 L_{11}$$

$$D_{\mathrm{H_2O}} = \frac{RT}{c^2_{\mathrm{H_2O}}} \frac{\mathrm{d}c_{\mathrm{H_2O}}}{\mathrm{d}\ln a_{\mathrm{H_2O}}} L_{22}$$

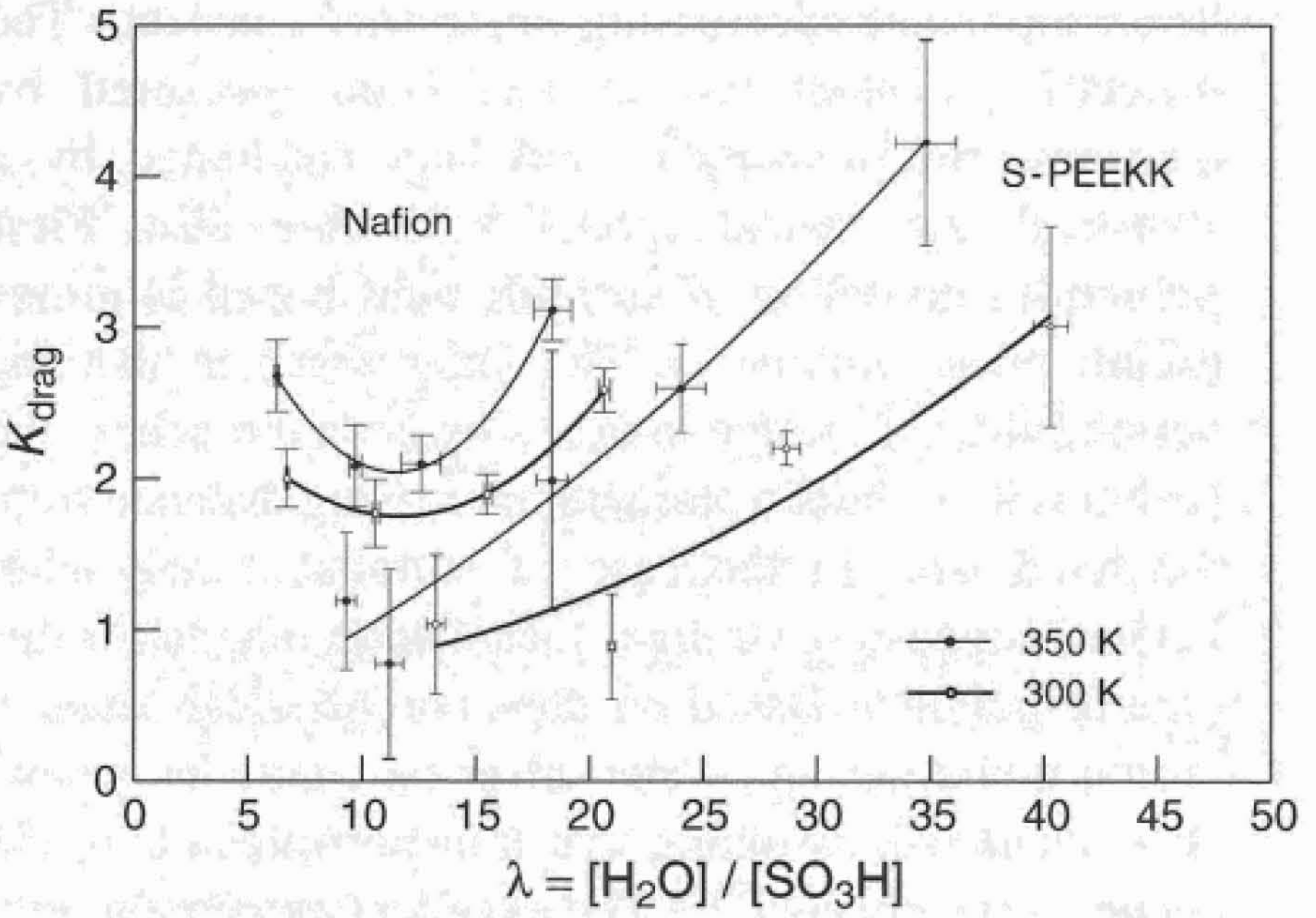


Figure 6. Electroosmotic drag coefficient of water in Nafion 117 and a sulfonated poly ether ketone as a function of the degree of hydration at two different temperatures (data from Refs. [9, 10]).

Hence, K_{drag} simply corresponds to the number of water molecules per proton "dragged" through the membrane.

Recent advances in electrophoretic (E-) NMR[9, 26] allow one to determine this parameter as a function of water content and temperature, and a few characteristic results are shown in Figure 6. The electroosmotic drag is generally higher for Nafion® compared to sulfonated poly ether ketones; it increases strongly with increasing hydration but only weakly with increasing temperature. These trends may also be qualitatively explained by the characteristic differences of the microstructure and chemistry of the two types of membranes. The water velocity profiles around a drifting protonic charge within a channel depend on the water-proton interaction, the viscosity of the water (which has some distribution across the channel), and the dimensions of the channel.[10] Assuming the proton conductance to be dominated by transport within the center of the channels (see above), where the properties of water approach those of bulk water, the proton-water interaction should be similar in both membranes providing the water content is not too low. Then, the lower electroosmotic drag of sulfonated poly ether ketones is mainly the result of the narrower channels (Figure 1) but is also affected by the viscosity distribution within the channels, which becomes increasingly apparent at low water levels. For identical channel sizes (as revealed from the microstructural analysis),[9, 10] electroosmotic drag in sulfonated poly ether ketones is still lower than in Nafion®, which can easily be explained by the stronger bonding of the water directly interacting with the polymer (see hydration isotherms, Figure 2). From a hydrodynamics perspective, the water-poly ether ketone interface has a more negative slip, which may be treated as a reduced effective channel diameter. It should be mentioned that K_{drag} hardly falls below unity, since protons are actually transported as hydronium ions at low levels of hydration (see above). The increase of K_{drag} at low water levels, which is only observed for Nafion® (Figure 6), is not well understood yet, but the appearance of a true pumping effect may be considered as a possible explanation. The shallow minimum of K_{drag} falls into the range $\lambda = 12-14$ at room temperature, corresponding to a water vapor saturated membrane (see also Figure 2), for which electroosmotic drag coefficients between 1 and 1.4 (slightly below the data in Figure 6) were reported earlier.[27a]

Water permeation, i.e., water flux as a result of a total pressure gradient, is also affected by channel diameter and polymer-water interaction, but in addition to this, percolation effects have to be included. At high water contents where the proton conductivities of both types of polymer are almost identical, the water permeability of plain sulfonated poly ether ketones is only about a factor of two lower than for Nafion®. As is observed for proton conductivity, water permeation decreases more strongly with decreasing water volume fraction in sulfonated poly ether ketones than in Nafion®.[10]

3.2.4 *Behavior in water/methanol mixtures*

Since the membranes considered are also envisaged as separators in DMFCs, their behavior in water/methanol mixtures is of particular interest. As can be seen from the swelling as a function of the water/methanol ratio (Figure 7), the presence of methanol has a tremendous effect on the membrane morphology.[27a–e] For both Nafion® and sulfonated poly ether ketones, swelling progressively increases with

