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The influence of absorbed methanol on the swelling and conductivity properties of cation-exchange membranes
Evaluation of nanostructure parameters

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ABSTRACT

In this work, we have measured the swelling properties (thickness, area, density, solvent content), and the conductivity of two different cation-exchange membranes (Nafion®117 and CM2), as functions of methanol content (X_{MeOH}) and LiCl concentration in the external solution. The volume fraction of electroneutral solution in the membrane (f_2) was found by using the microheterogeneous model of Gnusin. The values of f_2 as well as the porosity of Nafion®117 obtained as functions of the methanol content are compared with those calculated on the basis of the nanostructure model developed by Haubold et al. Generally a good agreement is noticed. It is found that the volume of regions occupied by side chains with fixed ion-exchange groups increases with methanol content, that determines the total swelling and growth in porosity of Nafion®117. This swelling is accompanied however by a small decrease in the pore core region volume, free of polymer chains. The latter results in a decrease in f_2, found also from conductivity measurements. The lower ionisation of the inner solution caused by the presence of less polar and less ionising solvent, such as methanol, produces a decrease in the membrane conductivity, which is partially compensated by swelling of side-chain regions. The conductivity (κ^*) of CM2 membrane, which is reticulated and swells only slightly in the presence of methanol, decreases much more in comparison with non-reticulated and strongly swelled Nafion in pure methanol solution: $\kappa^*_{\mathrm{CM2}} \approx 0.05\,\mathrm{mS\,cm^{-1}}$ and $\kappa^*_{\mathrm{Nafion}} \approx 6\,\mathrm{mS\,cm^{-1}}$.

1. Introduction

The understanding of relationships between the behaviour of ion-exchange membranes (IEMs) and their structure is important for improving the membranes and various membrane techniques. The effect of organic solvents present in aqueous solutions produced on membrane properties and structure is of particular interest taking into consideration such applications as electrodialysis treatment of water–organic solutions [1–3] or direct methanol or ethanol fuel cells [4,5]. Many studies [6–10] showed that the structure of IEMs is very sensitive to the presence of organic solvents.

It is well known that the functional properties of IEMs are determined by their nano-scale structure. Effectively, due to phase separation within such membranes occurring even in dry state and becoming much stronger when swelling, ion and solvent conducting channels of 1–4 nm in diameter are formed. The morphology of these channels is very important, and a number of structural models were developed in order to interpret membrane properties [6,11–18]. The basic model was proposed by Gierke and Hsu [11]. It consists in representing the membrane as a periodic structure. A structural unit is of 4–10 nm size and includes a region usually named cluster, which contains functional sites attached to the macromolecular chains as well as mobile solvent molecules and ions. The mobile particles are inside the cluster while the fixed solvated ions form its walls (Fig. 1, [16]). The clusters are linked between them by more or less wide channels (1–6 nm in diameter) thus making a connected network. Generally, the membrane contains also hydrophobic domains, enveloping the clusters and channels, and formed by bundles of chains devoid of charged sites. The models developed or applied by different authors [12–18] differ by details, sometimes important, such as the geometrical shape of clusters and channels and their spatial distribution [12,13]; they specify the morphology at dry state [14] and its evolution when

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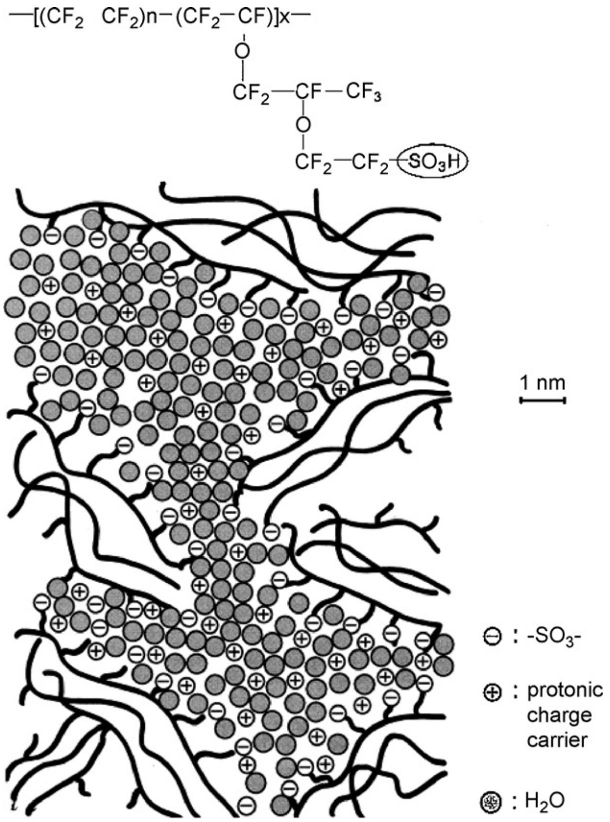

Fig. 1. Schematic representation of the microstructure of Nafion® 117 derived from SAXS experiments (Kreuer et al.).

