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Features of the adsorption of methylene blue and ascorbic acids on a polymer membrane „Nafion“

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Transmittance coefficient of polymer membrane „Nafion“ during adsorption of methylene blue and ascorbic acid from aqueous solutions onto the membrane was investigated by infrared (IR) Fourier spectrometry. A change in the membrane color and transmittance in the IR range during swelling of the polymer in the studied solutions was found, which is associated with chemical reactions occurring in the „membrane−solution“ system. It was found experimentally that the adsorption and desorption rates of distilled water, oxidized Methylene blue (Mb^+) and reduced colorless leuco-form of methylene blue (MbH^0) on the polymer membrane are close and lie within the following limits: adsorption rate 0.029−0.031 min^{-1}, desorption rate 0.010−0.011 min^{-1}. The adsorption and desorption rates of ascorbic acid from aqueous solution were 0.021 and 0.08 min^{-1}, respectively. During the sorption of Methylene blue leuco-form, we detected a change in membrane color. Thus, a redox reaction occurred in the membrane. Upon prolonged drying of the membrane, due to the proton-exchange properties of the membrane, the leuco-form of methylene blue oxidized to the initial state of Mb^+. This fact may indicate the manifestation of metachromatic properties of the system „Nafion — Methylene blue“. The system consisting of Methylene blue adsorbed on sulfonated perfluorocarbon can be considered as a model of dehydrogenase, a biocatalyst capable of hydrogen transfer. The „Nafion“ membrane, due to its high cationic conductivity, promotes proton transfer and thus affects the rate of redox reactions involving Methylene blue.

Keywords: „Nafion“ membrane, polymers amphiphilic properties, Methylene blue, ascorbic acid, optical properties, infrared spectrum.

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Introduction

Polymer membranes from Nafion ($Nafion^{TM}$), developed by DuPont, are being intensively studied in various fields of physics, chemistry and hydrogen energy [1–11]. Nafion is a polymer (Teflon) frame with terminal sulfo groups attached to the Teflon base [8]. The main perfluorocarbon chain of the membrane is the hydrophobic part of the macromolecule. Side chains with sulfo groups have hydrophilic properties and are able to adsorb water molecules.

Nafion swollen in water has the so-called amphiphilicity [4] — inside Nafion has a structure like cylindrical micelles with filled water structures of size 2−3 nm. At the boundary of these channels, there is dissociation of terminal sulfo groups:

$$R\text{–}SO_3H + H_2O \Leftrightarrow R\text{–}SO_3^- + H_3O^+,$$

and the inner surface of the channels becomes negatively charged. Therefore, cations are effectively drawn into the channels, which is used for the spatial separation of H^+ and OH^- ions in hydrogen energy installations. Its proton conductivity strongly depends on the concentration of water in the polymer, which increases with increasing amount of water inside the membrane during swelling [8].

Rationale

On the one hand, the polymer membrane „Nafion“ taking into account scaling, has some similarities with the cell membrane. On the other hand, aqueous solutions of various forms of methylene blue (MB) are used in the fight against COVID-19 [12–14]. The MB dye belongs to the family of phenothiazines, heterocyclic compounds, at the base of which there are three rings — two carbon and one more with inclusions of nitrogen and sulfur Methylene blue was the first phenothiazine derivative (as drugs based on it are called). The hydrated form contains three molecules of water per unit of methylene blue. Methylene blue is obtained from N,N-dimethylaniline ($C_8H_{11}N$) [15–17].

Therefore, from a fundamental and applied point of view, research into the interaction of the polymer membrane „Nafion“ with these solutions is relevant. Studying such interaction was the goal of this paper. The studies involved soaking the polymer membrane in aqueous solutions of various forms of MB and ascorbic acid (ASA).

The MB molecule is capable of forming various forms. The radical cation Mb^+ can exist in four equilibrium configurations and form dimers and H-aggregates. In addition, the MB dye is capable of being reduced to the neutral semiquinone radical Mb^0 and further to the colorless leucoform. The spectrum of the semiquinone radical Mb^0 has five maxima in the visible area: 420, 436, 585, 610, 640 nm [17]. Depending on the composition of solutions and the acidity of the medium, a transition of Mb^+ into various neutral (leucoform, semiquinone radical) and positively charged forms is possible. The neutral leucoform MbH^0 arises as a result of the reaction

$$Mb^+ + 2e^- + H^+ \to MbH^0. \quad (1)$$

The resulting radical MbH^0 is easily oxidized back to Mb^+ under the action of oxygen [16]. If MbH^0 adds one more proton, then it goes into the protonated leucoform MbH_2^+ [6]. Thus, an MB molecule in various environments is capable of transitioning from one form to another, accepting one or more electrons, or accepting or donating a proton.

