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Experiments with Fourier transform spectrometry of Nafion, a water-swollen polymeric membrane, are described. The transmittance spectra of liquid samples and Nafion, soaked in these samples, were studied, depending on the deuterium content in water in the spectral range 1.8–2.15 μm. The experiments were carried out using two protocols: in the first protocol we studied the dynamics of Nafion swelling in H$_2$O + D$_2$O mixtures for the deuterium concentrations $3 < C < 10^4$ ppm, and in the second protocol we studied the dynamics of swelling in pure heavy water ($C = 10^6$ ppm). For liquid mixtures in the concentration range $3 < C < 10^4$ ppm, the transmittance spectra are the same, but for Nafion soaked in these fluids, the corresponding spectra are different. It is shown that, in the range of deuterium contents $C = 90$–500 ppm, the behavior of transmittance of the polymer membrane is non-monotonic. In experiments using the second protocol, the dynamics of diffusion replacement of residual water, which is always present in the bulk of the polymer membrane inside closed cavities (i.e., without access to atmospheric air), were studied. The experimentally estimated diffusion coefficient for this process is ≈6·10^{-11} cm^2/s. *Published by AIP Publishing.* https://doi.org/10.1063/1.5022264

I. INTRODUCTION

The microstructure of swollen polymeric membranes made of Nafion[1] is of substantial research interest because of their use in low-temperature hydrogen cells.[2–4] Nafion membranes have a nanostructure reminiscent of that of ternary microemulsions. Actually, Nafion is a Teflon base (substantially hydrophobic), to which hydrophilic sulfonic groups are bound. A Teflon chain with a small sulfonic group can be considered as a typical amphiphilic structure consisting of a long hydrophobic "tail" and polar hydrophilic "head." Moreover, the sulfonic groups together with absorbed water molecules assemble into nanoscale clusters within the polymeric matrix. Thus the water-filled channels in Nafion are analogous to water nanodroplets surrounded by surfactants within a hydrophobic matrix (Teflon, in our case). Thereby, we deal with a system, similar to the dispersions being referred to as ternary microemulsions, where Teflon plays the role of "solid oil." The mesoscale structures composed of spherical or cylindrical micelles, which form microemulsions in aqueous mixtures, are widely described in the literature; see, e.g., Refs. 5–7 and the references therein.

As was shown by neutron scattering, see, e.g., Ref. 8, the Nafion membrane separates a hydrophobic matrix from water-filled spherical or bicontinuous cavities, which are analogous to micelles in microemulsions. The surface of the aqueous regions is presumably charged due to the dissociation of terminal sulfonic groups,

$$\text{R—SO}_3\text{H} + \text{H}_2\text{O} \Leftrightarrow \text{R—SO}_3^- + \text{H}_3\text{O}^+. \quad (1)$$
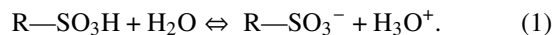
The uncompensated negative charge remains at the membrane interface. The water content in the cavities (the degree of swelling) increases with time and with increasing temperature and pressure.[9] The Nafion spectra, studied with small-angle X-ray and neutron scattering, exhibit a broad maximum and an increase in the scattering intensity at very small angles with the amount of swelling.[10–13] This structural evolution of Nafion membranes from a water-free state to a high degree of swelling has been studied in the experimental measurement of ionic conductivity, as well as on SANS and SAXS, see Refs. 14–18, and neutron reflectivity.[19]

Nafion swelling was further studied via SAXS with grazing incidence radiation and with atomic force microscopy.[20,21] What emerged was that bundles of polymer fibers at the aqueous polymer surface are oriented upon swelling perpendicular to the surface, while for Nafion in contact with the vapor phase, the bundles of polymer fibers are oriented in parallel to the surface. A qualitative model for explaining this phenomenon

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has been put forward in Ref. 22. Again this reproduces the birefringence behavior of the oil-water and oil-air interfaces and those of microemulsions.[5]

Our Nafion studies have also been motivated by the apparently peculiar phenomenon: At the surface region of water-swollen Nafion a special region is formed from which micron-sized colloid particles are pushed out. Therefore, this area was called the excluded zone (EZ); see Ref. 23. The size of the excluded zone can amount to hundreds of microns, and under certain experimental conditions this structure can remain practically unchanged for several days: see the monograph[24] and the references therein. It was suggested that the EZ represents a special phase state of water, which is characterized by a high degree of water ordering on the scale of several hundred microns. This controversial hypothesis ignores the existence of Gibbs-Marangoni effects[25] that might well explain the matter. It also is reminiscent of the extensive work of N. Ise and collaborators[26] on stability of suspensions of highly dialyzed latex spheres that remain stable for months, with enormous distances between the latex particles. These extensive observations have never been accommodated within classical theory. Furthermore, while investigating the swelling of polymers, one should account for the existence of some new forces, arisen due to conduction processes, developing between polymeric fibers; see Refs. 27 and 28. These forces are very long range and strictly non-additive.