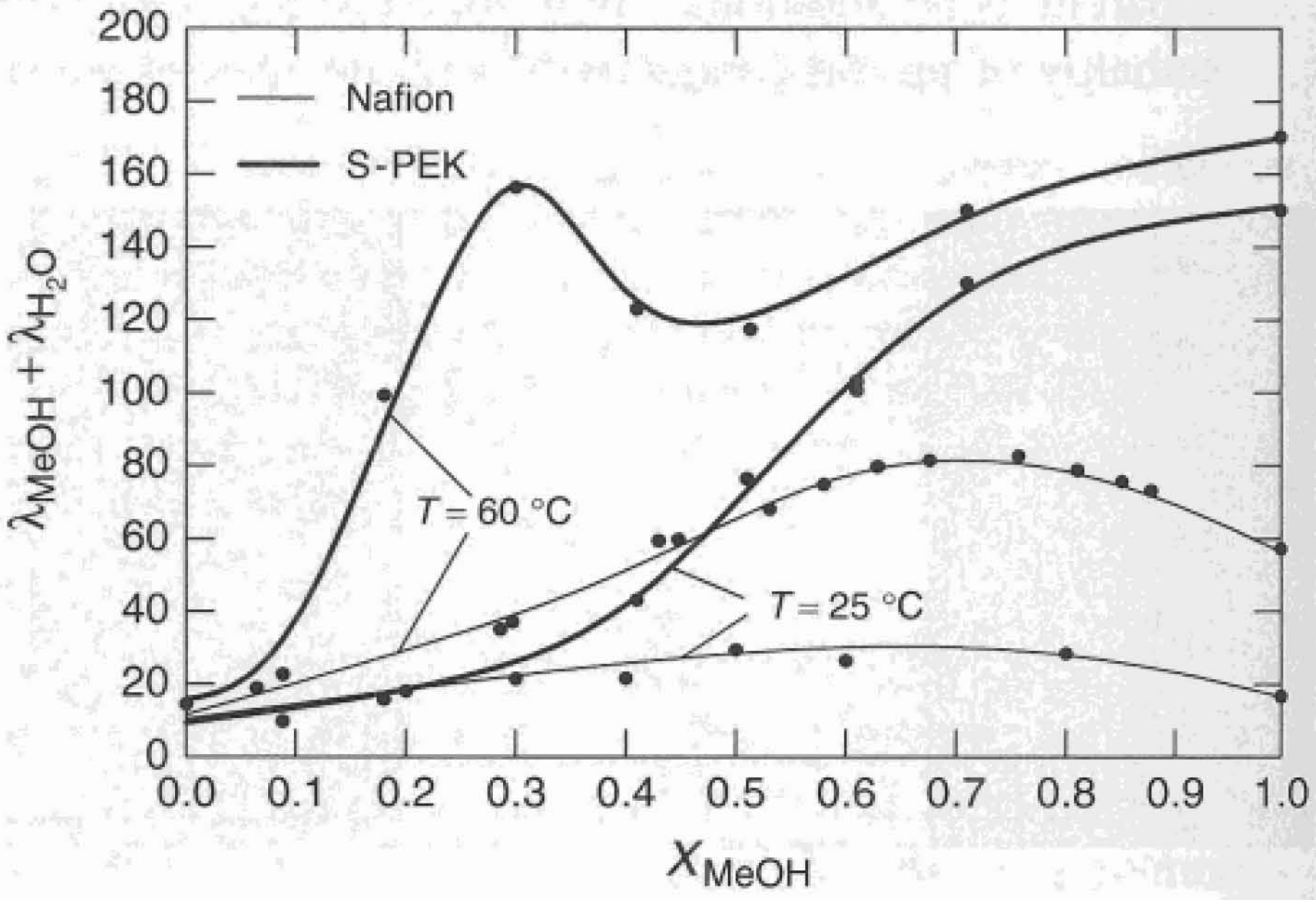


Figure 7. Swelling of Nafion® and a sulfonated poly ether ketone as a function of the methanol mole fraction of water/methanol mixtures for two different temperatures.[27] Note, that the data from Ref. [27b–e] show similar trends for Nafion®, however, with lower swelling for intermediate water/methanol ratios.

increasing methanol concentration. While swelling passes through a shallow maximum at very high methanol concentrations in the case of Nafion® significant, plain sulfonated poly ether ketones show a stronger increase of swelling in the presence of methanol especially at low methanol concentrations. For high ion exchange capacities ($>1.4\,\mathrm{meq\,g^{-1}}$) even dissolution in water/methanol mixtures is observed. Analysis of the water/methanol ratio in the membrane compared to the surrounding solution does not show any fractionalization for not too low solvent uptake ($\lambda > 10$) indicating that water and methanol are absorbed in the same part of the microstructure, i.e., the hydrophilic domain only.[27, 27b–e] With its lipophilic $-CH_3$ and hydrophilic $-OH$ part methanol obviously behaves like a surfactant improving the wetability of the polymer by the water/methanol mixture, thus opening up the microstructure prior to complete dissolution.

The transport coefficient affected the most by this increased swelling is the electroosmotic drag, which has recently been measured for water and methanol as a function of their respective mole fractions. The normalized electroosmotic drag coefficient, $K^{\circ}_{\mathrm{drag}}$ (drag coefficient divided by the mole fraction of the considered molecule), for both water and methanol in Nafion® at room temperature, pre-treated in water/methanol mixtures at 60 °C (see Figure 7), are shown in Figure 8. To a good approximation, the data for water and methanol are identical and increase to values higher than 30 for methanol rich-mixtures. Data taken from the microstructural analysis (see above) indicates that the electroosmotic drag coefficient roughly increases with the fourth power of the channel diameter, which is reminiscent of a Hagen–Poiseuille-type behavior. Only for low solvent levels (narrow channels), does K_{drag} not fall below unity because the proton remains hydrated with at least one water molecule (hydronium ion). Since swelling of plain sulfonated poly ether ketones is even higher than in Nafion® the electroosmotic drag also increases more with increasing methanol concentration (Figure 8).

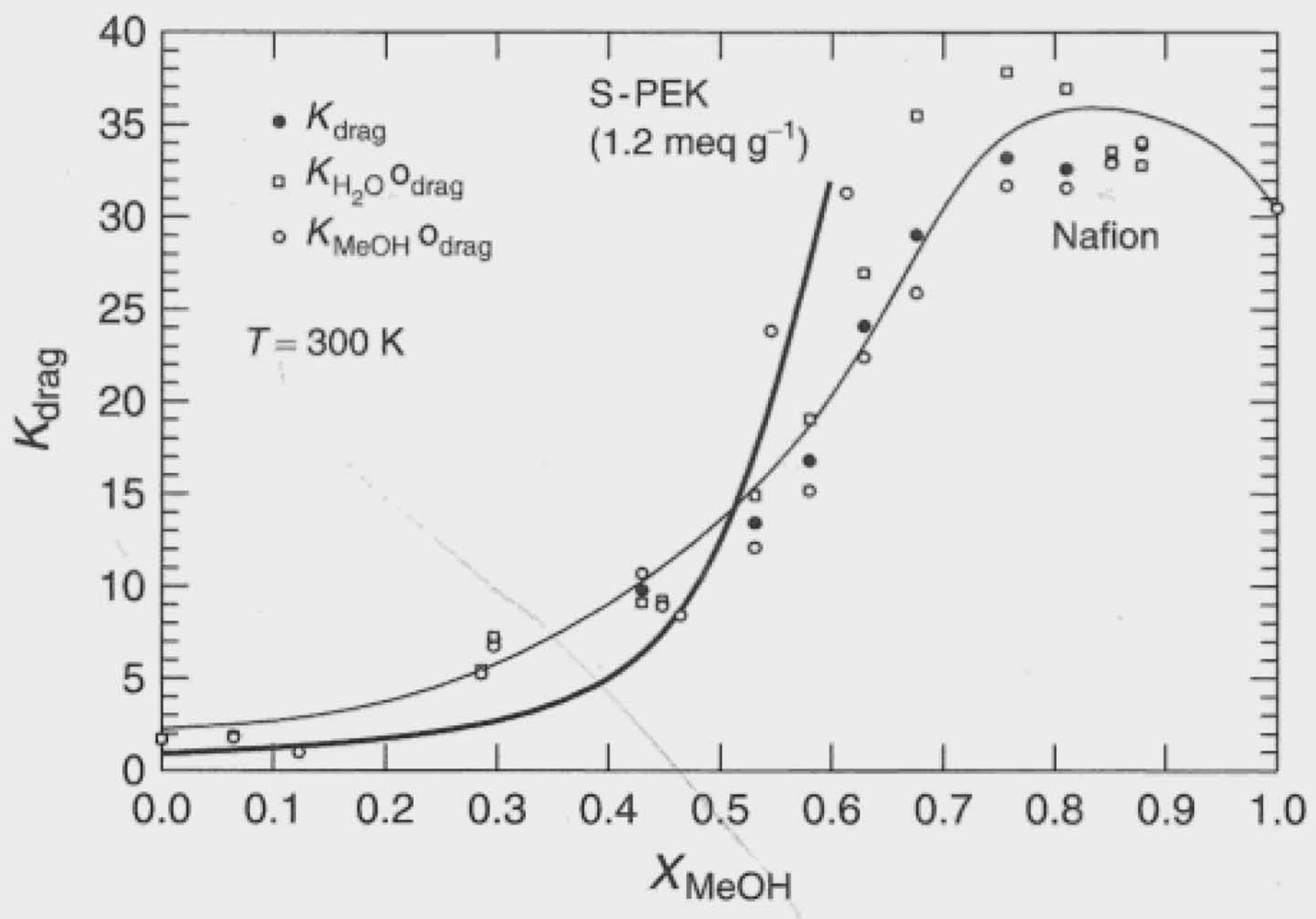


Figure 8. Normalized electroosmotic drag coefficient ($K^{\circ}_{i\mathrm{drag}} = K_{\mathrm{drag}}/x_i$) and the total drag coefficient of water and methanol (see text) in Nafion 117® and a sulfonated poly ether ketone pre-treated in water/methanol mixtures at 60 °C (see also Figure 7).[27]