Methylene blue has attracted the attention of researchers for many years due to its wide range of biochemical activities. It was found that MB has a strong antiviral effect, which was proven back in 2018 in the treatment of Ebola virus and MERS−CoV, which causes acute Middle East respiratory syndrome. In oncology, MB is known as a powerful photosensitizer. It actively exhibits an antiviral effect when exposed to light and its administration promotes the destruction of pathological cells.

The participance of MB (at low concentrations of < 2 mg/kg) in the fight against COVID-19 can be considered as a way to fight against methemoglobinemia [12]. The reversible oxidation-reduction system formed by the original form Mb^+ and the reduced protonated leucoform MbH_2^+ transfers an electron and a proton from the donor (for example, nicatinamide adenine dinucleotide NADH, the reduced form of flavin adenine dinucleotide $FADH_2$ or ASA) to methemoglobin met-Hb(Fe^{3+}), helping to restore it to hemoglobin Hb(Fe^{2+}). MB also blocks ACE2 receptors, which play one of the main roles in the progression of COVID-19 [13]. According to the paper [14], MB functions as an alternative electron carrier in mitochondria, which accepts electrons from NADH or $FADH_2$ and transfers them to CoQ or Cyt-c, bypassing the blocking of complex I/III in the electron transport chain (ETC), which allows the ETC to continue functioning and the production of adenosine triphosphate (ATP) in the cell.

In the present work, by recording the IR spectrum, the transmittance of a polymer membrane was measured when it was soaked in aqueous solutions of methylene blue (Mb^+), its leucoform (MbH^0) and a solution of ascorbic acid (ASA), as well as during subsequent drying of the membrane. The state of the membrane was recorded with a Fourier transform infrared spectrometer in the near IR range at room temperature. The phenomenon of swelling of a perfluorosulfonate polymer under the influence of water is important not only for clarifying the operational properties of the membrane, but also for studying its thermodynamic, electrical and optical properties.

The unusual sorption properties of the polymer sulfonated fluoroplastic membrane „Nafion" are due to its structure. IR spectra of the membrane were obtained after its swelling in aqueous solutions of Mb^+, ASA, the reduced colorless leucoform MbH^0 obtained as a result of the reaction of the dye with ASA, and subsequent drying of the membrane. The purpose of the paper — using the tendency of the polymer membrane „Nafion" to proton conductivity, to study adsorption from aqueous solutions of MB and ASA, as well as to identify the features of the vibrational spectrum of molecules and the presence of deviations in the characteristics of spectral lines in the wavelength range corresponding IR radiation.

Experimental part

The study of the IR spectrum of aqueous solutions Mb^+, MbH^0, ASA and membrane „Nafion" was carried out on an analytical IR Fourier spectrometer FS2201 in the wave range 370−7800 cm^{-1} with a nominal resolution of maximum 1 cm^{-1}, absolute error of the wave number scale was $\pm 0.05\,cm^{-1}$. We used plates of polymer N117 (SigmaAldrich, USA) with a thickness of $L_0 = 175\,\mu m$ and a size of 1×1 cm. Soaking in aqueous solutions of MB and ASA and subsequent drying were carried out. The polymer plate was placed in a cell with windows made of CaF_2, which are transparent to IR radiation in a wide spectral range (the long-wavelength transparency limit corresponds to $3\,\mu m$). The distance between the windows (cuvette thickness) was $180\,\mu m$.

The following liquids were used as research objects: double-distilled water, ASA solution, which was obtained by dissolving 33 g ASA (99.99%) in 100 ml distillate. An aqueous solution of MB was prepared by diluting 0.6 g Mb^+ 100 ml water and brought to absorbance $D = 1$. The initial blue structure of the dye Mb^+ has a spectrum with the following absorption maxima: $\lambda(\text{dimer}) = 615$ nm and $\lambda(\text{monomer}) = 665$ nm. An aqueous solution of Mb^+ with ASA was prepared in proportions 5 : 1. The process of soaking the membrane in distilled water and aqueous solutions Mb^+, MbH^0 (LMS) and ASA was carried out in a Petri dish. The pH values of the initial solutions were: double-distilled product pH 6.74, aqueous solutions Mb^+ pH 5.41, ASA pH 3.42.

