The research of time dependence polymeric membrane swelling in water with various deuterium content

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Abstract. Experiments on the 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 examined, depending on the deuterium content in water within the spectral range 1.8 - 2.15 μm. The experiments were carried out according to two protocols: with the first protocol we studied the dynamics of Nafion swelling in H2O + D2O mixtures for the deuterium concentrations 3 < C < 10^4 ppm, and with 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 with 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), was studied.

1. 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, see refs [5 - 7] and references therein. As was shown by neutron scattering, see, e.g., ref [8], this membrane separates a hydrophobic matrix from water-filled spherical or bicontinuous cavities, similar to oil in microemulsions. The surface of the aqueous regions is presumably charged due to the dissociation of terminal sulfonic groups:

R⎯SO3H + H2O⇌ R⎯SO3− + H3O+ (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 experimental measurement of ionic conductivity, as well as on SANS and SAXS, see refs [14 - 18], and neutron reflectivity [19]. From a fundamental point of view an ionic double layer without salt behaves peculiarly, is not accessible to classical colloid theory and is determined by
hydration, which is also highly counterion and coion ion-specific. That specificity and its implications will be explored extensively in following publications.

Our Nafion studies have also been motivated by an 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 [12]. 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 [13] and 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 [14] that might well explain the matter. It also is reminiscent of the extensive work of N. Ise and collaborators [15] on stability of suspensions of highly dialyzed latex particles 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 [16, 17]. These forces are very long range and strictly non-additive.

This work is a reasearch of the dynamics of Nafion swelling in water with FTIR techniques [18]. We remark on how our research fits into a wider context: Our aim was to study the dynamics of swelling of Nafion in water over a wide range of deuterium content. 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 $\text{H}_2\text{O}$, $\text{HDO}$, and $\text{D}_2\text{O}$ 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 [19 - 23]. Furthermore, deuterium effects have much biological impact, which are not understood, see, for instance, the monograph ref[24]. 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 content 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].

2. Materials and methods

In our experiments we used deuterium depleted water samples (DDW), deuterium content at a level of 3 ppm, manufactured by "Almaz" Ltd, Russia. The DDW water 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 $\approx$ 157 ppm; we will refer to these samples as "natural" water), and deuterium water samples (deuterium oxide, 99.9 atom%, content of deuterium $= 1\cdot10^6$ ppm, "Cambridge Isotope laboratories", UK) were used. Water samples with deuterium contents of 3, 50, 90, 300, 500, $10^3$, $10^4$, $10^5$, 2.5·$10^5$, 5·$10^5$, 7.5·$10^5$, and $10^6$ ppm (pure $\text{D}_2\text{O}$) were used. These samples were prepared by bulk dilution of DDW and $\text{D}_2\text{O}$. In addition, we investigated the samples of deionized Milli-Q water (specific resistance at 25 °C is 18 MΩ-cm, deuterium content is 157 ± 1 ppm). 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 figure 1. The spectrometer has the following characteristics:

- Maximum spectral range: 6000 – 400 cm\(^{-1}\);
- Tunable spectral resolution: 8 – 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 sec. 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 by 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.

![Figure 1. Schematic of Fourier spectrometer AF-01.](image)

**3. Experimental part**

At first studied the transmittance (in dimensionless units) of liquid samples in the spectral range 1.25 - 10 μm. As is well known, see [33, 34], the main mechanism of water absorption in this range is due to symmetric and antisymmetric stretching vibrations of the OH bonds of the H\(_2\)O 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\(_2\)O molecule; this band is centered at a wavelength of \(\lambda = 1.923\) μm.

The liquid sample was poured into a cell, the windows of which were made of CaF\(_2\), transparent in the investigated spectral range (the transparency boundary in the long-wavelength region corresponds to 

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to $\lambda = 3 \, \mu m$); the thickness of the liquid layer in the cell corresponded to 90 $\mu m$, 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 $4 \times 4 \, mm^2$, 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 minutes. 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 figure 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 measurement included 16 successive taking the spectrum and took several minutes; each point on the spectrogram corresponded 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. The plate was then removed from the cell, and its transmittance spectra were taken immediately after ($t = 0$), and 1 hour later ($t = 1 \, hour$). After these experiments, the plate was dried for two days in a drying cabinet, 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 [14], the isolated cavities containing residual water have a size of $\sim 15 \, \AA$; 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.

4. Discussion of experimental results

Panoramic spectra of the transmittance of a mixture of H$_2$O and D$_2$O near $\lambda = 1.923 \, \mu m$ are shown in figure 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, with a deuterium content in the range of $7.5 \cdot 10^5 - 10^6 \, ppm$, the transmittance minimum near $\lambda = 2.0 \, \mu m$ is slightly red-shifted, which is obviously due to the superposition of the contributions from D$_2$O and HDO molecules. According to [34], for the D$_2$O molecule, there exists an absorption resonance at a wavelength of $\lambda = 1.97 \, \mu m$, related to a combination of symmetric and antisymmetric stretching vibrations; we note that this line has the lowest intensity (the oscillator strength) among those shown in figure 2. At the same time, for the HDO molecule, the absorption line in this range corresponds to $\lambda = 2.02 \, \mu m$, which, according to data [33, 34], can be attributed to a combination of asymmetric stretching and bending vibrations of this molecule. With a deuterium content of $5 \cdot 10^5 \, ppm$ (50 volume % of D$_2$O), 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, 12; this is obviously connected with the different oscillator strengths of the corresponding molecular vibrations in the H$_2$O - D$_2$O mixture. As follows from the run of curves 9 - 12, the oscillator strengths are controlled by the isotopic composition of the mixture.
Figure 2. Transmittance spectra for the water samples with various deuterium content. 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 \times 10^5 ppm, 11 - 5 \times 10^5 ppm, curve 12 - 7.5 \times 10^5 ppm, curve 13 - 10^6 ppm (pure heavy water).