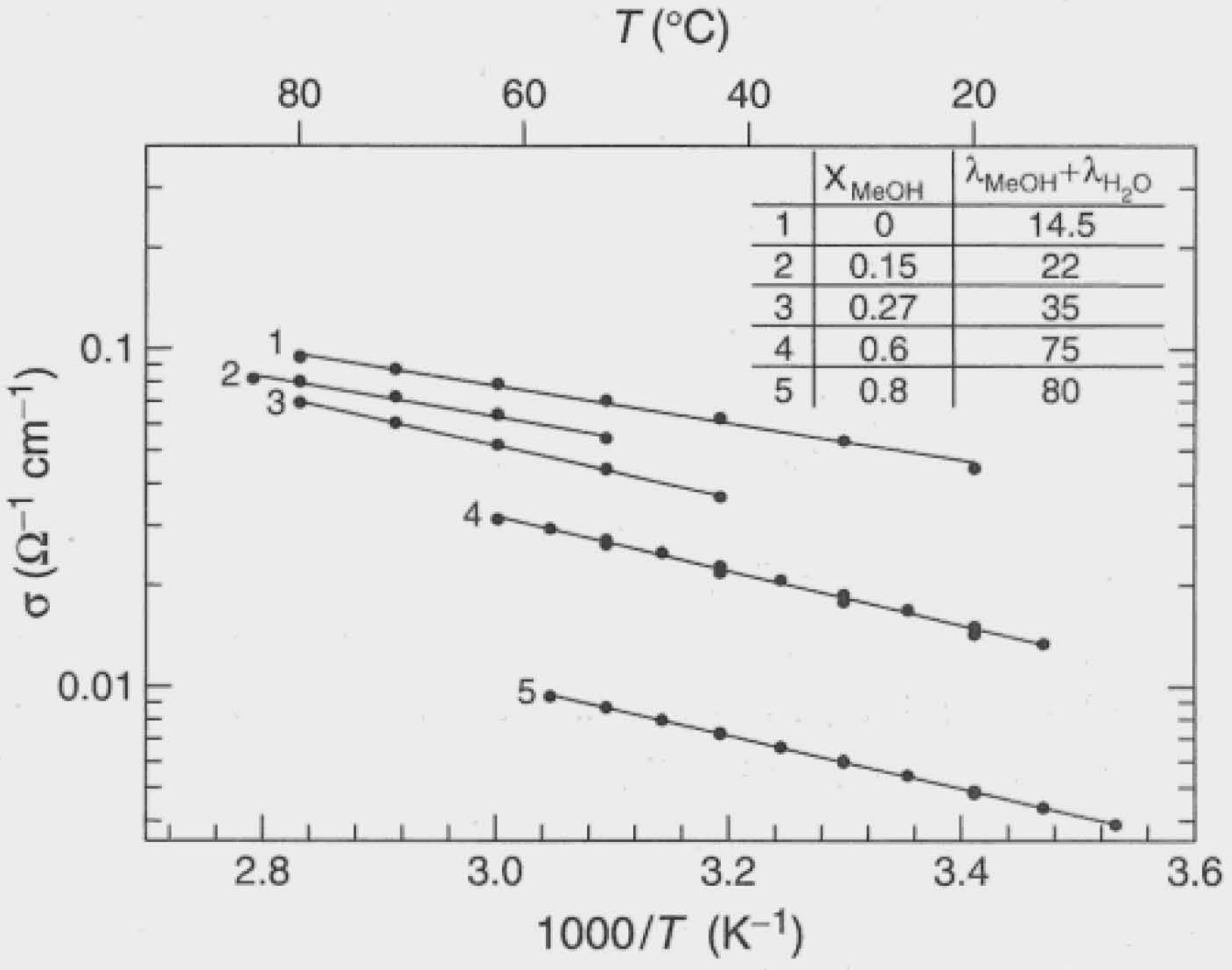


Figure 9. Proton conductivity of Nafion 117® soaked in different water/methanol mixtures at 60 °C (see also Figure 7).[27]

Interestingly, methanol has the opposite effect on the proton conductivity (Figure 9). At increasing methanol mole fraction, proton conductivity decreases significantly although the total solvent uptake increases. Since the diffusion coefficient of both water and methanol increases, the conductivity decrease is most likely due to a decreasing dissociation of the acidic function in the presence of methanol. Because of the lower acidity of the sulfonic acid function in poly ether ketones, an even stronger decrease in the proton conductivity with increasing mole fraction of methanol is expected.

3.3 Membrane modification by cross-linking and blending

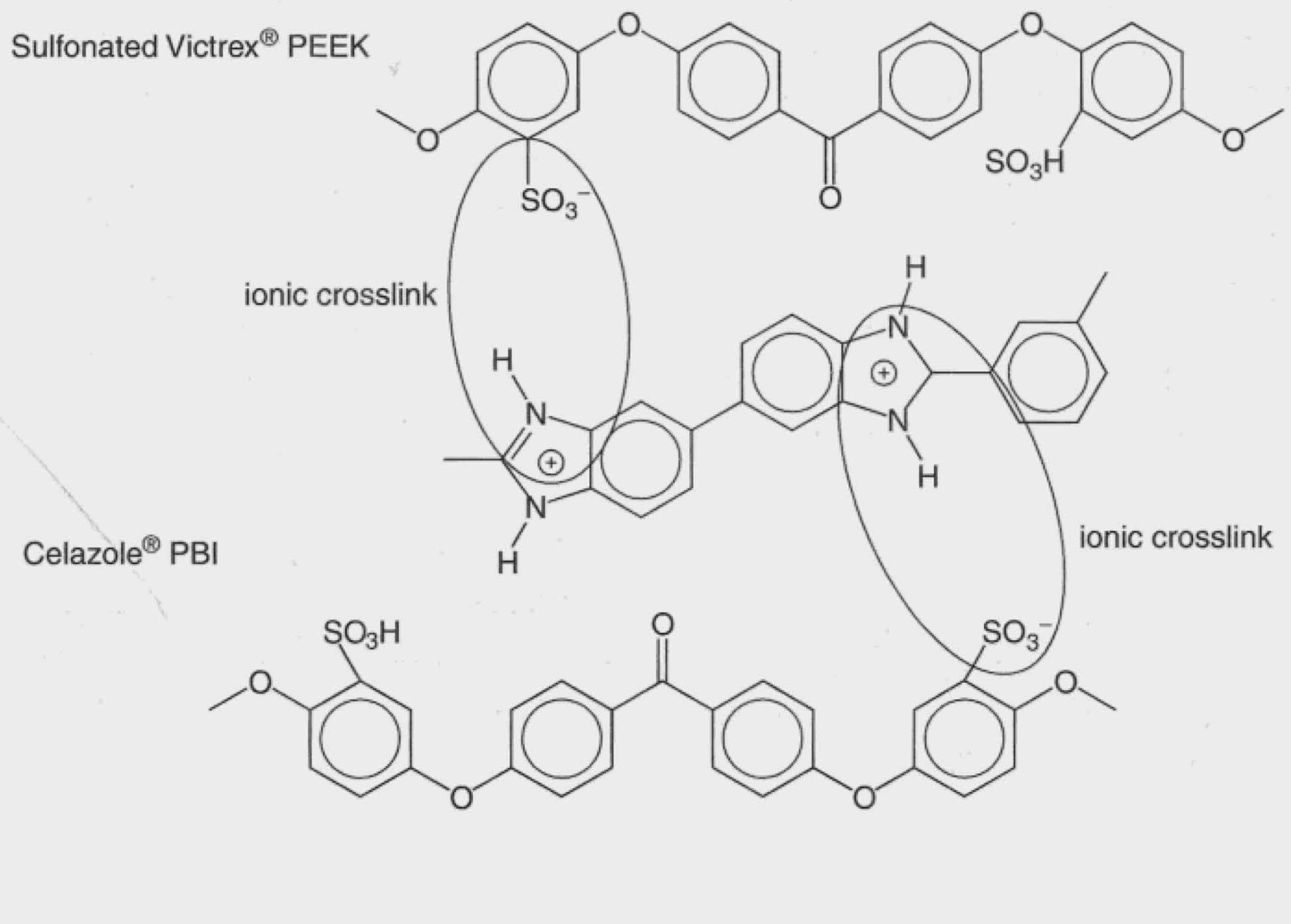
Based on the differences in the microstructures of sulfonated poly arylenes and Nafion® along with the consequences for the morphological stability, cross-linking and blending were envisaged to improve the properties of plain sulfonated poly arylenes.[13] In one of the early pieces of work on sulfonated poly arylenes[5] cross-linked varieties had already been presented. Part of the sulfonic acid groups had first been transferred to sulfonyl *N*-imidazolides before these were reacted with 4,4′-diaminodiphenylsulfones forming sulfonamide cross-links. In the particular case reported (sulfonated Victrex® PEEK) swelling was, indeed, reduced from 430% to 180% at the expense of about 50% of the proton conductivity. More recently, a process comprising of the alkylation of sulfonate groups with αω-dihalogenoalkanes of different chain lengths has been developed for cross-linking sulfonated Udel® PSU.[28, 29]

In the first route, mixed sulfonate/sulfinate PSU has been obtained by partial oxidation of sulfinated PSU with NaOCl. The residual sulfinate groups were then used for the cross-linking reaction.[28] In a second route, blends of sulfinated and sulfonated PSU have been cross-linked, resulting in cross-linked PSU-sulfinate in which sulfonated PSU is entangled.[29] Particularly for short alkane-cross-linkers, both routes reduced swelling compared to the very high swelling of plain sulfonated PSU up to temperatures of at least 80 °C; again at the expense of the conductivity, which hardly exceeded a value of $10^{-2}\,\mathrm{S\,cm^{-1}}$ for cross-linked membranes. But the more severe problem with this type of cross-linking appears to be the brittleness of such membranes in the dry state increasing the risk of membrane fracturing.