The transmittance of solutions $K = I/I_0$ was measured, where I and I_0 — the intensities of transmitted and incident IR radiation, which, according to Lambert- − Bouguer−Beer law, are associated with the relation

$$I = I_0 \exp(-kL), \quad (2)$$

where k — extinction coefficient, L — distance between the cuvette glasses. In L this paper L was constant and was determined by a thin metal plate (thickness $L = 0.18$ mm) between the cuvette glasses. The solution was injected into the liquid cuvette using a syringe.

The strongest absorption of IR radiation in distilled water for aqueous solutions Mb^+, ASA and the colorless leucoform MbH^0 is realized for the stretching vibration band

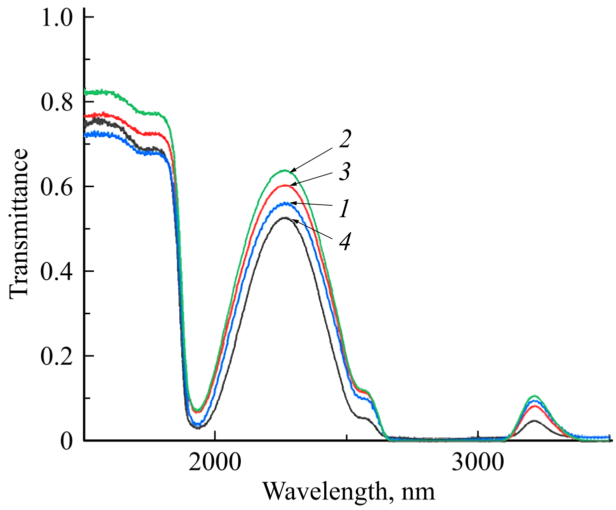

Figure 1. Combined IR spectra in the area of the spectral minimum: *1* — Mb^+, *2* — MbH^0, *3* — ASA, *4* — H_2O.

in the range 2.7–3.3 μm. Therefore, in experiments on IR Fourier spectroscopy, the spectral range of 1.8–2.2 μm was studied. After processing the spectral lines of solutions for the $\lambda \sim 1930$ nm area, a combined spectrum of the solutions under study was constructed (Fig. 1). The infrared spectrum of an aqueous solution of MbH^0, reduced from MB upon interaction with ASA, has a similar appearance. The minimum of the transmission coefficient at a given wavelength corresponds to the characteristic vibrational motion of the molecule under the influence of IR radiation.

Then the transmittance spectrum of the membrane was measured when it was soaked in solutions. Below there are the results of measuring the IR spectrum of the membrane (relative transmittance on the line $\lambda \sim 1930$ nm) upon soaking (and subsequent drying) in distilled water, as well as in aqueous solutions of Mb^+, ASA, MbH^0. Measurements of the IR spectrum of these solutions and the membrane soaked in them allowed to specify the features of the process of water adsorption, MB, its leucoforms and ASA by the membrane.

Since there was a review of aqueous solutions, the IR spectra of the compounds were compared with the IR spectrum of water. Figure 1 shows the transmittance spectra of IR radiation of distilled water and the studied solutions of — ASK, Mb^+ and MbH^0. It follows from the experiment that for distilled water and the studied aqueous solutions the width of the spectral line is almost the same and the minimum transmittance coefficient on average corresponds to a wavelength of 1931.4 nm. The transmittance of the IR spectrum in the region $\lambda \sim 1930$ nm for water is less than that of the studied aqueous solutions (Fig. 1).

An experimental study of the reduction process of the biochemically active compound MB in the field of low-frequency harmonic vibrations with a frequency from 7 to 30 Hz showed that the kinetics of the redox reaction of MB with ASK [18] changes. Therefore, a study of the kinetics of the reduction reaction of Mb^+ upon interaction with ASA was carried out in the paper. Registration of the IR spectrum of a mixture of aqueous solutions of Mb^+ and ASA at different times allowed us to indirectly measure the rate of reaction (1) reduction of Mb^+ by an aqueous solution of ASA to the formation of the leucoform MbH^0 by measuring the transmittance of IR radiation. Information about the rate of this reaction is necessary to account for the time interval during which we can obtain the reduced, in particular the protonated leucoform of MbH_2^+, which transfers an electron and a proton from the donor (for example, NADH, FADH $_2$ or ASA) to methemoglobin met-Hb (Fe^{3+}), helping to reduce it to hemoglobin Hb (Fe^{2+}). Figure 2 shows the time dependence of the transmittance of IR radiation at a wavelength of 1930 nm for a solution in which there is reaction Mb^+ with ASA. The approximation of the obtained dependence and its derivative give the average value of the transmittance change rate. This can be interpreted as the reaction average rate of of MbH^+ with ASA, which results in the formation of a colorless reduced form of MbH^0. The average reaction rate for the reduction of the MB solution with an aqueous solution of ASA for the selected concentration was 0.14 min^{-1}. The total time for the reduction of the oxidized form Mb^+ to the form MbH^0 was approximately 15 min.

