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Effect of the treatment of MF-4SC membranes on the cross sensitivity of Donnan potential sensors to cations in the aqueous solutions of organic ampholytes

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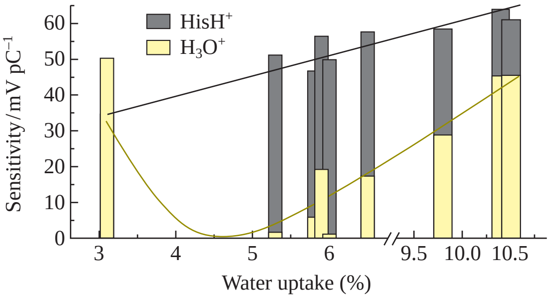
Methods of directional variation of properties of perfluorinated sulfo cation-exchange membranes were proposed based on the use of the effect of 'memory' to changes in their structure under the influence of external factors (heat treatment at various humidity or mechanical effect). The relationship between water uptake, transport properties of MF-4SC membranes, and sensitivity of Donnan potential (DP) sensors to the determined organic cations and interferent hydronium ions was established. Lowering sensitivity of DP-sensors to the interferent hydronium ions at a decrease in diffusion permeability and increase in conductivity of the membranes was reached.



Ion-exchange polymer membranes, particularly, Nafion perfluorinated sulfo cation-exchange membranes (MF-4SC, Dow, Aquivion), are widely used due to their unique mechanical and transport properties.[1–3] Multifold possibilities for the analysis of water-organic environments allow one to use cross sensitive Donnan potential (DP) sensors based on such membranes. The reactions of ion exchange and protolysis are potential-determining reactions in the potentiometric determination of the ions of organic ampholytes in water solutions. The possibility of determining the ionic forms of organic ampholytes at various pH values has been scarcely discussed in the literature. A major problem is a decrease in the accuracy of potentiometric determinations of organic ions at pH < 7 due to the influence of hydronium ions on the response of sensors.[4] Therefore, a search for the ways of decreasing the sensitivity of DP-sensors to hydronium ions in water-organic solutions is of considerable current interest. The use of Nafion and MF-4SC hybrid membranes containing different dopants was proposed for the directional variation of the properties of DP-sensors in the solutions of organic ampholytes (amino acids and pharmaceutical substances).[4,5] The other possible way to change the properties of the Nafion type membranes is treatment at various temperatures and relative humidities (RHs) and also the mechanical deformation.[6–10] A change in the membrane properties as the result of such treatment opens possibilities for varying the concentration of organic and inorganic ions in membrane pores and, therefore, the sensitivities of DP-sensors to them.

The aim of this work was to relate the water uptake and transport properties of MF-4SC membranes and the sensitivity of DP-sensors to the determined and interfering ions in solutions of organic ampholytes. Membranes were treated thermally and mechanically deformed at various RHs for varying the membranes properties and the sensitivity of sensors. The water uptake, ion conductivity and diffusion permeability of membranes were measured.[†]

The characteristics of DP-sensors based on pretreated MF-4SC membranes (ion exchange capacity, 0.75 mmol g^{-1}; thickness, 140±10 μm in a hydrated state) in the K$^+$ form were determined in the solutions of histidine hydrochloride (HisHCl) with concentrations from 1.0×10^{-4} to 1.0×10^{-1} M (pH 3.63–5.02), in which the amino acid predominantly occurred as monovalent cations, at room temperature according to a published procedure.[4] It was found that the sensitivity of DP-sensors to the interfering H$_3$O$^+$ ions decreased by a factor of ten with the use of the membrane held at 90 °C and RH = 95%, in comparison with the initial one (Table 1). It is associated with a change in the size of pores and

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[†] The thermal analysis of samples was carried out using a Netzsch-TG 209 F1 thermobalance under argon in platinum crucibles in a temperature range of 25–150 °C (heating rate, 10 K min^{-1}). For standardization, all membranes were first removed from water and equilibrated at RH = 95%. The ionic conductivity was measured at 30 °C in contact with deionized water. The measurements were carried out using a Z1500J (Elins) impedance meter (frequency range, from 10 Hz to 2 MHz) and carbon/membrane/carbon symmetric cells with an active surface area of ~1 cm^2. The membrane diffusion permeability for a 0.1 M KCl solution was measured in the following way. The sample was placed in a cell consisting of two chambers separated by the membrane. The volume of each chamber was 32 cm^3. A solution of KCl was placed at the one side of the membrane, while the other chamber was filled with deionized water. During the experiment, the change in the specific conductivity of the solution was measured by an Expert-002 conductometer (Econix-Expert) in a chamber filled with deionized water. The membrane diffusion permeability was found as $P = (dC/dt)Vl/(S\Delta C)$, where V is the solution volume, cm^3; l is the membrane thickness, cm; ΔC is the concentration gradient, mol cm^{-3}; and t is time, s (error in the determination of P is less than 1%).