This work is a study of the dynamics of Nafion swelling in water with FTIR techniques.[29] We remark on how our study fits into a wider context: Our aim was to study the dynamics of swelling of Nafion in water over a wide range of deuterium contents. As is known,[1] when a polymeric membrane is subjected to swelling, nanometer-sized channels are formed in the process; in our experiments, these channels are filled with water, having different isotopic composition. In the spectral range, investigated in our experiments, the molecules of H_2O, HDO, and D_2O have different positions of the absorption resonances, and, besides, these resonances have different oscillator strengths. This allows us to study the temporal behavior of the intensities of different spectral bands, i.e., we actually can investigate the dynamics of swelling of the polymer membrane. Studies of isotope effects in various polymers with ordinary and heavy water have become possible recently.[30–34] Furthermore, deuterium effects have much biological impact, which are not understood; see, for instance, the monograph (Ref. 35). In addition, as noted in Ref. 23, the size of the still unexplained exclusion zone when Nafion was soaked in heavy water appeared less compared to the case of soaking in natural water. Systematic studies of Nafion swelling dynamics in water with different deuterium contents have not previously been carried out. These matters are of interest because as far as we know, hydrogen fuel cells with the use of the Nafion membranes are basically manufactured with natural water, for which the ratio D/H is equal to the so-called standard mean ocean water (SMOW) ratio with a very narrow area of deuterium content: D/H = 157 ± 1 ppm; see Ref. 36.

IR-spectroscopic studies of swelling Nafion in water with various deuterium contents have been initiated quite a long time ago; see, for example, Ref. 37 and the references therein;

the dynamics of swelling Nafion in deuterated water with the use of FTIR spectroscopy were also studied in recent work.[38] Using the FTIR technique, it is possible to effectively study the diffusion of water molecules inside the pores of a polymer membrane.[39] Note finally that we in our group also investigate the properties of Nafion soaked in various liquids with the chemiluminescence[40] and fluorescence spectroscopy; see Refs. 41–43.

II. MATERIALS AND METHODS

In our experiments, we used deuterium depleted water (DDW) samples, with a deuterium content at a level of 3 ppm, manufactured by "Almaz" Ltd., Russia. The DDW samples were prepared by low-temperature vacuum distillation; the concentration of deuterium was monitored at the Liquid Water Isotope Analyzer-24 ("Los Gatos Research," USA) using multi-pass laser absorption spectroscopy. In addition, samples of deionized Milli-Q water (specific resistance 18 MΩ·cm at 25 °C, deuterium content is 157 ppm; we will refer to these samples as "natural" water), and heavy water (D_2O) samples ("Cambridge Isotope laboratories," UK) with 99.9 at. % content of deuterium ($\approx 1 \times 10^6$ ppm) were studied. Besides, water samples with deuterium contents of 3, 50, 90, 300, 500, 10^3, 10^4, 10^5, 2.5×10^5, 5×10^5, and 7.5×10^5 were used. These samples were prepared by bulk dilution of DDW and D_2O. Nafion plates (DuPont, USA; plate thickness $d = 175$ μm) were soaked in these liquids.

