Study of the luminescence from polymeric membrane swollen in water with various content of deuterium; isotopic effects

N F Bunkin¹,²,³, U A Bashkina¹, N G Bolikov¹, I S Bereza¹, I I Molchanov¹ and V A Kozlov¹

¹ Bauman Moscow State Technical University, 2nd Baumanskaya St. 5, Bld.1, Moscow, 105005 Russia
² Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, Moscow, 119991 Russia
³ E-mail: nbunkin@mail.ru

Abstract. The paper describes the experiments with the irradiation in the near UV range of a swollen surface of Nafion polymer membrane in the grazing-incidence pumping geometry. The pump radiation caused a photoluminescence from the Nafion interface in a certain spectral range. The photoluminescence signal proved to be an important parameter for describing the swelling of the polymer in water. It is shown that luminescence is generated due to the presence of sulfonic groups, anchored to the ends of the perfluorovinyl ether groups forming a tetrafluoroethylene (Teflon) base. The dynamics of Nafion swelling was studied depending on the content of deuterium in water. In the case where the polymer is swollen in water with different deuterium content, isotopic effects appeared to be largely manifested.

1. Introduction

Recently, the polymer membranes made of Nafion™, developed by DuPont, have been very intensively investigated; see, for example, the review [1]. The interest in these studies is linked to the use of Nafion in low-temperature hydrogen cells; see [2 - 4]. Nafion membranes are characterized by the spatial separation at the nanoscale between the hydrophobic matrix and the water-filled spherical cavities. Namely, as was shown in experiments with neutron scattering [5], water in the water-swollen Nafion membrane is localized in cavities within the polymer matrix. On the boundary of these regions, double ionic layers (the so-called ionic domains) are formed as a result of the dissociation of water-contact terminal sulfonic groups, accompanied by proton tearing off:

\[
\text{R}-\text{SO}_3\text{H} + \text{H}_2\text{O} \Leftrightarrow \text{R}-\text{SO}_3^- + \text{H}_3\text{O}^+. \quad (1)
\]

The proton passes into the bulk water, and an uncompensated negative charge remains at the membrane interface. At the same time, the water content in the cavities (the degree of swelling) increases with the growth of swelling time, as well as with increasing temperature and pressure [6]. 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 a rise of the degree of swelling [7 - 10]. The structural evolution of Nafion membrane from the water-free state to a high degree of swelling was studied in detail in [11].

We should also refer to [12], where Nafion swelling was investigated with the help of small-angle X-ray scattering in the scheme of grazing incidence of incident radiation, and also with atomic force microscopy. In that research it was found that the bundles of polymer fibers on the surface are oriented...
upon swelling mainly perpendicular to the surface, while for Nafion in contact with the vapor phase, the bundles of polymer fibers are oriented parallel to the surface.

Nafion studies are also highly motivated due to the fact that near the surface of Nafion swollen in water a special region is formed, from where colloid micron-sized particles are pushed out. Therefore, this area was called the excluded zone (EZ) [13]. 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 [14] and references therein. It was suggested that EZ represents a special phase state of water, which is characterized by a high degree of ordering at the scale of several hundred microns.

The present work is devoted to the study of the dynamics of Nafion swelling in water with the use of luminescent techniques. These techniques are widely used in polymer studies, see, for example, [15 - 20]. Here, we develop a technique for studying the swelling of Nafion, using photoluminescence spectroscopy; the very preliminary results obtained by us with this technique have been published in [21 - 23].

The aim of our experiments was to study the dynamics of swelling Nafion in water with different deuterium content. Studies of isotope effects in the interaction of various polymers with ordinary and heavy water are undoubtedly relevant and have been actively developed lately, see, for example, [24 - 28]. These studies are also interesting from the viewpoint of biological applications. Experiments with mammals have shown that replacing 25 % of protium atoms by deuterium atoms in living tissues results in sterility, which is sometimes irreversible. Higher concentrations of deuterium lead to a rapid death of the animal; thus, mammals die at about 50 % deuterium water in their body. At the same time, the fish and inferior invertebrates die at 60 - 70 % content of deuterium in water, while the protozoa are able to adapt up to 70 % deuterium content, and some algae and bacteria are able to survive in almost pure heavy water [29]. At the molecular level, it is not known what the target for the action of deuterium is. Apparently, it makes sense to talk about the general toxic effect caused by the inhibition of certain biochemical reactions. It is known that "classical" chemical reactions in deuterium water develop more slowly than in natural water, and hydrogen bonds involving deuterium are amplified. Therefore, proton-exchange systems and systems with high proton mobility are the most susceptible to the replacement of protium by deuterium. Such systems in the cell are the ion channels of membranes and enzymes, which play the role of catalysts for biochemical reactions. The most vulnerable of enzymes is the respiratory chain of higher animals. It is shown that deuterium water significantly reduces the activity of cytochrome oxidase and a number of other parts of the electron transport chain of mitochondria, which is a key enzyme in the respiratory chain [30]. In heavy water, biosynthesis of proteins [31] and DNA [32] develops much slower. It has been established that deuterium water can affect the biosynthesis of secondary metabolites. For example, D₂O inhibits the synthesis of serotonin, which in turn can cause serious psychological problems [33]. It was shown that deuterium water significantly reduces the activity of the ionic (cation) channels of cell membrane [34], which leads to a slowing down of the propagation rates of nerve impulses [35]. Interestingly, deuterium water acts not only on the membranes, but also on the glycocalyx, which covers the membrane [36]. The toxic effect of deuterium water can be realized not only by inhibiting biochemical reactions. It is known that the lifetime of singlet oxygen is significantly increased in deuterium water [37], which leads to the formation of dangerous compounds such as active oxygen species, namely hydrogen peroxide, superoxide radical, hydroperoxide radical, etc. [38]. The level of the toxic effect of deuterium water increases with the growth of its concentration in the body. At present, the literature describes a large number of negative effects in highly diluted deuterium solutions (the ratio D/H is 500 - 1000 ppm), where deuterium content is only 3 - 10 higher than in natural water [39, 40].