In contrast to directional covalent bonds, ionic cross-linking may strengthen the membrane without introducing brittleness. These are formed by blending a sulfonated polymer, e.g., in its $\mathrm{Na^+}$-form, with a basic polymer. Subsequent ion-exchanging in acid leads to the formation of the acid $\mathrm{H^+}$-form of the sulfonated polymer, which then reacts with the basic blend component. While weakly basic polymers act only as proton acceptors in hydrogen bonds with the acidic polymer, strongly basic polymers may be fully protonated by the acidic polymer introducing ionic interactions between the blend components. When there is an excess of acidic sites to basic sites in the blend, ionic or hydrogen bond cross-links exist along with unneutralized sulfonic acid functions, which may still act as a source for protonic charge carriers in the presence of water. Accordingly, ionically cross-linked blends of highly sulfonated Udel® PSU and Victrex® PEEK as acidic components and weakly basic poly-sulfoneorthosulfonediamines or more basic PBI (PBI Celazole®) in different ratios according to different effective equivalent weights have been prepared.[30, 31]

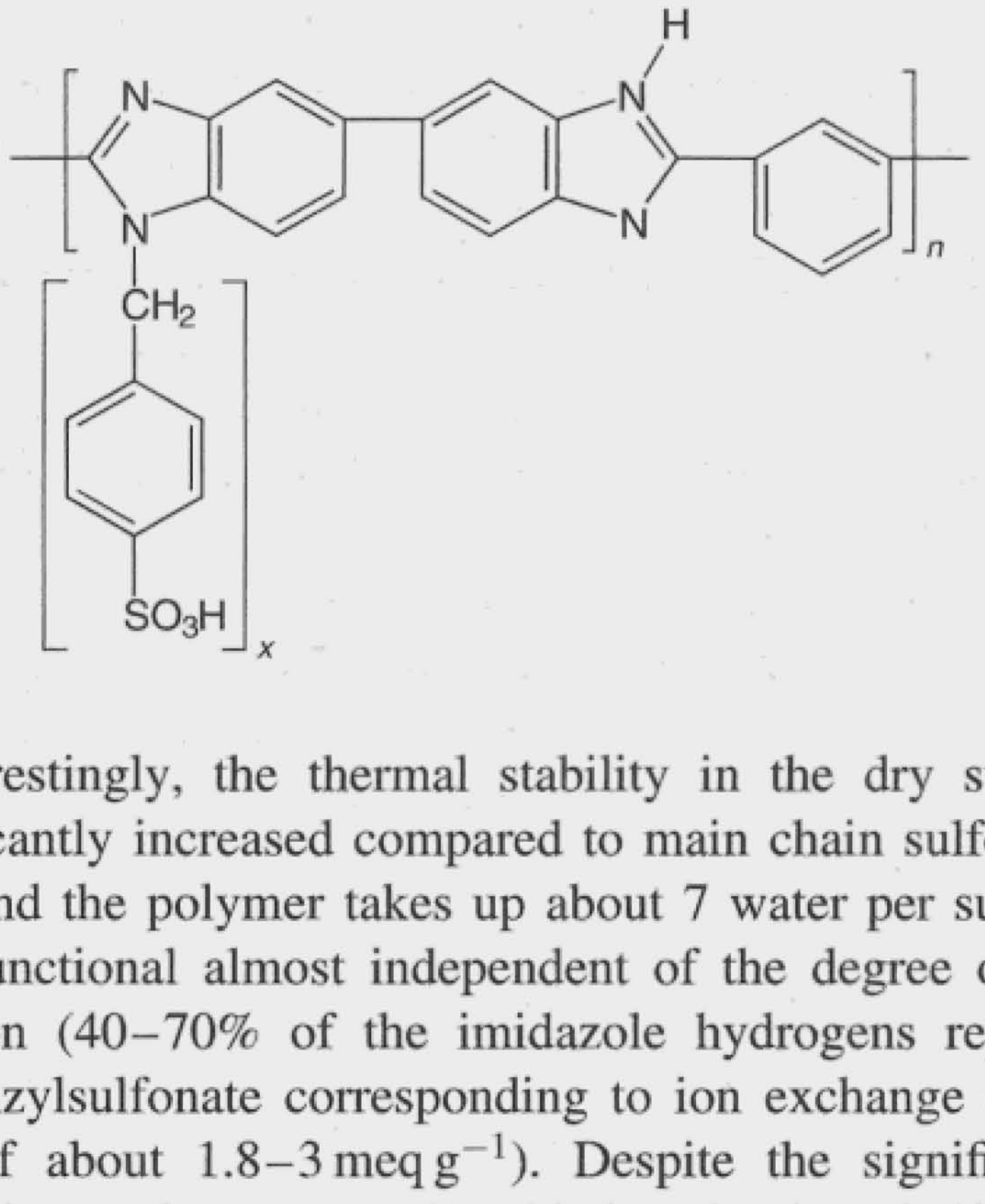
This type of blending causes the water-soluble acidic polymer to become virtually insoluble. Swelling in water and brittleness in the dry state are reduced compared to plain sulfonated polymers of similar ion exchange capacity. As expected, these effects increase with increasing amount and basicity of the basic component. But even for the best systems (blends of sulfonated PEEK and PBI, see scheme above), swelling is still higher than for covalently cross-linked membranes, indicating that ionic cross-links start to hydrolyze in water at temperatures above about 80 °C. Additionally, under these conditions irreversible reactions start to occur as indicated by the appearance of a strong aromatic smell and a loss of ion exchange capacity (unpublished results from the author's laboratory). It is also worth mentioning that the hydration behavior and transport properties of such blends resemble those of plain sulfonated poly ether ketones (unpublished results from the author's laboratory), but the advantageous properties are conserved to somewhat higher temperatures since the morphological stability is increased. Furthermore, the flexibility in the dry state is even better than for uncross-linked membranes. This has also been achieved by blending sulfonated poly ether ketones with inert polymers such as PES.[10]

In order to combine the reduced swelling of covalently cross-linked membranes with the flexibility of ionically cross-linked membranes, the development of combined covalently/ionically cross-linked blend membranes is currently underway.[31]



4 GRAFTED PBI

Since aromatic PBIs are well known for their remarkable thermal stability and vapor barrier properties, they have been considered not only as constituent of proton conducting complexes (adducts) with oxo-acids (see **High-temperature membranes**, Volume 3), but also as the backbone of sulfonated polymers conducting protons in the hydrated state.[32, 33] While main chain sulfonated PBI, which is referred to as "stabilized PBI" due to its remarkable thermal, mechanical and chemical durability,[34] does not swell in water and hence does not show noticeable proton conductivity, PBI in which the imidazole hydrogen is replaced by a sulfonated aryl or alkyl substituents shows interesting hydration and conductivity properties. For instance, polybenzimidazole-N-benzylsulfonate is directly obtained by forming a PBI anion via reaction with a soluble base (e.g., LiH) and subsequent reaction with sodium (4-bromomethyl) benzenesulfonate.[32]



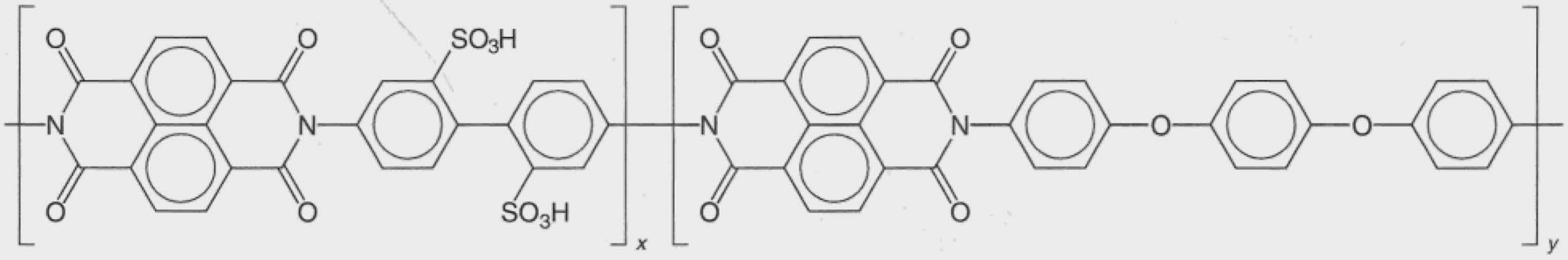
Interestingly, the thermal stability in the dry state is significantly increased compared to main chain sulfonated PBI, and the polymer takes up about 7 water per sulfonic acid functional almost independent of the degree of sulfonation (40–70% of the imidazole hydrogens replaced by benzylsulfonate corresponding to ion exchange capacities of about 1.8–3 $\mathrm{meq\,g^{-1}}$). Despite the significantly higher ion exchange capacity, this is only about half of the water uptake of Nafion® or sulfonated poly ether ketones. Unfortunately, no temperature dependent swelling data are available as yet. If this low swelling was maintained to high temperatures, which is to be expected from the vitreous character of the PBI backbone, the comparatively low conductivity ($<10^{-2}\,\mathrm{S\,cm^{-1}}$ at 40 °C and 100% RH) may even be acceptable for certain applications where low electroosmotic drag is required. This has not yet been confirmed experimentally, but is expected to be low at low degrees of hydration (see above).

As is the case for sulfonated polyarylene main chain polymers, grafted PBI suffers from a loss of flexibility in the dry state, which actually can not be recovered by repeated soaking in water. This raises the question of specific interactions between the unprotonated imidazole N and the acidic function, which has not yet been addressed. It is worth mentioning that for alkyl substituted varieties, some of the drawbacks seem to be less severe.[35] The high flexibility of the side chains reduces the brittleness and leads to a higher water uptake. Unfortunately, proton conductivity barely exceeds a value of $10^{-3}\,\mathrm{S\,cm^{-1}}$.

5 SULFONATED BLOCK COPOLYMERS (NAPHTHALIC POLY-IMIDES)

A very interesting approach to controlling the sulfonation sequence along the polymer backbone has recently been advanced by using sulfonated monomers in the polymerization of different phthalic and naphthalic polyimides. After phthalic polyimides had been found to be insufficiently stable under fuel cell conditions, the focus was shifted to sulfonated polyimides based on 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA).[36] In a first step NTDA is polymerized with a diamine monomer containing two sulfonate groups (4,4′-diaminodiphenyl 2,2′-disulfonic acid (BDSA)) after the latter has been neutralized to obtain solubility in m-cresol. The ratio of NTDA and BDSA in the first step is varied to control the length of the ionic sequence. In a second step, remaining NTDA monomers are introduced with either 4,4′-oxydianiline (ODA) or an equimolar mixture of 4,4′ and 3,4′-ODA in order to space the ionic blocks by hydrophobic sequences.