The experiments were performed with an analytical Fourier-spectrometer AF-01, designed in the Scientific and Technological Center of Unique Instrumentation of the Russian Academy of Sciences. The schematic diagram of the spectrometer is shown in Fig. 1. The spectrometer has the following characteristics:
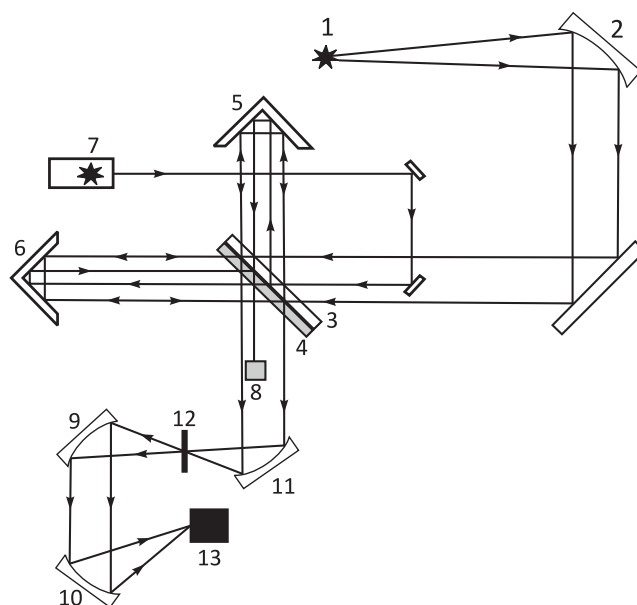

FIG. 1. Schematic of Fourier spectrometer AF-01. 1—Source of IR radiation; 2, 9, 10, 11—off-axis parabolic mirrors; 3, 4—beam splitter and compensator (transparent in the IR range); 5—fixed reflector; 6—movable reflector; 7—He–Ne laser; 8—receiver of laser radiation; 12—sample; 13—IR receiver.

- maximum spectral range: 6000–400 cm^{-1};
- tunable spectral resolution: 0.08–0.1 cm^{-1};

The impossibility of misalignment and high stability are provided by replacing flat mirrors in the classical Michelson interferometer, which is the basis of the Fourier spectrometer, by reflectors in the form of high-precision mirror trihedra with a precision of ±1 s. The optical scheme of the AF-01 Fourier spectrometer provides an intermediate focus for inserting the samples under study. The movable reflector is shifted by a highly stable electromagnetic drive for a distance of ≈8 cm. The movement of this reflector is monitored using a He–Ne laser, built into the Michelson interferometer.

IR radiation in this spectral range was generated with a high-temperature ceramic source and was received with a pyroelectric sensor.

III. EXPERIMENTAL PART

We first studied the transmittance (in dimensionless units) of liquid samples in the spectral range 1.25–10 μm. The main mechanism of water absorption in this range is due to symmetric and asymmetric stretching vibrations of the OH bonds of the H_2O molecule and corresponds to approximately $\lambda = 3$ μm. Since we are dealing with samples of large thickness (100–200 μm), the transmittance was measured in the vicinity of a weaker absorption band, which is attributed to a combination of asymmetric valence and flexural vibrations of the H_2O molecule; this band is centered at a wavelength of $\lambda = 1.923$ μm; see Refs. 44 and 45.

The liquid sample was poured into a cell with the windows made of CaF_2, which is transparent in the investigated spectral range (the transparency boundary in the long-wavelength region corresponds to $\lambda = 3$ μm); the thickness of the liquid layer in the cell corresponded to 90 μm, which is about the thickness of the Nafion plate.

The experiments were carried out according to two protocols. The first experimental protocol included studies of dry Nafion plates with a size of 4×4 mm^2 as well as plates of the same size that were previously soaked in the liquid samples for different times (the soaking time was varied up to several weeks) in total darkness at a fixed temperature (25 °C); the soaking time was fixed with an accuracy of 1 to 2 min. Prior to the measurement, the Nafion plate was withdrawn from the liquid and mounted in a special holder that was inserted into one of the arms of the Michelson interferometer of the FTIR setup; see Fig. 1. Special attention was paid to the removal of liquid droplets from the polymer surface; these droplets were blown off by a stream of compressed dust-free nitrogen. The measuring procedure included 16 successive recordings of the spectrum and took several minutes; each point on the spectrogram corresponds to averaging over the experimental dependences, obtained this way.