Table 1 Water uptake, ionic conductivity (σ), and diffusion permeability (P) of MF-4SC membranes and sensitivity of DP-sensors on their basis to the (b_1) $HisH^+$ and (b_2) H_3O^+ ions (membranes in K^+ form, treated in a hydrated state).

Membrane treatment conditions	Water uptake (%)	σ (at 30 °C)/ 10^{-3} Ω^{-1} cm^{-1}	P 0.1 M KCl/ 10^{-8} cm^2 s^{-1}	b_1/ mV pC^{-1}	b_2/ mV pH^{-1}
90 °C, RH = 60%	3.1	1.66	0.0067	35±4	32.7±1.5
90 °C, RH = 95%	6.0	3.49	1.32	50±3	1.2±1.1
Without treatment	6.5	5.3	5.62	58±2	17.3±0.7
$t_{ht}{}^a$ = 100 °C	9.8	7.91	9.13	59±2	28.8±0.9
t_{ht} = 120 °C	10.4	7.69	16.2	64±2	45.4±0.9
t_{ht} = 140 °C	10.5	7.82	22.7	61±2	45.5±0.9

[a] t_{ht} is the hydrothermal treatment temperature.

Table 2 Water uptake and ionic conductivity (σ) of MF-4SC membranes and sensitivity of DP-sensors on their basis to the (b_1) $HisH^+$ and (b_2) H_3O^+ ions (membranes in K^+ form, treated in a dry state).

Membrane treatment conditions	Water uptake (%)	σ (at 30 °C)/ 10^{-3} Ω^{-1} cm^{-1}	b_1/ mV pC^{-1}	b_2/ mV pH^{-1}
80 °C, ambient RH	5.3	3.65	51±2	1.6±0.9
80% deformation (at room temperature), 80 °C, ambient RH	5.9	4.11	57±2	19.3±0.9
80% deformation (at room temperature), 100 °C, ambient RH	5.8	4.39	47±3	5.9±1.0

transport channels of the membrane and in the volume of free solution – electrically neutral solution in membrane pores, which is not included into the area of double layer near the charged pore wall and is similar in composition to the external solution. These microstructure parameters determine the possibility of transition of large volume organic cations into the membrane. A part of water molecules left the membrane pores during thermal treatment at lower humidity (RH < 100%) of the membranes in a hydrated state (Table 1). We expected that the diameter of transport channels, which connect membrane pores, decreased during such a treatment, and it resulted in ionic transport difficulty. In particular, this is evidenced by a significant decrease in the water uptake and diffusion permeability (by a factor of 4) as a result of the membrane treatment at 90 °C and RH = 95% in comparison with the initial one (Table 1). High sensitivity of the DP-sensor based on the membrane treated at 90 °C and RH = 95%, to the $HisH^+$ ions (50 mV pC^{-1}) allows us to consider that water molecules are capable of moving into the membrane phase in contact with the test solution. Apparently, the interaction of bulk amino acid ions with fixed membrane groups at a small volume of intrapore space excludes a part of protons from ion exchange and levels their influence on the sensor response.

A decrease in relative humidity down to 60% during the treatment of the membranes results in a decrease in the volume of pores. This is confirmed by a sharp reduction in water uptake (by a factor of 2), conductivity (by a factor of 3), and diffusion permeability (by about 3 orders of magnitude) as compared with the initial values (Table 1). At the same time, the sensitivity of the DP-sensor based on the membrane treated at 90 °C and RH = 95% to the $HisH^+$ ions diminished, and that to the H_3O^+ ions greatly increased in comparison with the initial values (Table 1). This validates the difficulty of bulk $HisH^+$ cations transfer into the membrane, while the hydronium ions enter the membrane without restriction.