The number of monomeric units X in the sulfonated part was varied from 1 to 9 while keeping the ratio X/Y constant (3/7 corresponding to an ion exchange capacity of about 1.3 $\mathrm{meq\,g^{-1}}$) for most polymers except for a few samples with higher ion exchange capacity. The vitreous character of the polymer steams from the phenylene bonds



in the sulfonated part while the unsulfonated hydrophobic part has some residual flexibility.

For all hydrophilic sequence lengths X, the water uptake under 100% relative humidity is around $\lambda = 10H_2O/{-}SO_3H$, which is close to the value observed for sulfonated poly ether ketones (Figure 2). But the amount of water taken up when the membrane is soaked in water increases with increasing block length X and reaches a value of $\lambda = 30$ for $X = 9$. Surprisingly, proton conductivity passes through a maximum at $X = 3$ ($\sigma = 1.8 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ at room temperature) indicating that the microstructure changes qualitatively with X. As opposed to phthalic polyimides, where the size of the ionic domain varies linearly with the block length, the microstructural changes in naphthalic polyimide are more complex as indicated by SAXS measurements.[36] In fact, only for $X = 3$ is a distinct ionomer peak observed corresponding to a typical separation of 25 nm which does not correspond to the length of the ionic sequence (7 nm). For all sulfonation patterns, the absence of typical Porod behavior at high momentum transfers suggests the absence of sharp interfaces between the hydrophobic and hydrophilic parts and some structural regularity within the hydrophilic part. The overall picture which emerges from the SAXS study is that the hydrophobic parts probably aggregate during the film forming process forming lammelar or disk-like domains surrounded by highly solvated ionic sticks. The latter form a continuous hydrophilic domain in which hydrophilic islands are embedded (Figure 10).

This microstructure also explains the residual volume change upon water uptake. The anisotropy of the volume change and also of the proton conductivity suggest that the hydrophobic lamellae do align parallel to the membrane surfaces. Unfortunately, no data on electroosmotic drag and permeation are available at present. These are expected to strongly depend on the fine structure of the hydrophilic domain (see above). Swelling data at higher temperature have not been reported yet, but the significantly lower swelling in pure methanol compared to water at room temperature,[37] which is a unique feature of this class of membranes, provides an interesting perspective for DMFC applications.

It should be noted that the limited solubility of naphthalic polyimides in m-cresol has recently been improved by introducing phenyl ether bonds and/or bulky groups.[38]

6 SULFONATED POLY-PHENOXYPHOSPHAZENES (POP)

The chemical and thermal stability and the high flexibility of polyphosphazene backbones and the ease of chemically attaching various side chains to this backbone has already enabled the successful development of the fully polymeric Li^+ conducting electrolyte methoxy-ethoxy-ethoxy-phosphazene (MEEP) for battery applications.[39] Functionalization of poly-dichlorophosphazene with methylphenoxy groups leads to poly-bis-3-methylphenoxyphosphazene, which can easily be sulfonated with SO_3 in 1,2-dichloroethane (DCE) to yield high ion exchange capacities (up to $2.0\,\mathrm{meq\,g^{-1}}$).[40]

SAXS data clearly show nano-separation as a function of ion-exchange capacity and degree of hydration,[41] which closely resembles that in sulfonated poly ether ketones. Additionally, diffraction intensity in the wide-angle range indicates some two-dimensional short-range order, which

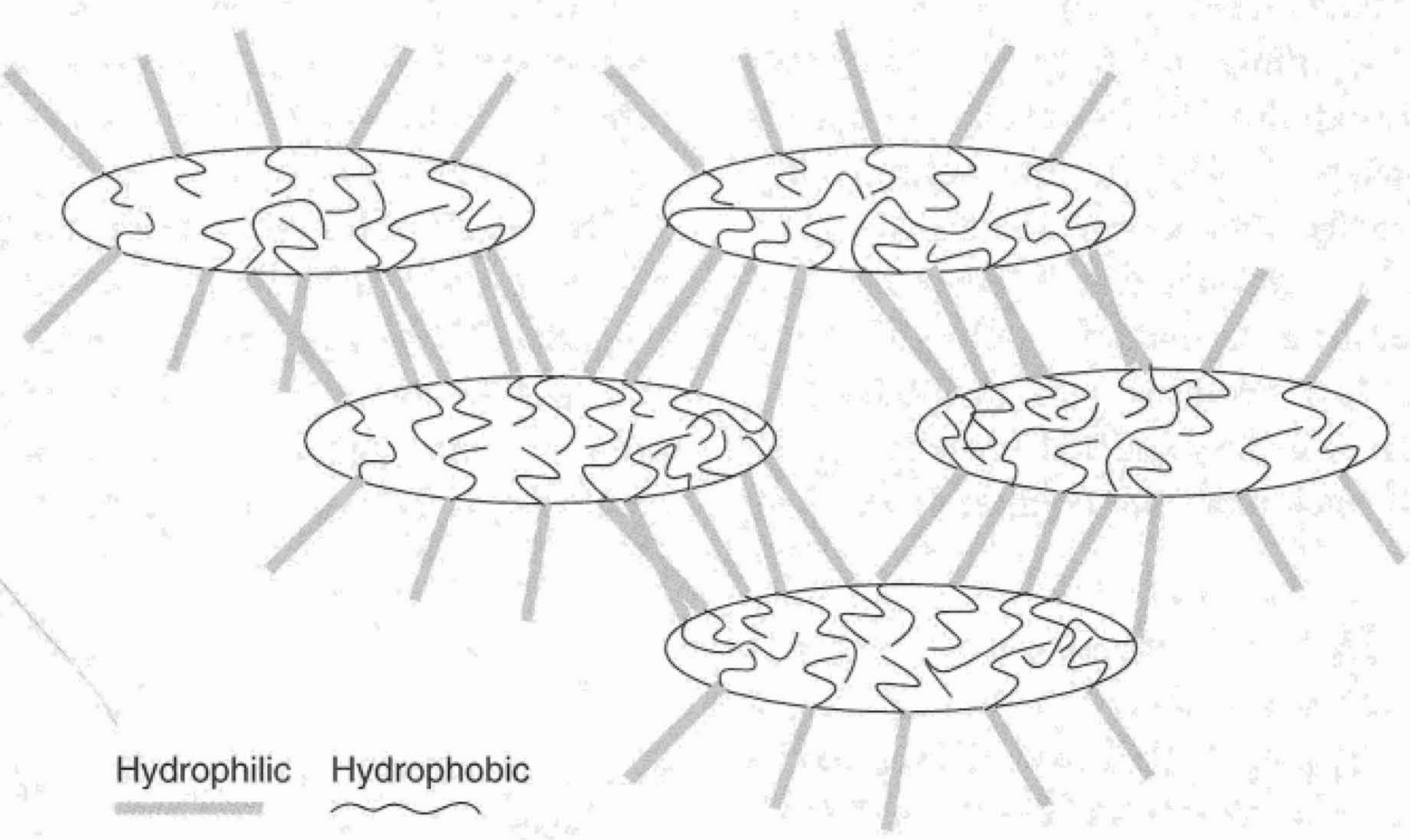
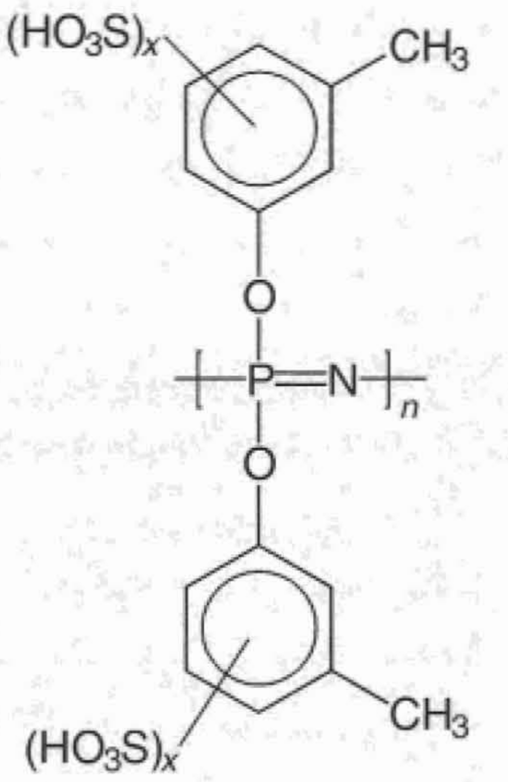


Figure 10. Schematic illustration of the suggested microstructure of a naphthalic polyimide[36] (see text).



is not completely disrupted by swelling. Proton conductivities as a function of the water volume fraction have been interpreted in terms of a percolation threshold at significantly higher water contents than for Nafion®.[42] Apart from all the effects discussed for sulfonated poly ether ketones (Section 3.2.3.1), this finding is in accordance with a less pronounced hydrophobic/hydrophilic separation as compared to Nafion®. Although these microstructural features are reminiscent of the poly ether ketones and the chemical character of the sulfonic acid function is also expected to be similar, the reported transport coefficients show distinctly different behavior. While the proton conductivity shows a similar dependence on the water content as observed for sulfonated poly ether ketones ([41] and Figure 4), the water and methanol diffusion coefficients are more than one order of magnitude lower. The water diffusion coefficients were actually obtained from the desorption kinetics[40] and the mutual diffusion of methanol and water from the equilibration rate of a membrane containing CH_3OD and D_2O with surrounding D_2O.[42] In both cases, the driving force is a gradient of the activities (chemical potentials) of water and/or methanol, and the obtained chemical diffusion coefficients are related to the component *i* self-diffusion coefficients by the corresponding thermodynamic factors ($d\ln a_i/d\ln c_i$). For water, this factor approaches zero for activities close to unity (Figure 2), i.e., the chemical driving force for equilibrating concentration gradients almost vanishes. Therefore, tracer or self-diffusion data are required to determine whether POP shows transport behavior that is qualitatively different to other hydrated sulfonated polymers. This also holds for water and methanol crossover, which, on the basis of the available diffusion data, is likely to be lower. As pointed out above, however, the complex relation between self-diffusion, chemical diffusion, electroosmotic drag and permeation make such ad hoc conclusions problematic.