Next, we will review the results of studying the dynamics of the process of adsorption and desorption of the studied solutions by Nafion. The swelling of the polymer in water is mainly determined by the primary hydrophilic phase — the presence of sulfo groups. Functional sulfo groups are grouped inside spherical cavities with a diameter of approximately 40 Å [19]. The second hydrophilic phase is a system of cavities connected by narrow channels with a diameter of 10 Å, which contain hydrated cations.

The two-phase structure of Nafion determines its amphiphilic properties. Side chains can aggregate and form

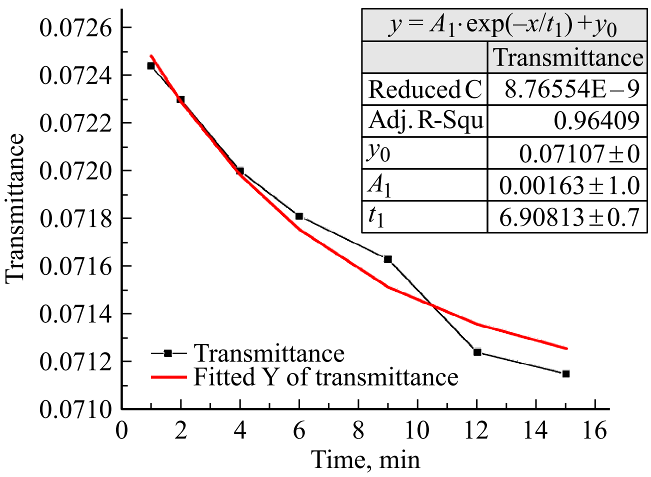

Figure 2. Time dependence of the minimum transmittance of an aqueous solution at the reaction Mb^+ with ASA at a wavelength 1930 nm.

rod-like aggregates with long relaxation times. If a sample of Nafion is moistened with water, first its hydrophobic qualities appear — Nafion resists the penetration of water inside and remains almost dry. However, after some time (approximately 190 min [7]) the hydrophilic phase begins to appear and water is absorbed into the membrane.

The dried Nafion film takes on the color of the solution — yellowish after soaking in an aqueous solution of ASA. The change in membrane color occurs as a result of the sorption of ASA on Nafion. When Nafion is soaked in an aqueous solution Mb^+ (blue color of the solution), a color change occurs and the polymer becomes blue, and the solution itself becomes lighter. Thus, the membrane actively adsorbs Mb^+. When the membrane is soaked in a colorless aqueous solution — reduced form MbH^0 — the polymer at the beginning of soaking acquires the color of the solution and becomes colorless. Next, after sufficient exposure to the solution, the polymer turns a slightly light blue color. Then, after drying the film in air for a very long time, its color changes again — the membrane acquires a turquoise color. The color change indicates metachromasy of MB upon adsorption on the Nafion polymer. The property, expressed in a change in the color of the dye upon adsorption, appears quite rarely and is associated with the proton activity of the membrane. For MB forms, this property is known only for adsorption on phosphates. Apparently, here the MbH^0 solution penetrated into the membrane pores and then the oxidation reaction of the leucoform MbH^0 to the oxidized form Mb^+ occurred.

The peculiarities of adsorption of the test solutions on Nafion are primarily related to the fact that Nafion has high ionic conductivity. Since Nafion is a proton-exchange membrane, upon adsorption of MB forms in the membrane, not only physical swelling, but chemical processes occur as well. This can be judged by the change in the spectra during the adsorption of substances from aqueous solutions: the blue-colored cation Mb^+, its colorless leucoform MbH^0, which has no charge, and also the relatively weak ASA, which has small dissociation constants — the first stage is $pK_1 = 4.17$, and the second stage is $pK_2 = 11.57$.

