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Water state and ionic conductivity of grafted ion exchange membranes based on polyethylene and sulfonated polystyrene

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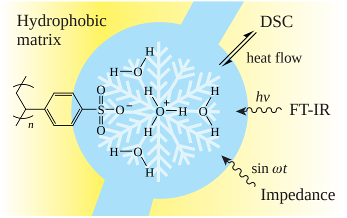
The reasons of changes in the mobility of proton-containing groups (water molecules and hydrated protons, $H_{2n+1}O_n^+$) of ion exchange membranes at various temperatures and water uptake are considered by an example of membranes based on polyethylene and grafted sulfonated polystyrene.



Ion exchange membranes are widely used in electrodialysis, electrochemical synthesis,[1–3] alternative power generation,[4–7] sensor devices,[8,9] *etc.* NAFION© perfluorinated sulfonic-acid membranes have the best transport properties,[10,11] but they are expensive. Thus, the development of new membranes, *e.g.*, by the graft polymerization of monomers to an inexpensive polymer (polyethylene) followed by the sulfonation of grafted moieties, is of interest.[12,13] The transport properties of such materials depend on the water content and state.[14]

In this work, we used IR spectroscopy, differential scanning calorimetry (DSC) and ionic conductivity measurements to study changes in the state of water and hydrated protons located in membrane pores. The membranes of polyethylene grafted with sulfonated polystyrene were used as an example.

The membranes were obtained by the graft polymerization of styrene on preirradiated polyethylene films followed by polystyrene sulfonation. We studied membrane samples containing 65% polystyrene (MSK-65), which has high proton conductivity. The variation of ionic conductivity in them, like in other ion exchange membranes, is determined by the degree of hydration of the protons of functional groups localized in the pore and channel system of the membranes. Furthermore, the environment humidity exerts a strong effect on the degree of hydration. Thus, these membranes are convenient for studying conductivity changes as a function of water uptake and temperature.

The vibrations of proton-containing groups in the IR spectra of the test materials were observed in the characteristic regions of stretching (3700–2800 cm^{-1}) and bending vibrations (1600–1700 cm^{-1}). In water-rich materials in contact with liquid water (water uptake, ~42 H_2O per SO_3H group), water molecules formed a dynamically disordered ice-like network of hydrogen bonds. They exhibited a bending vibration band at 1640 cm^{-1}. At a 95% relative humidity, there were about nine water molecules per sulfonic group, four of which formed the $H_9O_4^+$ ion. The broadened bending vibration band can be described as a sum of two lines at 1640 and 1705 cm^{-1} with close intensities. On a decrease in humidity to 20%, the band of water bending vibrations (1640 cm^{-1}) disappeared completely. Since electrostatic interactions give a maximum contribution to the energy of hydrogen bonds,[15] the strongest hydrogen bonds are formed by proton hydrates, in which hydrogen ions have the largest positive charge. In view of this, the stretching vibration bands of the form containing the smallest amount of water were most strongly shifted to lower frequencies, *viz.*, 3400, 3200 and 3050 cm^{-1}. The intensity of the high-frequency spectrum component increased with water uptake, and its maximum shifted to higher frequencies (3420 cm^{-1}). This corresponds to a gradual weakening of hydrogen bonds due to the weaker polarization of water molecules that are remote from protons. Thus, in membranes equilibrated with water, a considerable increase in water uptake occurred due to the sorption of water molecules involved only in the formation of comparatively weak bonds such as $HO{-}H{\cdots}OH_2$ or $HO{-}H{\cdots}OSO_2^-$.

To understand the state of water in membranes, we studied them by DSC in a temperature range from –100 to 50 °C. An endothermal transition with a maximum at 2 °C was observed in the membranes equilibrated with pure water [Figure 1(*a*)]. It resulted from the melting of water molecules located in

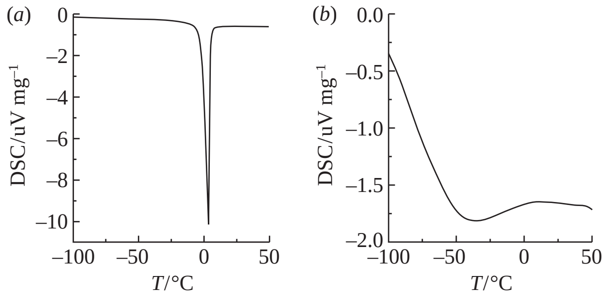


Figure 1 Calorimetry data for an MSK-65 membrane (*a*) equilibrated with water and (*b*) at a relative humidity of 30%.

membrane pores and remote from their walls along which the majority of protons were localized.[16] This is a so-called electrically neutral solution; *i.e.*, weakly bound water is localized near the center of pores, and it contains almost no protons. This endo effect amounts to ~100 J g^{-1}. Based on this, the amount of this weakly bound water can be estimated at ~20 molecules per sulfonic group. The water melting effect nearly disappeared even at 95% humidity. Note that the heat spent for membrane heating at low humidity in the low-temperature region consistently increased up to –35 °C, passed through a weakly expressed maximum, and then approached a constant value at temperatures above 0 °C [Figure 1(*b*)]. The shape of this heat capacity plot resembles that for a phase transition. The absence of a distinct maximum with a discontinuity point is an exception.