As opposed to sulfonated poly ether ketones, POP membranes show surprising oxidation resistance (in hot hydrogen peroxide/ferrous ion solution), but like most sulfonated polyarylenes, plain POP dissolves in liquid methanol at room temperature. However, photo cross-linking with benzophenone as the photoinitiator[40] significantly improves the swelling in water and water/methanol mixtures.

7 PERFORMANCE IN HYDROGEN AND METHANOL FUEL CELLS

A few hydrocarbon-based membranes have already been tested in fuel cells. The sulfonated poly ether ketones display current/voltage characteristics in hydrogen fuel cells similar or even better than that for Nafion®, and have been reported by several laboratories (e.g., Ref. [8]). This is surprising considering the lower proton conductivity of sulfonated poly ether ketones for a given water content. In fact, high conductivity strongly depends on the presence of liquid water (Figure 11), and a sharp decrease in conductivity is observed for water activities below the dew point of water (see also Figure 4). Obviously, high hydration is maintained under the usual fuel cell conditions. The lower electroosmotic drag of water (see Figure 6) reduces the problem of dehydrating the membrane at the anode side, and the generally thinner membranes (20–40 μm compared to 100 μm for Nafion 117®) allow for a more effective back transport of water from the cathode to the anode side by permeation (at high water activity where the chemical driving force disappears) and by chemical diffusion (at low water activities). There

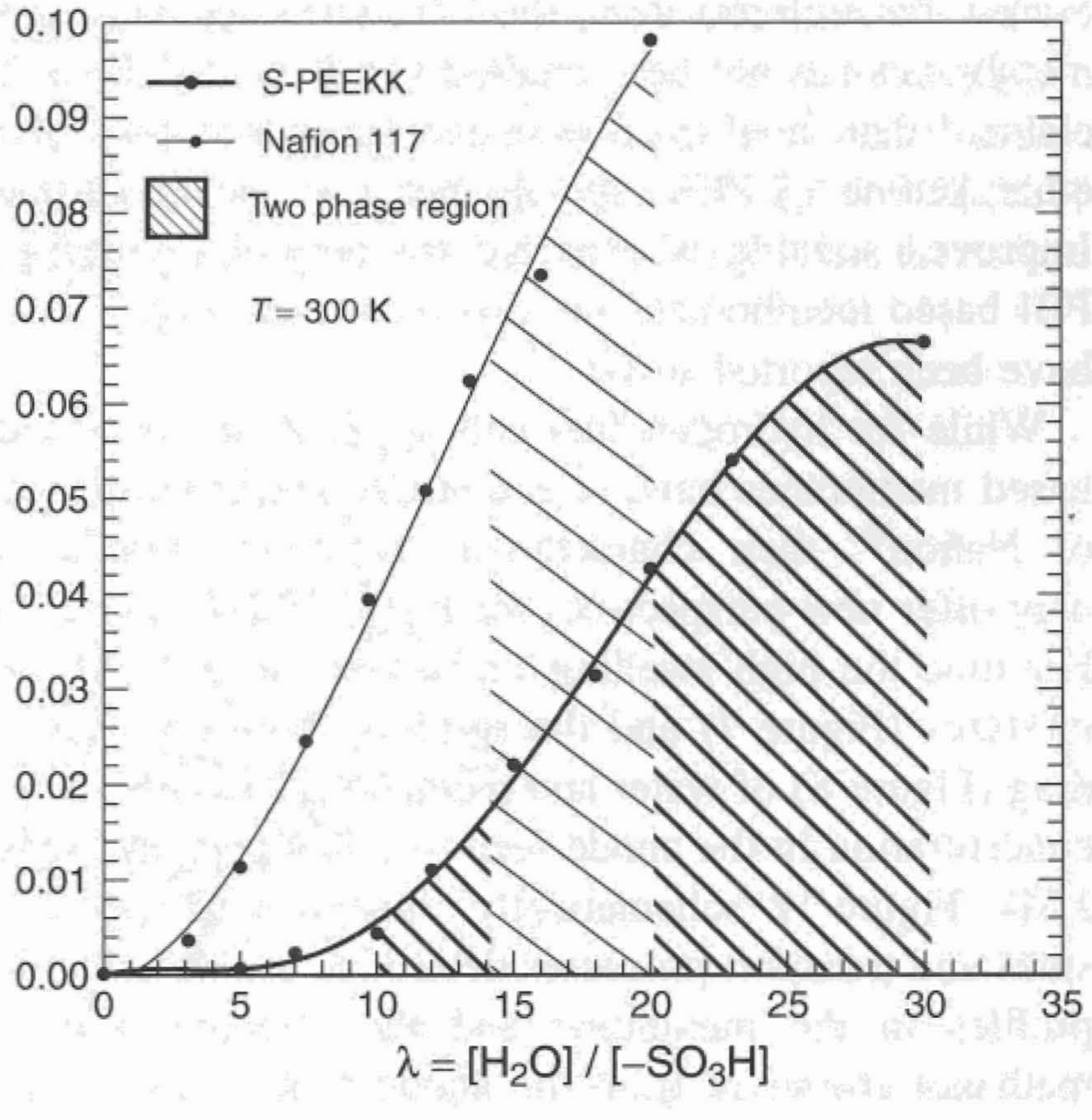


Figure 11. Proton conductivity of Nafion 117® and a sulfonated poly ether ketone as a function of the degree of hydration. The regimes where water is present as a distinct second phase is shaded.[13]

are also indications that lower ohmic resistance of the membrane/electrode interface is more favorable for the performance of hydrocarbon based membranes. The good performance is also a direct indication of low hydrogen and oxygen permeability, which is not treated explicitly in this chapter (it should be noted however that ionomers as additive of the gas diffusion electrodes require at least some gas permeability). Long term tests of sulfonated poly ether ketones (e.g., Ref. [8]) and poly-imide membranes[36] have already demonstrated that these may function in a hydrogen fuel cell at a typical temperature of $T = 80\,^\circ\mathrm{C}$ for several thousand hours. Although such membranes readily dissolve in hydrogen peroxide solutions, they are apparently resistant to oxidation under the conditions of an operating fuel cell.

But the failure of single cells and the closer inspection of membranes even after successful long term operation reveal different types of irreversible changes (unpublished results from different laboratories). As a result of the brittleness in the dry state, membranes may simply develop cracks, when the membrane is not uniformly humidified. Under wet conditions, on the other hand, plain sulfonated polyarylenes tend to slowly lose some ion exchange capacity, toughness, and finally their morphological integrity. Although the precise reasons for this behavior are not yet clear, one should keep in mind that for linear, uncross-linked polymers the cleavage of a very low portion of bonds may have a drastic effect on the morphological stability. Both brittleness in the dry state and decreasing toughness in the wet state are reduced for ionically cross-linked membranes, but unfortunately, the long term behavior of such membranes has not been studied yet. Recently, it has been claimed that flexible cross-linked sulfonated poly arylene ether ketone (S-PEK) membranes may be accessible.[43] Improved stability is expected for poly-phosphazene and PBI based membranes, but also for these no fuel cell tests have been reported so far.

While for hydrogen fuel cell applications, hydrocarbon based membranes have to essentially match the properties of Nafion®, their characteristic microstructural features may offer new perspectives for liquid DMFC applications. For this, the high swelling of Nafion® in water/methanol mixtures (Figure 7) and the resulting high electroosmotic drag (Figure 8) of water and methanol, limits the methanol concentration in the anode feed to a few percent (typically 1 M). Figure 12 schematically illustrates which sources, sinks and transport processes determine the water/methanol profiles in the membrane and the effective water and methanol crossover from the anode to the cathode. Finite element type calculations using available thermodynamic and transport data clearly show that water and methanol crossover is dominated by electroosmotic drag for not too low protonic currents. K_{drag} is lower in hydrocarbon based membranes (Figure 6) provided that exaggerated swelling is prevented. This may be achieved by cross-linking, and the surprisingly good performance of unoptimized MEAs using sulfonated poly arylene ether ether ketone (S-PEEK)/PBI blends as the membrane material[31] demonstrates the appeal of this approach.