Another experimental protocol included the soaking of Nafion only in heavy water. In the experiments with this protocol, the transmittance spectrum of the initially dry Nafion was first taken. Then the plate of Nafion was placed in a quartz flask with heavy water, the flask was sealed, and the plate soaked in heavy water; the swelling time varied from a few hours to

several weeks. After the swelling, the plate was removed from the cell, and its transmittance spectra were taken immediately ($t = 0$), and upon drying in atmospheric air for 1 hour ($t = 1$ h). After these experiments, the plate was dried for two days in a drying cabinet ($T = 30$ °C, relative humidity $H < 1\%$), and then its transmittance spectrum was studied once again. It is obvious that in the process of drying the plate the total amount of heavy water, which was contained inside the open pores of the membrane, should completely evaporate. As is known (for more detail, see Ref. 1 and also Fig. 7 in Ref. 14), there always exists in a dry/dried Nafion a certain amount of residual water inside closed cavities in the membrane bulk; this water cannot evaporate because of the absence of contact with atmospheric air. Following Ref. 14, the isolated cavities containing residual water have a size of ~15 Å; dissociation of terminal sulfonic groups develops at the "polymer–residual water" interface, [see (1)], i.e., the surface of the polymer is negatively charged, while the cavities with residual water have an excess of positive charge. Summarizing, the experiments with the second protocol allow us to study the kinetic processes for residual water.

IV. DISCUSSION OF EXPERIMENTAL RESULTS

Wide-range spectra of the transmittance of a mixture of H_2O and D_2O near $\lambda = 1.923$ μm are shown in Fig. 2. As is seen from the figure, in the range of deuterium content $3 < C < 10^4$ ppm, the transmittance spectra are practically the same within the experimental error. At the same time, for deuterium content, ranging within 7.5×10^5–10^6 ppm, the transmittance minimum near $\lambda = 2.0$ μm is slightly red-shifted, which is obviously due to the superposition of the contributions from D_2O and HDO molecules. According to Ref. 45, for D_2O
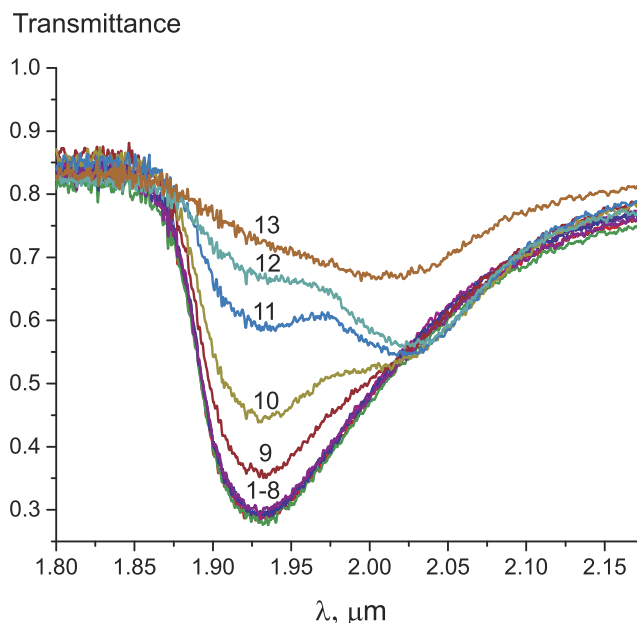
Transmittance

FIG. 2. Transmittance spectra for the water samples with various deuterium contents. Curve 1 relates to 3 ppm. Curves 2–8 are from samples: 2—50 ppm, 3—90 ppm, 4—157 ppm, 5—300 ppm, 6—500 ppm, 7—10^3 ppm, 8—10^4 ppm. The others are successively 9—10^5 ppm, 10—2.5·10^5 ppm, 11—5·10^5 ppm, 12—7.5·10^5 ppm, 13—10^6 ppm (pure heavy water).

molecules, there exists an absorption resonance at a wavelength of $\lambda = 1.97$ μm, related to a combination of symmetric and asymmetric stretching vibrations; we note that this line has the lowest intensity (the oscillator strength) among those shown in Fig. 2. At the same time, for HDO molecules, the absorption line in this range corresponds to $\lambda = 2.02$ μm, which, according to data,[44,45] can be attributed to a combination of asymmetric stretching and bending vibrations of this molecule. With a deuterium content of 5×10^5 ppm (50 vol. % of D_2O), we observe two transmittance minimums with approximately equal intensities. We also note that the intensity of the HDO absorption peak decreases with increasing deuterium content; see curves 11 and 12; this is obviously connected with the different oscillator strengths of the corresponding molecular vibrations in the H_2O–D_2O mixture. As follows from the run of curves 9–12, the oscillator strengths are controlled by the isotopic composition of the mixture.