The lines of the IR transmission spectrum for water molecules in the area $\lambda \sim 1930$ nm correspond to a combination of stretching (asymmetric) and bending vibrations. The transmittance coefficient (Fig. 3) at the maximum depth of penetration of water molecules into the polymer due to prolonged soaking is approximately $K \sim 0.36$. This is more than for other studied solutions. The following feature of the obtained results is noteworthy. When the polymer is dried, the transmittance is higher than that of the original sample. Water made the polymer more transparent after swelling and drying.

A qualitatively different result was obtained when the polymer membrane was soaked and dried in an aqueous solution of ASA (Fig. 4). The average membrane transmittance value corresponding to the maximum penetration of the ASA solution is approximately $K \sim 0.44$, and for water $K \sim 0.36$ This is the first feature of the results

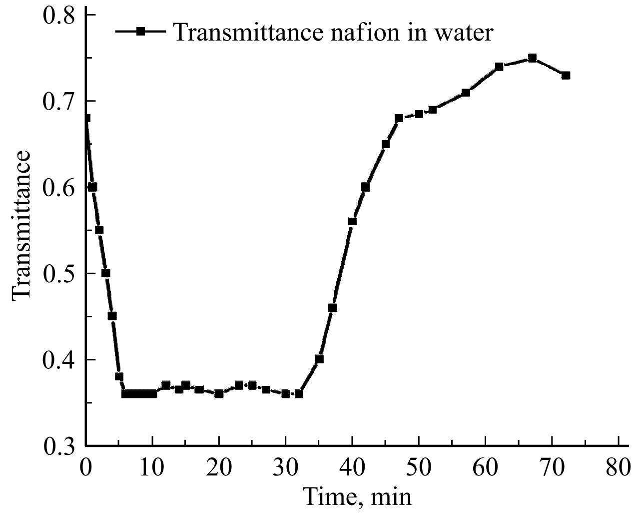

Figure 3. Transmittance of Nafion when soaked in double-distilled water and subsequently dried in air.

Rate of adsorption and desorption processes of substances on Nafion

Substance in solution	Rate adsorption, min^{-1}	Rate desorption, min^{-1}
H_2O	0.032	0.009
ASA	0.021	0.008
Mb^+	0.031	0.011
MbH^0	0.029	0.010

obtained: the polymer membrane after soaking in ASA is more transparent than after soaking in water. The second difference between the obtained results and the adsorption of distillate: the adsorption rate of ASA is less (table) than the rate of water adsorption, as well as the desorption time ASA. The third difference: the difference in the transmittance coefficients of the original (dry) sample of Nafion ($K \sim 0.65$) and that dried after soaking in an ASA solution ($K \sim 0.72$, Fig. 4).

The obtained IR spectra of aqueous solutions of the initial positively charged form Mb^+ and the reduced colorless leucoform MbH^0 coincide in principle. In both cases, they have approximately the same minimum membrane transmittance when soaked ($K \sim 0.36$); both adsorbents leave the polymer more transparent after drying compared to the initial state. Here, however, there is some difference: the polymer after desorption Mb^+ remains more transparent ($K = 0.63$) than after desorption of the leucoform ($K = 0.59$). Meanwhile, water is desorbed from the polymer, and the membranes themselves acquire the color of the solution in which they were soaked. Subsequently, a chemical reaction occurs in the membrane, which has been soaked in a solution of leucoform MbH^0, as evidenced by a change in the color of the membrane. The subsequent

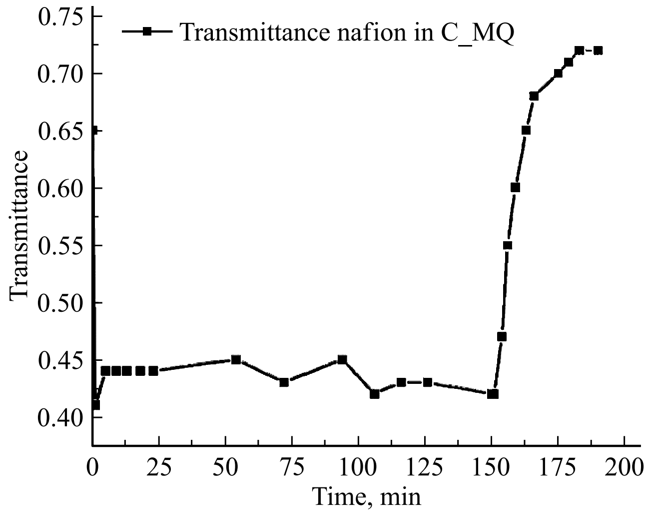

Figure 4. Transmittance of Nafion when soaked in aqueous solution of ASA and subsequently dried in air.