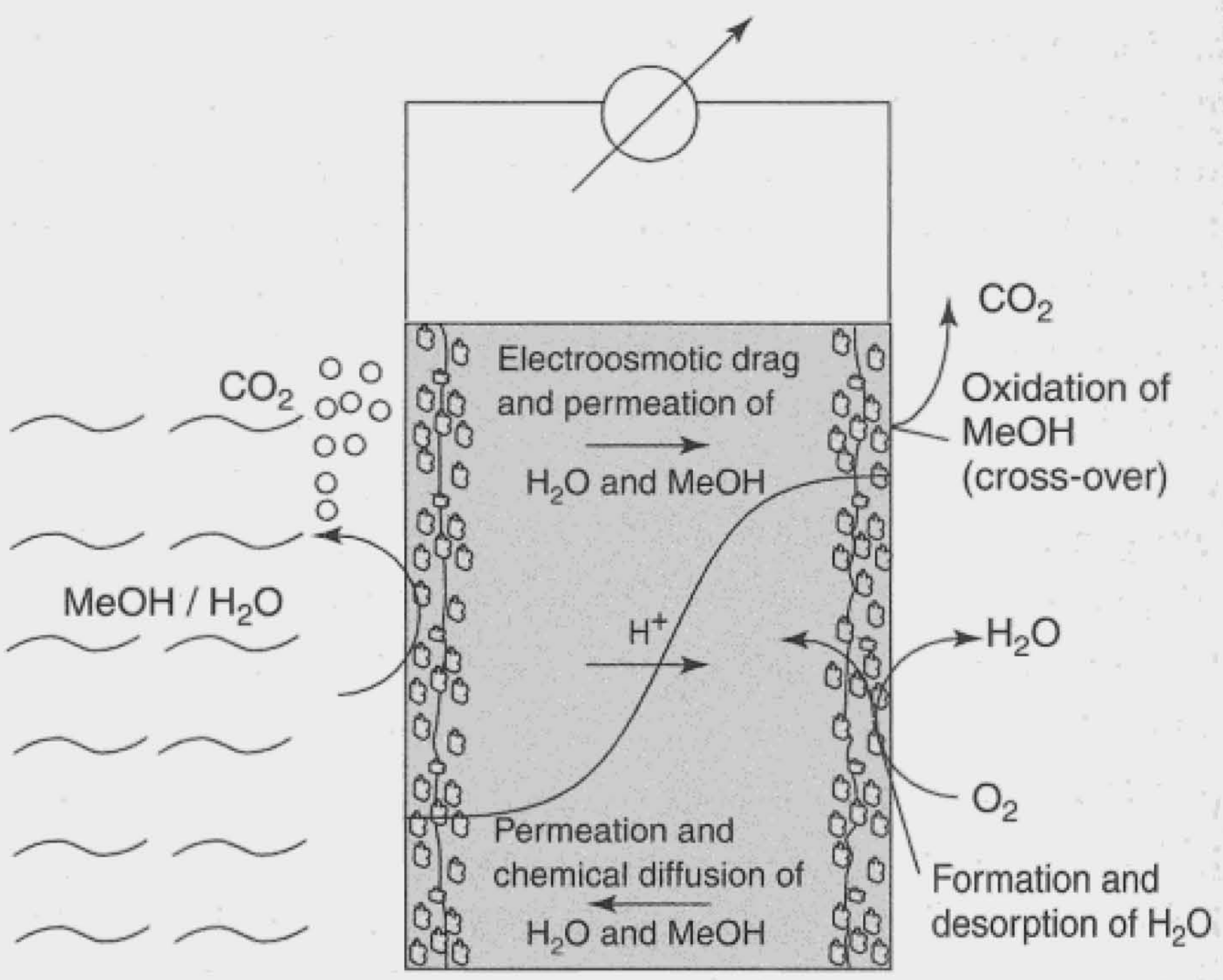


Figure 12. Schematic illustration of the different sources, sinks and transport processes determining the water/methanol profiles in the membrane and crossover from the anode to the cathode.

8 AN UNCONVENTIONAL APPROACH

Since the very high proton conductivity of all of the above discussed membrane materials relies on water activities close to the dew point of water, the maximum operation temperature is approximately given by the boiling point of water, i.e., $100\,^\circ\mathrm{C}$ at $p = 10^5$ Pa, which is a characteristic limitation for conventional membranes. It has been shown, however, that intercalation of heterocycles (e.g., imidazole, pyrazole, and benzimidazole) leads to proton conductivities between 150 and 250 °C, which are comparable to the conductivities of hydrated polymers.[44] Indeed, such heterocycles form similar hydrogen bond networks to water, and the transport properties in the liquid state are also similar to water for a given temperature relative to the melting point (e.g., for a mixture of benzimidazole with 10 m/o H_3PO_4 a conductivity of $5 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ is observed at $200\,^\circ\mathrm{C}$).[45] Of course, the volatility of heterocycles prevents them from being used in open electrochemical systems, such as fuel cells. In contrast to using water as the proton solvent, which is usually supplied to the membrane by humidifying the anode and cathode gases and is produced at the cathode by the electrochemical reaction, the use of heterocycles as the proton solvent requires their immobilization in the polymer membrane in such a way that high mobility of the protonic charge carriers is still guaranteed. While proton mobility in hydrated polymers has large contributions from the diffusion of hydrated protons (see also Figure 4), proton mobility in an environment of immobilized heterocycles must completely rely on structure diffusion, comprising proton transfer between heterocycles and solvent reorganization. For oligomeric model systems consisting of polyethylene oxide segments (spacers) terminated by imidazole groups, such a mechanism has recently been confirmed experimentally.[46] Such oligomers are highly viscous oils which locally aggregate in such a way that dynamical hydrogen bonds are formed between terminating groups of different oligomers (Figure 13). It is within this hydrogen bonded structure, that high mobility of protonic defects (excess protons) is observed ($D_\sigma > 10^{-6}\,\mathrm{cm^2\,s^{-1}}$). Recently, this mechanism has even been confirmed for fast proton transport at medium temperature (150–250 °C) in fully polymeric systems comprising similar soft spacers in their architecture (recent work from the authors laboratory). But before this class of materials may be considered for fuel cell applications, chemically more stable spacers have to be found and the poisoning of the anode, which has been observed for monomeric imidazole as a proton solvent,[47] has to be excluded.

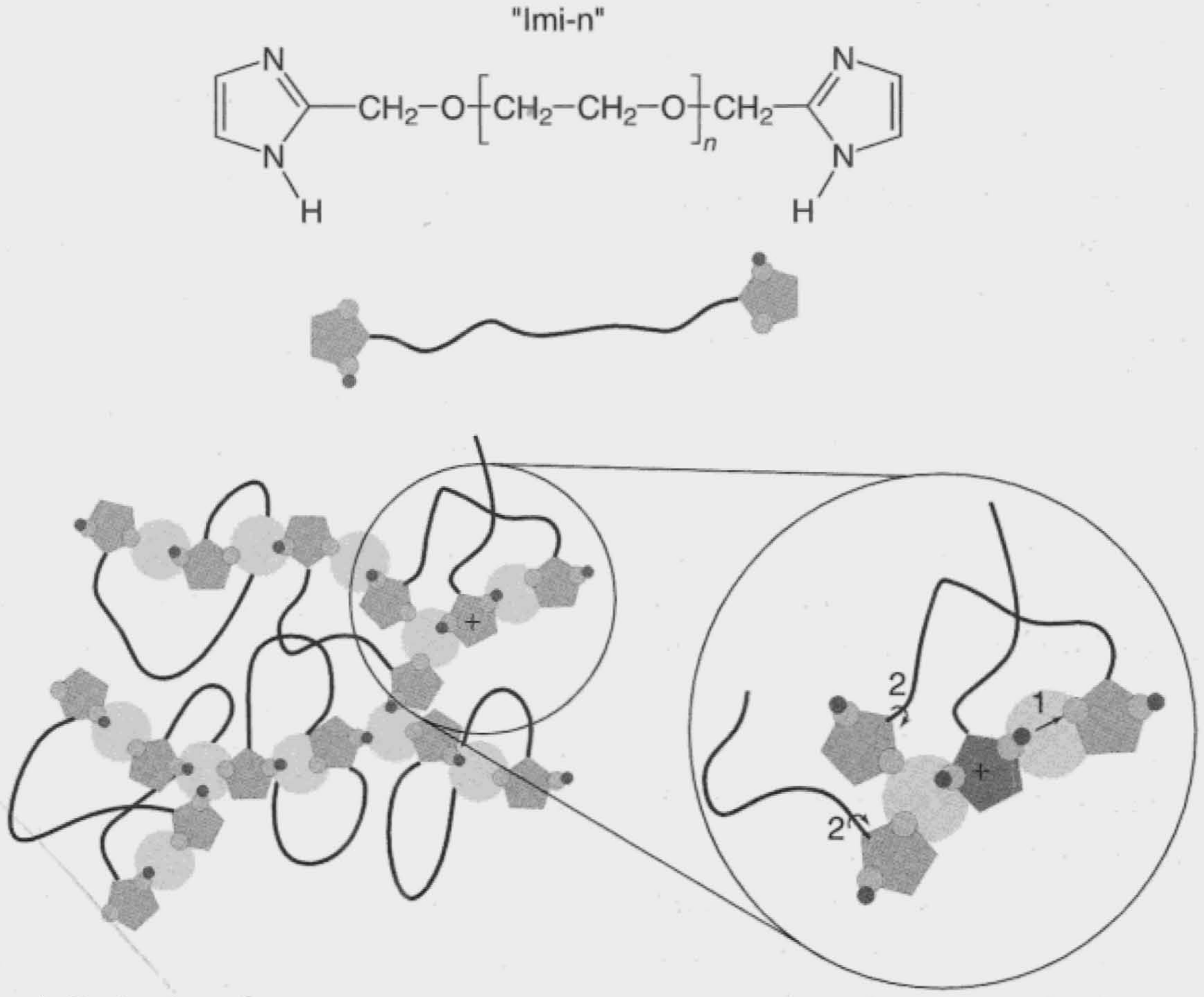
9 SUMMARY AND OUTLOOK

Many sulfonated fully aromatic high performance polymers combine good durability and high proton conductivity in the wet state, making them interesting low-cost alternatives for perfluorosulfonic polymers (e.g., Nafion) as membranes in hydrogen fuel cells. However, a number of constraints have to be considered, some of which may be overcome by membrane modifications.