In Fig. 3, we exhibit the transmittance spectra of the Nafion plate, which was previously soaked in liquid samples with a deuterium content within the range 3–10^4 ppm for 30 min [panel (a)]; and for three days [panel (b)]. Transmittance spectrum of dry Nafion is also shown in the graphs (orange curve), i.e., dry Nafion contains some amount of residual water, which can be assumed to be natural water (deuterium content $C = 157$ ppm, cf. orange and magenta curves). When Nafion is soaked in liquid samples with a deuterium content in the given range, the isotopic effects are revealed: unlike the spectra of liquid samples, Nafion transmittance depends on the content of deuterium in this range. Note also that for 30 min soaking the spectral dependence for the dry Nafion goes lower than the curve for Nafion soaked in a sample with a deuterium content of 500 ppm, while after soaking for 3 days the transmittance spectra for all deuterium contents go lower than that for dry Nafion. We cannot explain this feature of water with a deuterium content of 500 ppm inside the Nafion matrix for short times of swelling.

In Fig. 4, we exhibit the dependence of the transmittance at the wavelength $\lambda = 1.92$ μm, which corresponds to the minimum value for the given spectral range, for 30 min and 3 days of soaking correspondingly. As can be seen, in contrast to pure liquid samples, the transmittance of Nafion behaves non-monotonically vs the deuterium content in the range $C = 90$–500 ppm. Note that a decrease in the transmittance in this range indicates that some special regime of swelling is kept for both swelling times. It is interesting that the transmittance at 3 ppm does not change with the soaking time.

In Figs. 5(a) and 5(b), we show the Nafion transmittance, measured after soaking in heavy water for 7 [panel (a)] and 28 days [panel (b)], respectively. Denoting the time after removal the Nafion plate from the flask with D_2O as τ, we show, here, the spectrograms, obtained immediately after removal of the plate from the flask with heavy water and inserting it in the interferometer arm ($\tau = 0$, red curve) and 1 h after removal (blue curve). In addition, the spectrograms of initially dry Nafion (orange curve) and Nafion, dried after soaking (black curve), are given. Note that the spectral band at the wavelength $\lambda = 1.97$ μm, specific for D_2O molecules, is absent in the Nafion transmittance spectrum. Vertical arrows indicate
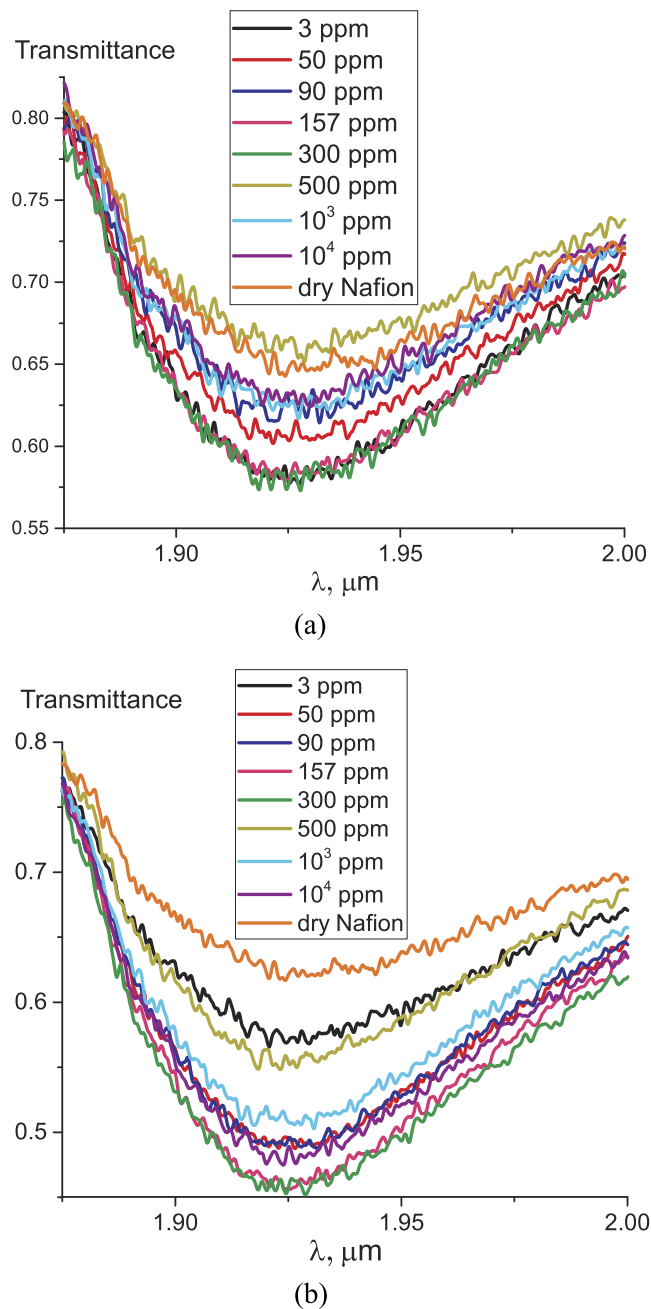