In figure 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 minutes (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 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 will not give any comments on this.

Figure 3. Transmittance spectrum of Nafion, soaked in liquid samples with various deuterium content; (a) - for 30 minutes of soaking, (b) – for 3 days of soaking.
In figure 4 we exhibit the dependence of the transmittance at the wavelength $\lambda = 1.92 \, \mu m$, which corresponds to the minimum value for the given spectral range, for 30 minutes 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; the experimental scatter in this graph corresponds to the size of squares. The non-monotonic behavior of the transmittance with respect to the soaking time can be attributed to the fact that general increase in the deuteration of polymer sites affects curvature (bending) of the polymer chains and hence their packing, but preferential adsorption of excess deuterium around hydrophilic sites that change molecular forces between polymer strands and again affects packing and density of the polymer. Note that a decrease in the transmittance in the range of deuterium concentrations $50 - 10^3$ ppm indicates that here we deal with some special regime of swelling, which is kept for both swelling times. It is interesting that the transmittance at 3 ppm does not change with the soaking time. At present, we are conducting more detailed researches of the time dependences of the Nafion transmittance for soaking in water with different deuterium content.

![Figure 4. Dependence of the transmittance at the wavelength $\lambda = 1.92 \, \mu m$ vs the deuterium content for 30 minutes and 3 days of swelling accordingly.](image)

In figure 5 (a) and (b) we show the data of measurements of the Nafion transmittance after soaking in heavy water for 7 (panel (a)) and 28 days (panel (b)), respectively. The spectrograms, obtained immediately after removal of the polymer plate from the flask with D$_2$O and inserting in the interferometer arm ($t = 0$, red curve) and 1 hour after removal (blue curve) are plotted. In addition, spectrograms of initially dry Nafion (orange curve) and Nafion, dried after soaking (black curve), are given. Note that the spectral band at the wavelength $\lambda = 1.97 \, \mu m$, specific for D$_2$O molecule, is absent in the Nafion transmittance spectrum. Vertical arrows indicate the interval $\Delta(t) = F(t) - F(0)$, where $F$ is the measured value of the transmittance (in arbitrary units) at the wavelength $\lambda = 1.923 \, \mu m$. Here, $F(0)$ corresponds to the initially dry Nafion (the soaking time $t$ is zero), and $F(t)$ corresponds to the dried Nafion, which was soaked for the time $t$; in this figure this time is equal to 7 and 28 days, accordingly. The dependence $\Delta(t)$ allows us to study on a qualitative level the dynamics of the isotope composition of residual natural water ($C = 157$ ppm) upon soaking in D$_2$O.

As follows from the graphs obtained, immediately after the removal of the plate from D$_2$O (see the red curves in figure 5), the spectral bands near the wavelengths $\lambda = 1.923 \, \mu m$ and $\lambda = 2.02 \, \mu m$, which are related to resonances of the H$_2$O and HDO molecules, are clearly seen in the transmittance spectrum. This is possible only in the case where the residual H$_2$O water is mixed with D$_2$O 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 ($t = 0$) in figure 5 with curve 11 in figure 2 (for this curve,
the deuterium content $C = 5 \cdot 10^5$ ppm, which is related to 50 vol. % of D$_2$O in the H$_2$O + D$_2$O mixture), we can conclude that immediately after removing the soaked membrane from the flask with heavy water, the D$_2$O content in the bulk of Nafion exceeds 50 vol. %.

After one hour of settling in atmospheric air ($t = 1$ hour, 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 HDO and H$_2$O mixture inside the pores of 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 figure 2.

As follows from figure 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 $\Delta$. 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$_2$O 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 figure 5 (a) and (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$_2$O.

In figure 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 figure 2, with deuterium content $C = 10^5$ 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 (the curves 1 - 8), but there is no resonance transmittance band at the wavelength $\lambda = 2.02 \mu m$; the latter is clearly seen in the curves 10 - 12, figure 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, residual molecules of H$_2$O, which exist in the bound state in the polymer bulk inside closed cavities (see figure 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 figure 7. 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, we obtain for the residual water diffusivity the estimate \( D = \frac{d^2}{\tau_{\text{diff}}} \approx 2.5 \times 10^{-10} \) cm/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.

![Graph showing \( \Delta(t) \) vs. time](image)

Figure 6. Dependence of \( \Delta(t) \); the dotted line indicates the time of reaching the stationary level.

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 in a cabinet, since this water is contained in closed cavities in the membrane bulk, i.e. 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, [35 - 38]; the results of studies of the bound water diffusion in the Nafion membrane are presented in refs [39 - 42]. 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 in a cabinet (provided that the solubility of the membrane can be neglected) seems likely to be a thermodynamically reversible process.

At the same time, following [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 the water content, the water pools diameter increases, while the inter-pool distance increase is not substantial, which leads to 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 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 diffusion regime was observed for the first time.

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