While the sharp decrease in conductivity with decreasing water content is a direct consequence of the inherently lower acidity and nano-separation compared to perfluorosulfonic polymers, the poor mechanical properties (brittleness in the dry state and increasing softness in the wet state) may be improved by blending and/or crosslinking.

On the other hand, the low electroosmotic drag (especially observed in sulfonated poly ether ketones) reduces the problem of membrane dehumidification and provides an interesting perspective for liquid DMFCs. However, for this application the tremendous swelling in water/methanol mixtures has to be reduced significantly, which also may be achieved by appropriate blending and/or crosslinking.

While proton and water transport are generally related in the above types of membranes, pure proton conductivity in low humidity environment at higher temperature may be achieved with heterocycles (e.g., imidazole) as proton



1: Proton transfer
2: Structural reorganization by hydrogen bond

Figure 13. Schematic illustration of imidazole aggregation and diffusion of protonic defects in the oligomeric system Imi-n. (Reproduced from Schuster *et al.* (2001)[46] with permission from Elsevier Science.)

solvent in fully polymeric systems, which may be relevant for fuel cells using water/methanol vapor as a fuel.

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REFERENCES

1. *J. Membr. Sci.* (special issue), 185 (2001).
2. C. A. Linkous, *Int. J. Hydrogen Energy*, **18**, 641 (1993).
3. I. Colon and D. R. Kelsey, *J. Org. Chem.*, **51**, 2627 (1986).
4. M. Rehan, A. D. Schlüter and G. Wegner, *Macromol. Chem.*, **191**, 1991 (1990).
5. R. Nolte, K. Ledjeff, M. Bauer and R. Mülhaupt, *J. Membr. Sci.*, **83**, 211 (1993).
6. P. Genova-Dimitrova, B. Baradie, D. Foscallo, C. Poinsignon and J. Y. Sanchez, *J. Membr. Sci.*, **185**, 59 (2001).
7. J. Kerres, W. Cui and S. Reichle, *J. Polym. Sci.*, **A34**, 2421 (1996).
8. B. Bauer, D. J. Jones, J. Rozière, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, A. Peraio, S. Besse and E. Ramunni, *J. New. Mater. Electrochem. Syst.*, **3**, 93 (2000).

8a. F. Wang, M. Hicker, Q. Ji, W. Harrison, J. Mecham, T. A. Zawodzinski and J. E. McGrath, *Macromolecular Symp.*, **175**, 387 (2001).

9. M. Ise, 'Polymer Elektrolyt Membran: Untersuchungen zur Mikrostruktur und zu den Transporteigenschaften für Protonen und Wasser', Ph.D. Dissertation, University of Stuttgart (2000); also available on the world wide web: **http://elib.uni-stuttgart.de/opus/volltexte/2000/662/**
10. K. D. Kreuer, *J. Membr. Sci.*, **185**, 29 (2001).
11. G. Gebel, *Polymer*, **41**, 5829 (2000).
12. T. D. Gierke, G. E. Munn and F. C. Wilson, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1687 (1981).
13. K. D. Kreuer, Th. Dippel and J. Maier, *Proc. Electrochem. Soc.*, **95–23**, 241 (1995).
14. K. D. Kreuer, *Solid State Ionics*, **97**, 1 (1997).

14a. M. Doyle, M. E. Lewittes, M. G. Roelofs and S. A. Perusich, *J. Phys. Chem. B*, **105**, 9387 (2001).

15. K. D. Kreuer, Th. Dippel and J. Maier, *Mat. Res. Soc. Symp. Proc.*, **293**, 273 (1993).
16. K. D. Kreuer, *Chem. Mater.*, **8**, 610 (1998).
17. N. Agmon, *Chem. Phys. Lett.*, **244**, 456 (1995).
18. M. E. Tuckerman, K. Laasonen, M. Sprike and M. Parrinello, *J. Chem. Phys.*, **103**, 150 (1995).
19. K. D. Kreuer, *Solid State Ionics*, **136–137**, 149 (2000).
20. K. D. Kreuer, A. Rabenau and W. Weppner, *Angew. Chem. Int. Ed. Engl.*, **21**, 208 (1982).
21. M. Eikerling, S. J. Paddison and T. A. Zawodzinski, *J. New Mater. Electrochem. Syst.*, **5**, 15 (2002).
22. G. Alberti, M. Casciola, L. Massinelli and B. Bauer, *J. Membr. Sci.*, **185**, 73 (2001).
23. S. J. Paddison, G. Bender, K. D. Kreuer, N. Nicoloso and T. A. Zawodzinski, *J. New Mater. Electrochem. Syst.*, **3**, 291 (2000).
24. R. Paul and S. J. Paddison, *J. Chem. Phys.*, **115**, 7762 (2001).
25. S. J. Paddison, R. Paul and K. D. Kreuer, *Phys. Chem. Chem. Phys.*, **4**, 1151 (2002).
26. M. Ise, K. D. Kreuer and J. Maier, *Solid State Ionics*, **125**, 213 (1999).
27. M. Schuster, K. D. Kreuer and J. Maier, Proc. SSPC-11. *Solid State Ionics*, in press (2002).

27a. Sh. Gottesfeld and T. Zawodzinki 'Polymer Electrolyte Fuel Cells', in "Advances in Electrochemical Science and Engineering", R. C. Alkire, H. Gerischer, D. M. Kolb and C. W. Tobias (Eds), Vol 5, Wiley-VCH, Weinheim, pp. 195–301 (1997).

27b. A. B. Geiger, J. Newman and J. M. Pransnitz, *AIChE J.*, **47**, 445 (2001).

27c. X. Ren, T. E. Spinger and Sh. Gottesfeld, *J. Electrochem. Soc.*, **147**, 92 (2000).

27d. E. Skou, P. Kauranen and J. Hentschel, *Solid State Ionics*, **97**, 333 (1997).

27e. D. Nandan, H. Mohan and R. M. Iyer, *J. Membr. Sci.*, **71**, 69 (1992).

28. J. Kerres, W. Zhang and W. Cui, *J. Polym. Sci.*, **A36**, 1441 (1998).
29. J. Kerres, W. Cui, R. Disson and W. Neubrand, *J. Membr. Sci.*, **139**, 211 (1998).
30. W. Cui, J. Kerres and G. Eigenberger, *Sep. Purification Technol.*, **14**, 145 (1998).
31. J. Kerres, *J. Membr. Sci.*, **185**, 3 (2001).
32. X. Glipa, M. El Haddaas, D. J. Jones and J. Rozière, *Solid State Ionics*, **97**, 323 (1997).
33. D. J. Jones and J. Rozière, *J. Membr. Sci.*, **185**, 41 (2001).
34. E. J. Powers and G. A. Serad, 'History and Development of Polybenzimidazoles' in "High Performance Polymers: Their Origin and Development", R. B. Seymour and G. S. Kirschenbaum (Eds), Elsevier, Amsterdam, p. 355 (1986).
35. M. Kawahara, M. Rikukawa, K. Sanui and N. Ogata, *Solid State Ionics*, **136–137**, 1193 (2000).
36. N. Cornet, O. Diat, G. Gebel, F. Jousse, D. Marsacq, R. Mercier and M. Pineri, *J. New. Mater. Electrochem. Syst.*, **3**, 33 (2000).
37. M. V. Motyakin, N. Cornet, G. Gebel and S. Schlick, *Bull. Polish Acad. Sci. Chem.*, **48**, 273 (2000).
38. C. Genies, R. Mercier, B. Sillon, N. Cornet, G. Gebel and M. Pineri, *Polymer*, **42**, 359 (2001).
39. P. N. Blonsky, D. F. Shriver, P. Austin and H. R. Allcock, *J. Am. Chem. Soc.*, **106**, 6854 (1984).

40. Q. Guo, P. N. Pintauro, H. Tang and S. O'Connor, *J. Membr. Sci.*, **154**, 175 (1999).

41. H. Tang and P. N. Pintauro, *J. Appl. Polym. Sci.*, **79**, 49 (2001).

42. R. Carter, R. F. Evilia and P. N. Pintauro, *J. Phys. Chem. B*, **105**, 2351 (2001).

43. J. Kerres, private communication (2001).

44. K. D. Kreuer, A. Fuchs, M. Ise, M. Spaeth and J. Maier, *Electrochim. Acta*, **43**, 1281 (1998).

45. K. D. Kreuer, 'New Proton Conducting Polymers for Fuel Cell Applications', in "Solid State Ionics: Science & Technology", B. V. R. Chowdari, K. Lal, S. A. Agnihotry, N. Khare, S. S. Sekhon, P. C. Srivastava and S. Chandra (Eds), World Science, Singapore, p. 263 (1998).

46. M. Schuster, W. H. Meyer, G. Wegner, H. G. Herz, M. Ise, M. Schuster, K. D. Kreuer and J. Maier, *Solid State Ionics*, **145**, 85 (2001).

47. C. Yang, P. Costamagna, S. Srinivasan, J. Benziger and A. B. Bocarsly, *J. Power Sources*, **103**, 1 (2001).