FIG. 3. Transmittance spectrum of Nafion, soaked in liquid samples with various deuterium contents; (a) for 30 min of soaking and (b) for 3 days of soaking.

the interval $\Delta(t) = F(t) - F(0)$, where F is the measured value of the transmittance at the wavelength $\lambda = 1.923$ μm and t is the soaking time; in this figure, this time is equal to 7 and 28 days, respectively. Here, $F(0)$ corresponds to the initially dry Nafion ($t = 0$), $F(t)$ is related to the dried Nafion. The dependence $\Delta(t)$ allows us to study qualitatively the dynamics of the isotope composition of the residual natural water ($C = 157$ ppm) upon soaking in D_2O.

As follows from the graphs, the spectral bands near the wavelengths $\lambda = 1.923$ μm and $\lambda = 2.02$ μm, coupled to the resonances of H_2O and HDO molecules, are clearly seen in the transmittance spectrum immediately after the removal of the plate from D_2O (see the red curves in Fig. 5). This is possible only in the case where the residual H_2O water
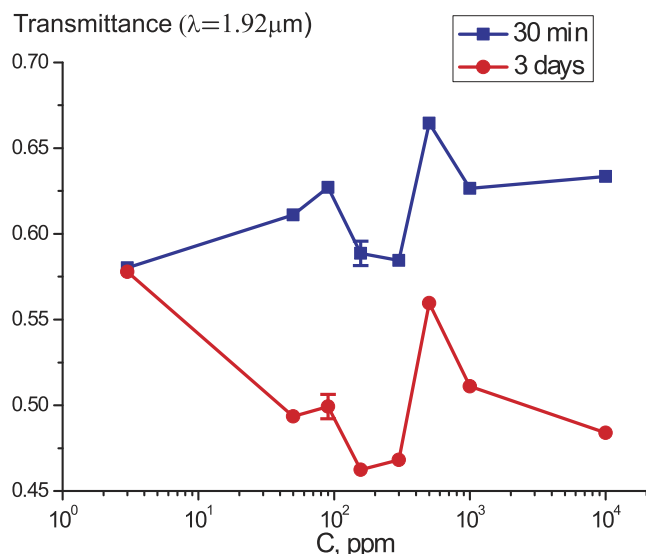
FIG. 4. Dependence of the transmittance at the wavelength $\lambda = 1.92\,\mu m$ vs the deuterium content for 30 min and 3 days of swelling accordingly.

is mixed with D_2O in the process of soaking Nafion in heavy water. At the same time, the content of residual water decreases in comparison with dry Nafion, which is manifested by an increase in the transmittance near the wavelength $\lambda = 1.923\,\mu m$. Comparing the spectrograms of red color ($\tau = 0$) in Fig. 5 with curve 11 in Fig. 2 (for this curve, the deuterium content $C = 5 \times 10^5$ ppm, which is related to 50 vol. % of D_2O in the $H_2O + D_2O$ mixture), we can conclude that immediately after removing the soaked membrane from the flask with heavy water, the D_2O content in the bulk of Nafion exceeds 50 vol. %.

After 1 h of settling in atmospheric air ($\tau = 1$ h, blue curves), the HDO spectral band at the wavelength $\lambda = 2.02\,\mu m$ completely disappears, while the transmittance near $\lambda = 1.923\,\mu m$ increases even more; see the blue curves in the graphs. We associate this with a change in the isotopic composition of the HDO and H_2O mixture inside the pores of the swollen polymer and the corresponding decrease in the oscillator strengths in this spectral range; this statement is justified by the run of the curves 9–13 in Fig. 2.