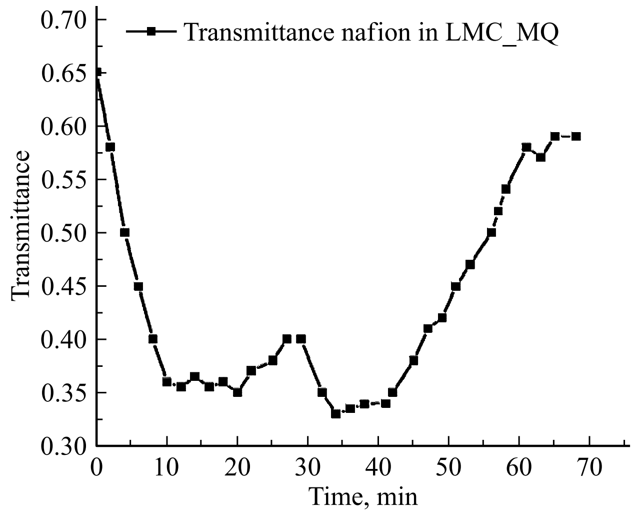

Figure 6. Transmittance of Nafion when soaked in aqueous solution MbH^0 and subsequently dried in air.

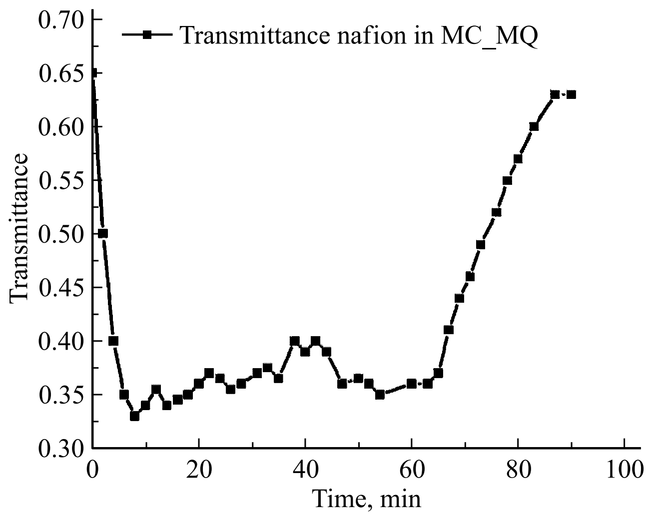

Figure 5. Transmittance of Nafion when soaked in aqueous solution Mb^+ and subsequently dried in air.

change in the color of the membrane indicates that the observed adsorption process is associated with the process of solution component diffusion into the membrane and is of a chemical nature.

Figure 5 shows the kinetics of adsorption of Mb^+ into Nafion during soaking of the membrane and its subsequent drying.

Analysis of the experiment results

The processes of adsorption and desorption of aqueous solutions Mb^+, MbH^0 and ASA on the polymer membrane „Nafion"were studied. From the analysis of IR spectra, the rate of active phases of adsorption and desorption of the substances under study on the polymer membrane in the aqueous solutions under study was determined. The rate of the sorption process (in min^{-1}) was calculated using the formula

$$v = \frac{dK_{\text{min}}(t)}{dt}.$$

Here K_{min} — membrane transmittance at a wavelength of 1930 nm.

Figure 6 shows the kinetics of adsorption of MbH^0 into Nafion during soaking of the membrane and its subsequent drying.

The calculation carried out on the basis of the experimental results (Fig. 3–6) showed (table) that, probably, due to the amphiphilic properties developing process by Nafion in double-distilled water, the rate of soaking of Nafion is significantly (3.5 times) greater than the rate of its subsequent drying. Water after drying leaves the polymer at the 1930 nm peak more transparent than it was before interacting with water (Fig. 3). Ascorbic acid is the slowest of all the studied compounds and is adsorbed from an aqueous solution on Nafion and desorbed from the polymer. Namely, the adsorption of ASA by the polymer occurs ~ 1.5 times slower than the adsorption of distilled water. It can be assumed that the polymer amphiphilicity plays a significant role here. By accepting protons from the acid, the polymer structure „rejects" the adsorption of negatively charged acid ions.