hydration [15], the effect of different solvent [6,16–18], the role of side polymer chains [6]. The most studies cited above concern the perfluorosulfonated membranes of Nafion-type (Gierke's, Haubold's, and others). The structure of other type of membranes is less studied. However, it is known that IEMs with hydrocarbon matrix are more hydrophilic; the range of pore radius is more large with higher mesopore contribution [9,19–21], in comparison with perfluorosulfonated IEMs. Heterogeneous membranes prepared from a mixture of ion-exchange resin and polyethylene particles [22–24] are characterized by bi-porous structure: micro- and mesopores with radius 2–10 nm are related to ion-exchange resin particles, and macropores with the radius of the order of 1 μm are confined between the resin and/or polyethylene particles [9,19–21].

Consider the nanostructure 3D model of Nafion membranes by Haubold et al. [6], which will be used in this study (Fig. 2a and b). The phase separation in Nafion results in formation of a hydrophobic fluorocarbon backbone phase non-accessible to water and methanol, and a hydrophilic region containing the side chains with fixed ionic groups on their edge [6]. Thus the side-chain region is detached; it constitutes a new structure element having a thickness $s/2$. These regions form the "shell" of a transport channel. The "core" of the channel is either empty (in dry state) or flooded by water–methanol solution. A basic structure unit (Fig. 2b) is characterized in addition to s by three other parameters: the distance, c, between two parallel planes passing through fixed ions belonging to opposite side-chain regions; and the lateral dimensions, a and b, which determine the cross-section of the structure unit. Note that in this model, the thickness of core region, c, does not vary with coordinates (thus being an average size) whereas in Gierke's and other similar models the spacing between the opposite pore walls is different in the clusters and channels.

Generally, one can distinguish two approaches to describe quantitatively membrane macro-properties starting from the membrane structure image and parameters describing this structure. In the first one, the ion and water transport is considered within the solution filling the pores/channels (charged space models) [25–27]. In the second approach, which is discontinuous, the membrane is presented as a microheterogeneous multiphase system and the transport modelling consists in describing the physicochemical properties of the entire membrane as functions of the properties of different phases and of their relative disposition [28–32].

Within the first approach, different types of modelling are developed, especially in the last 10 years [17,18]: atomic and molecular dynamics simulations [33], statistical mechanics modelling [34], application of Poisson–Boltzmann equations taking into account the interactions between individual ions, fixed and/or mobile, and solvent [27]. Between the numerous results giving a more comprehensible understanding of transport in nano-dimensional pores, it is found that the internal solution possesses bulk properties (at least, the dielectric permittivity, ε, reaches its bulk value (81) in the centre of pore), when the water content is higher than 10 water molecules per sulfonic acid group [16,17,27]. For lower degrees of hydration, ε is lower than 81 even in the pore centre.

Gnusin et al. [28,35,36] have developed, in the framework of the second approach, a "microheterogeneous model", which gives relatively simple relationships between some membrane macro-properties (such as the electrolyte uptake, the conductivity and the permeability towards electrolyte diffusion) and its structural parameters.

In the microheterogeneous model, three phases are distinguished: (1) the *electroneutral electrolyte solution* filling central regions of the pores, (2) the *gel phase* containing the charged *hydrophilic polymer domains* (i.e. the side polymer chains with fixed sites present at the pore's walls) surrounded by the *charged regions of the internal solution* compensating the charge of the fixed sites, and (3) the *hydrophobic domains* of polymer chains free of functional sites.

Taking into account the small dimensions of these three regions (often lower than 5 nm), that means they are only quasi-homogeneous, one can consider them as continuous and use the term "phase" with a great reserve. Mafé et al. [37] have developed a two-region model that can be considered as intermediate between continuous (space charge models) and discontinuous (multiphase models) approaches, thus giving a certain theoretical background for the latter when starting from the former.

In the mathematical description of ion and water transport, the gel phase can be joined together with the hydrophobic phase to form a "joint-gel" phase [28]. In this way, only two pseudo-phases are considered: the joint-gel phase and the electroneutral solution filling the spaces between different elements of the joint-gel phase. When assuming that the volume fractions of these two phases is given as well as the disposition of the one in relation to the other, the microheterogeneous model allows the calculation of the electrolyte uptake, membrane conductivity and diffusion permeability as functions of ion concentrations an diffusivities within the phases. In particular, if the external solution concentration is not too far from the so-called isoconductance concentration, c_{iso}, at which the conductivity of all membrane phases and the membrane as a whole are the same, the membrane specific conductivity, κ^*, may be approximated by the following equation:

$$\kappa^* = \bar{\kappa}^{f_1}\kappa_{\mathrm{s}}^{f_2} \tag{1}$$

where $\bar{\kappa}$ and κ_{s} are the specific conductivity of the joint-gel phase and internal electrolyte solution, respectively; f_1 and f_2 are the volume fractions of the joint-gel and solution phases, $f_1+f_2=1$; κ_{s} is