As follows from Fig. 5, the transmittance of dried Nafion (curves of black color) increases in comparison with that of the initially dry Nafion (orange curve), which is reflected by the length of segment Δ. This is apparently due to the change in the isotopic composition of the bound water in the bulk of polymer matrix. Our interpretation is that we are dealing with a diffusion driven replacement of H_2O molecules by HDO molecules; an indirect proof of this is a slight red shift of the transmittance minimum (with respect to $\lambda = 1.923\,\mu m$) upon soaking, which is indicated by the dashed lines in Figs. 5(a) and 5(b). Currently, we are carrying out more detailed measurements of the shifts of the resonance bands to the long-wave region in the process of soaking Nafion in D_2O.

In Fig. 6, we show the dependence of $\Delta(t)$; the experimental points are approximated by the curve $\Delta(t) = 0.055 \cdot [1 - \exp(-t/2.973)]$. For a qualitative analysis of the dependence obtained, consider the curve 9 in Fig. 2, with deuterium content
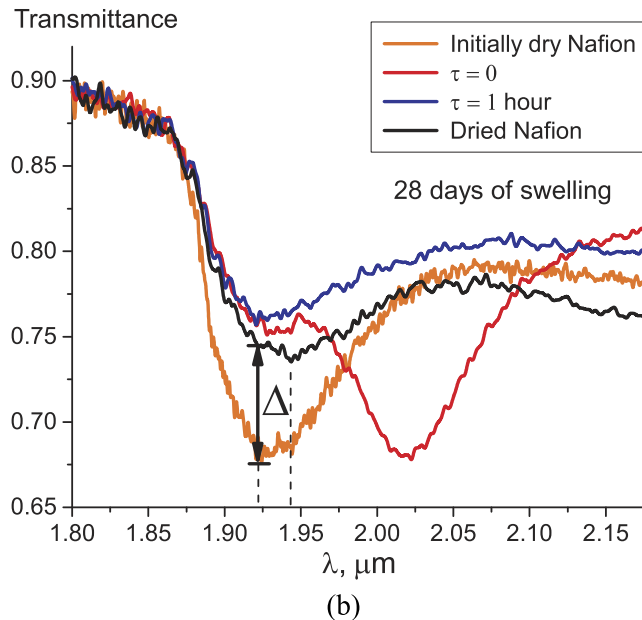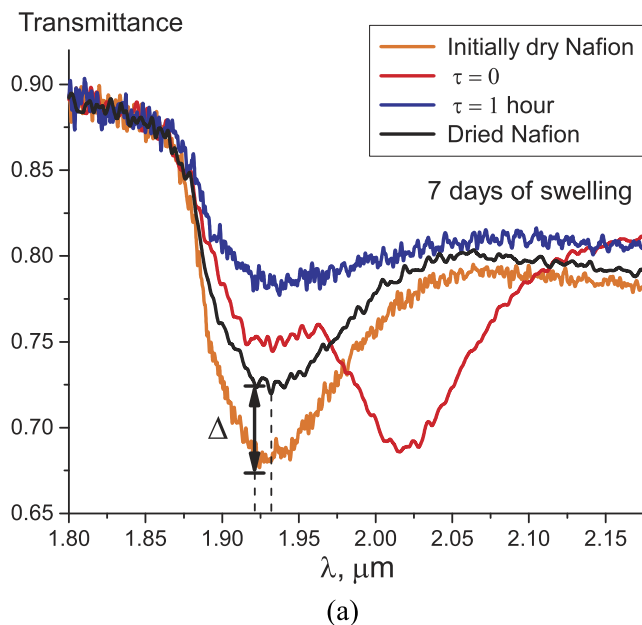

(a)

(b)

FIG. 5. The Nafion transmittance spectrum in the range 1.8–2.15 μm; orange curve is related to the initially dry Nafion; red curve is related to the spectrogram, recorded immediately after removal of the Nafion plate from the flask with heavy water; blue curve is related to the spectrogram, recorded 1 h after removal of the Nafion plate from the flask; black curve is related to the Nafion after drying in the drying cabinet. Case (a) is related to soaking for 7 days. Case (b) is related to soaking for 28 days. The dashed lines indicate the positions of the transmittance minima of the initially dry Nafion ($\lambda = 1.923\,\mu m$) and the dried Nafion.