It is due to the gradual unfreezing of molecular mobility that starts with water molecules in the first coordination sphere of protons ($H_5O_2^+$ or $H_9O_4^+$ ions). Note that, according to ^{1}H NMR data, the mobility of proton-containing groups in many hydrates of acids and acid salts manifests itself at around –90 °C. In these cases, the fraction of mobile protons increases with temperature due to the cooperative effect.[17] This process ceases at about 0 °C and all water is transformed to a high-mobility state, which corresponds to a plateau in DSC curves. A similar effect is also observed in the samples with high water uptake [Figure 1(*a*)]. However, a narrow peak of the melting of weakly bound water is imposed in this case.

The ionic conductivity of membranes characterizes the mobility of proton-containing groups therein, and it is directly related to the state of water molecules based on calorimetry data. In view of this, it appears appropriate to compare the above data with the conductivity *vs*. temperature plots near 0 °C, where the main changes in the mobility of proton-containing groups are observed. Since the proton conductivity is of activation nature, it grows with temperature. However, this Arrhenius plot for a highly hydrated sample is nonlinear and has a kink at about 0 °C (Figure 2). In this case, the activation energy decreases from 41 kJ mol^{-1} in the low-temperature region to 7.5 kJ mol^{-1} in the high-temperature region. According to calorimetry data, this is due to the transition of a considerable fraction of water to a high-mobility state. Though this transformation corresponds to a first-order phase transition, the plot contains no discontinuity. This phenomenon is unexpected at first sight but is actually quite understandable. Pure water, which is localized in the pore center and contains no admixtures, including protons, freezes near 0 °C. Hence, the number of charge carriers does not change in this process. Furthermore, even above the phase transition temperature, the electrically neutral solution localized in the pore center contains very few charge carriers. The majority of these carriers are located within the thin Debye layer near the pore walls. It is these water molecules and protons located in this layer that gradually pass into a mobile state in the low-temperature region. After the melting of weakly bound water, the conductivity increased only due to a gradual growth of the proton mobility in the Debye layer, whereas an additional contribution to the conductivity activation energy at low temperatures was caused by the transition of water within the Debye layer, along with the protons it contains, into a mobile state.

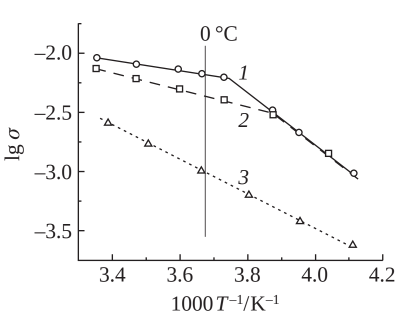


Figure 2 The temperature dependence of the conductivity of MSK-65 at humidities of (*1*) 100, (*2*) 95, and (*3*) 60%.

According to calorimetry data, the phase transition disappeared as the humidity decreased to 95%. In this case, the trend with a gradual transition of water within the Debye layer, along with the protons it contains, to a mobile state remained unchanged. Upon completion of this transition, the conductivity activation energy also decreased. However, the resulting conductivity was somewhat lower than that of the membrane equilibrated with water (Figure 2). This is because a decrease in the pore volume was inevitably accompanied by a decrease in the size of channels connecting them,[18] which limit the conductivity. A further humidity decrease to 60% was accompanied by a reduction in water uptake due to a decrease in the water content of the Debye layer and by an increase in the concentration of protons. As a result, the temperature of completion of its transition to a mobile state decreased, and no changes in the conductivity activation energy were observed down to –30 °C (Figure 2).

Thus, we examined the reasons of changes in the mobility of water molecules and proton conductivity of ion exchange membranes at various water uptakes and temperatures using polyethylene membranes with grafted sulfonated polystyrene as an example. We found that, though a first-order phase transition occurred upon the melting of water in electrically neutral solution, the temperature plots of proton conductivity contained no discontinuity points, and explained this unexpected phenomenon.

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