The rate of soaking of Nafion in an aqueous solution of ASA is approximately 2.6 times greater than the rate of its subsequent drying. Here it should be taken into account that sulfonated polytetrafluoroethylene is a cation – conductive polymer. Most likely, the main role in this case is not the size of the molecule. A small water molecule (or ion H_3O^+) and a relatively large molecule Mb^+ have the same rate for both adsorption and desorption. Most likely, the negative charge that ASA acquires after the release of a hydrogen cation complicates its adsorption on the polymer. In this case, the value of the transmittance coefficient of the membrane after drying the ASA is higher than the value of the transmittance coefficient of the original membrane (Fig. 4).

Of significant interest is the sharp difference in the rate of adsorption V_A from the rate $V_D$of subsequent desorption when drying Nafion. For all studied aqueous solutions, the ratio of these rates falls within the range, probably due to the amphiphilic properties developing process by Nafion. For distilled water $V_A/V_D \sim 3.6$. The positively charged oxidized form Mb^+ is adsorbed at the same rate as water, and is also slowly removed upon drying. When the Mb^+ form is soaked in an aqueous solution, the transmittance of IR radiation by Nafion at a wavelength of 1930 nm is only slightly less than that of the original sample (Fig. 5). This indicates residues of the Mb^+ solution in the membrane pores.

In a solution of the reduced colorless form MbH^0, the swelling of Nafion occurs almost three times faster compared to drying. The rate of adsorption of the MbH^0 form from an aqueous solution onto Nafion is close to the values for water and the initial Mb^+ form. The drying rates of Nafion in the studied solutions Mb^+ and MbH^0 are also approximately the same. However, the transmittance of IR radiation of Nafion soaked in a MbH^0 solution is noticeably lower (Fig. 6) than the similar value when soaked in a Mb^+ solution (Fig. 5). The spectral line width at $\lambda \sim 1930$ nm of the MbH^0 solution is 1.5% less than that of the Mb^+ and ASA solutions separately. This is presumably due to the presence of free radicals formed at intermediate stages of the oxidation-reduction process of interaction of the initial form Mb^+ with ASA.

It should be noted that the drying time of the membrane after soaking in distilled water and in an ASA solution is 1.6 times longer than the drying time when the membrane is soaked in aqueous solutions of Mb^+ and MbH^0.

The dynamics of the reduction reaction of the oxidized form Mb^+ to the form MbH^0 due to the reaction with ASA was studied using IR spectrometry in the near-IR wavelength range using spectral line analysis. Based on the obtained IR spectra, the rate of reaction Mb^+ with ASA was indirectly determined. The absorption (extinction) coefficient was determined, which was $12157.6\,m^{-1}$ for an aqueous solution of the form MbH^0. The change per unit time of the minimum transmittance of IR radiation was $0.14\ min^{-1}$ at wavelength $\lambda \sim 1930$ nm.

Conclusions

1. The interaction of MB and ASA with the surface of the Nafion polymer was studied using IR spectrometry in the near-IR wavelength range. The dynamics of soaking and subsequent drying of Nafion in aqueous solutions of ASA, MB and its leucoform were studied.

2. MB metachromasy was discovered: the dye, when adsorbed on the perfluorosulfonate membrane, reversibly changes its color.

3. The rate of the oxidation-reduction reaction Mb^+ with ASA was indirectly measured by IR spectroscopy. The change in the minimum transmittance of IR radiation at a wavelength of 1930 nm per unit time was $0.14\ min^{-1}$.

4. It was found that the rates of soaking of Nafion in double-distilled water and an aqueous solution Mb^+ are approximately the same and are maximum compared to other solutions. The lowest rate of soaking, and therefore sorption on Nafion, is found in the ASA solution. Meanwhile, the rate of ASA desorption turned out to be the lowest. Drying of Nafion in air after soaking in a MbH0 solution occurs more slowly than when drying after soaking in water and in a Mb^+ solution. The experimental facts obtained are a consequence of the amphiphilic properties developing process by the polymer membrane „Nafion".

5. Experimental studies have shown that Nafion with MB forms adsorbed on it can be considered as an analogue of the dehydrogenase biocatalyst: the membrane performs the function of transporting hydrogen. The reduced form of MB is able to activate the process of oxygen absorption, which is important in the fight against Covid-19, which is accompanied by a decrease in the oxygen content in the blood.

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