$C = 10^5$ ppm. We see that the transmittance near the wavelength $\lambda = 1.923\,\mu m$ grows in comparison with the case of $3 < C < 10^4$ ppm (curves 1–8), but there is no resonance transmittance band at the wavelength $\lambda = 2.02\,\mu m$; the latter is clearly seen in curves 10–12, Fig. 2. These two features—the increase in the transmittance near $\lambda = 1.923\,\mu m$ and the absence of transmittance minima at longer wavelengths—are also typical for spectrograms obtained for dried Nafion. We can infer that as the Nafion plate is soaking in heavy water, the residual molecules of H_2O, which exist in the bound state in
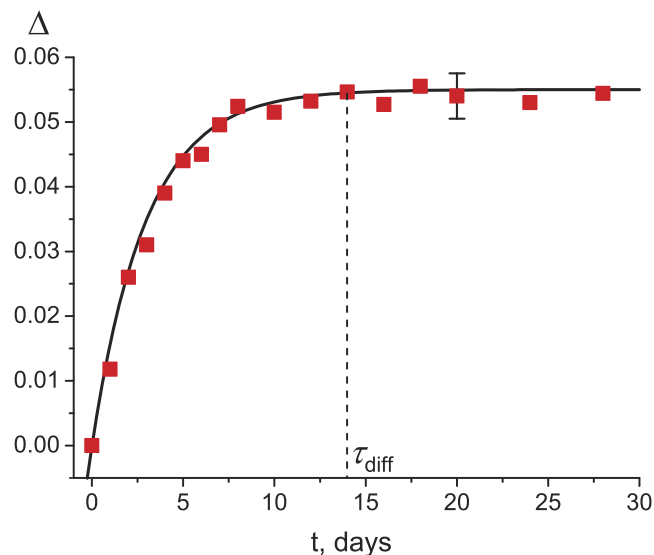
FIG. 6. Dependence of $\Delta(t)$; the dotted line indicates the time of reaching the stationary level.

the polymer bulk inside closed cavities (see Fig. 7 in Ref. 14), are partially replaced by HDO molecules, and that the deuterium content in such water seemingly lies in the range $10^4 \leq C \leq 10^5$ ppm. Such a replacement is controlled by diffusion kinetics; the diffusivity of residual water can be estimated from the graph in Fig. 6. Assuming that the steady-state level of $\Delta(t)$ is reached on the fourteenth day of soaking, i.e., the diffusion time is $\tau_{\text{diff}} \approx 1.21 \times 10^6$ s, and assuming that imbibition of water into the membrane takes place from both sides of the membrane, we obtain for the residual water diffusivity the estimate $D = d^2/(4\tau_{\text{diff}}) \approx 6 \times 10^{-11}$ cm^2/s, where d = 175 μm is the thickness of the Nafion plate. To the best of our knowledge, we have obtained the numerical estimate of the residual water diffusivity in the bulk of Nafion for the first time.

We emphasize once again that the observed diffusion replacement is related specifically to the molecules of residual water, which in principle cannot be removed by prolonged drying, since this water is contained in closed cavities in the membrane bulk; i.e., it does not come in contact with atmospheric air. At the same time, diffusion processes in open pores have been fairly well studied; see, for example, Refs. 46–49; the results of studies of the bound water diffusion in the Nafion membrane are presented in Refs. 50–52. It was shown that the diffusion kinetics of bound water in open pores is controlled by the humidity and temperature in the drying cabinet, as well as by the size and surface properties of the pores, and the water can be completely removed from the open pores by prolonged drying. Thus, the soaking of the polymer membrane followed by drying (provided that the solubility of the membrane can be neglected) seems likely to be a thermodynamically reversible process.

At the same time, following Ref. 14, as Nafion is being soaked in natural water, the following regimes are realized in the near-surface layer of the membrane. The swelling induces a modification of the cavities with residual water, which becomes spherical water pools with the ionic groups at the polymer-water interface; those pools were termed as

ionic domains. With growing water content, the water pools' diameter increases, while the inter-pool distance increase is not substantial, which leads to a percolation. At water volume fraction values larger than 0.5, an inversion of the structure occurs and the near-surface structure of the membrane corresponds to a connected network of rod-like polymer aggregates. Between the water volume fraction of 0.5 and 0.9, this rod-like network swells; the swelling is then due to an increase of the distance between the rods. Summarizing, with the soaking of Nafion in heavy water, the spatial structure of cavities with residual water is destroyed, and partial diffusion replacement of H$_2$O molecules by HDO molecules occurs. With the subsequent drying of the membrane, the spatial structure of cavities containing residual water is apparently restored, but the isotopic composition of this water has been changed. To the best of our knowledge, such a diffusion regime was observed for the first time.

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