In the case of the treatment of membranes under hydrothermal conditions, changes in the transport properties of samples and the sensitivity of DP-sensors based on them correlate well with changes in the water uptake (Table 1). Treatment of the membranes under a pressure of water vapor above one atmosphere contributes to the sorption of an additional amount of water molecules, which leads to an increase in the volume of pores and transport channels. An increase in diffusion permeability with hydrothermal treatment temperature was observed (Table 1) because the anion transport through the free solution located in the center of the membrane pore became easier. The ion conductivity of the membranes treated in this way grew by a factor of 1.5 in comparison with the initial conductivity, and it weakly depended on the treatment temperature (Table 1). It is associated with the fact that the cation transfer is carried out within the narrow Debye layer along the membrane pore walls, which is formed by functional groups, and the rate-determining stage is cation transfer through the narrow transport channels.

An increase in the water uptake of membranes was accompanied by a small rise in the sensitivity of DP-sensors to $HisH^+$ ions and even by a more sharp increase in the sensitivity to H_3O^+ ions (Table 1). Amino acid and hydronium ions are transferred into the membrane phase according to both exchangeable and non-exchangeable mechanisms under such conditions, and amino acid cations do not disturb interactions between protons and membrane sulfonic-acid groups at a high water uptake. The study of the membrane samples treated at various temperatures and relative humidity suggests that a decrease in water uptake and an increase in the selectivity of membranes allows us to level the influence of interfering H_3O^+ ions on the response of DP-sensors in the solutions of organic ampholytes.

Thermal treatment and mechanical deformation of the membranes in a dry state with the following hydration have an impact on the sensitivity of DP-sensors and on a ratio between the sensitivities to $HisH^+$ and H_3O^+ ions (Table 2). Such a treatment was accompanied by irreversible dehydration and led to a more rarefied arrangement of pores in the membranes in comparison with the initial sample, which was retained even after the subsequent hydration. This was confirmed by a significant decrease in the water uptake and conductivity of such membranes (Table 2). Note that similar values of the conductivity of membranes and the sensitivity of DP-sensors to the $HisH^+$ and H_3O^+ ions were reached for two samples: a membrane treated at 90 °C and RH = 95% (Table 1) and a membrane treated at 80 °C in a dry state (Table 2). Sensitivity of DP-sensors to the interfering H_3O^+ ions based on data for these samples decreased by factors of 14 and 11, respectively, as compared with the initial sample.

In summary, note that the sensitivity of DP-sensors to the $HisH^+$ ions monotonically increased with the water uptake of membranes (Figure 1). This is due to an increase in the membrane

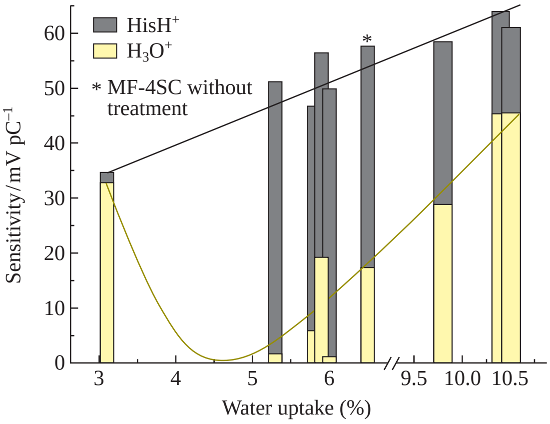

Figure 1 Sensitivity coefficients of DP-sensors to the $HisH^+$ and H_3O^+ ions depending on the water uptake of the MF-4SC membranes in a concentration range of 1.0×10^{-4}–1.0×10^{-1} M at room temperature.

pore space availability to bulky organic ions with rising the water uptake. At the same time, the dependence of the sensitivity of DP-sensors to H_3O^+ ions on the water uptake of MF-4SC membranes has an extreme character (Figure 1). A decrease in the water uptake of membranes at first diminishes the sensitivity of DP-sensors to H_3O^+ ions owing to their exclusion from ionic exchange caused by the interaction of high volume organic ions with fixed membrane groups at the small volume of intrapore space. A further decrease in the water uptake of the membranes makes difficult the transition of organic cations into the membrane phase and the sensitivity to the H_3O^+ ions entering the membrane without encumbrance increases.

Thus, the memory effect of ion-exchange membranes, which includes irreversible changes in the system of pores and transport channels under the influence of treatments at various relative humidities and temperatures and as a result of mechanical action, can be used for reducing the impact of interfering hydronium ions on the response of potentiometric DP-sensors in the solutions of organic ampholytes. Differences in the sensitivity of DP-sensors to the amino acid cations and H_3O^+ ions depend on the transfer of organic cations into the membrane and the intrapore space volume.

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