In parallel with the study of toxicology of deuterium water, the idea of the use of deuterium-depleted water (DDW, or protium water) for the human and animal organism is widely discussed. At present, in the literature one can find references to the fact that DDW can promote the normalization of certain biochemical parameters of the organism during its detoxification [41], including the cardiometabolic parameters [42]. At the same time, it is known that when the content of deuterium in
water is less than 100 ppm, there is a significant delay in cell fission [43], and the expression of the bcl-2 gene, responsible for suppressing the apoptotic death of many cell types, is also inhibited [44]. Probably, for biological systems there exists an optimum of deuterium content lying in the range of 100 - 200 ppm. We note in this connection that the ratio D/H in natural water corresponds to the so-called standard mean ocean water (SMOW), and is related to a very narrow area of deuterium content: D/H = 157 ± 1 ppm (log 157 ≈ 2.2), see [45].

2. Materials
In our experiments we used protium water samples (DDW, deuterium content at a level of 3 ppm), manufactured by "Almaz" Ltd, Russia. The protium water samples were prepared by low-temperature vacuum rectification; 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 ~ 157 ppm; we will refer to these samples as “natural” water), and deuterium water samples (deuterium oxide, 99.9 atom %, content of deuterium ≈ 1·10^6 ppm, "Cambridge Isotope laboratories", UK) were used. Samples of water with the deuterium content of 3, 90, 157, 300, 10^3, 10^4 and 10^6 ppm (in the latter case we are dealing with pure D_2O) were investigated. These samples were prepared by the corresponding bulk dilution of protium and deuterium water. In the obtained this way liquid samples, the Nafion plates (DuPont, USA; the plate thickness d = 175 μm) were subjected to soaking. Finally, we investigated solutions of Nafion in isopropyl alcohol (Sigma Aldrich, USA), and aqueous solutions of heparin C_{12}H_{19}NO_{20}S_3 (Belmedpreparaty, Belarus, weight content of 58 mg/ml) and chondroitin sulfate C_{14}H_{21}NO_{15}S (Belmedpreparaty, Belarus, weight content of 100 mg/ml).

3. Experiments with luminescence spectroscopy

3.1. Absorption coefficient of Nafion. Optimum wavelength choosing.
First, we used the Cary 100 UV-Vis spectrophotometer (Varian Inc., Australia) to study the absorption spectrum for dry (water-free) Nafion, as well as for Nafion swollen in natural water for an hour, 10 and 24 hours. Figure 1 shows the dependence of the optical density $D = \log \frac{\Phi_{in}}{\Phi_{out}} = [\kappa(\lambda) \cdot d] / \ln 10$, where $\kappa(\lambda)$ is the absorption coefficient. Here, $\Phi_{in}$ and $\Phi_{out}$ are the intensities of the incident and transmitted radiation at the wavelength $\lambda$. The samples of dry and swollen Nafion were kept in identical quartz cells. For a correct comparative analysis of the results, the optical densities of the water sample and the cell walls were subtracted from the curves, obtained for the swollen Nafion, with taking into account the reflection from the interface of dry and swollen membrane. As follows from the graphs, the absorption appears for the wavelengths $\lambda \leq 500$ nm. At the same time, the optical density decreases as the polymer is soaked.
Figure 1. Spectral dependences of the optical density $D(\lambda)$ of dry (red) and swollen in natural water of Nafion for an hour (green), 10 hours (magenta) and 24 hours (blue).

In finding the positions of the absorption bands of Nafion, we used the results of study [46], reporting on the existence of absorption bands centered on 196, 230 and 273 nm in dry Nafion; it was also obtained in [46] that the Nafion optical density decreases upon swelling in water. According to [46], the absorption at 196 nm is associated to the carbon-carbon double bond; the absorption at 230 nm is assigned to the diene structure, and the band at 273 nm is assigned to a chromophore containing a carbonyl group derived from a radical group. It was specially noted in [46] that these absorptions bands are not associated with the sulfonic group of Nafion. We note that the spectral range of our device was restricted by a wavelength of $\lambda = 200$ nm, and we could not measure the optical density at shorter wavelengths. At the same time, the tails of the spectral lines from the vacuum UV region should contribute to the results of our measurements. Obviously, the main contribution is made by the 196-nm band, which is closest to the measured spectral range (200-600 nm). In addition, we must take into account the Rayleigh scattering, which increases strongly when approaching the vacuum UV. To exclude these contributions from the absorption spectra in Figure 1, we represent the measured absorption coefficient $\kappa(\lambda)$ in the form

$$\kappa(\lambda) = b(\lambda) + \gamma(\lambda) + C_0,$$

where

$$b(\lambda) = \frac{\ln 10}{d} \left[ \log \frac{1}{1 - K \cdot \lambda^{-4}} \right] + \frac{C_{196}}{\alpha_{196} + (\lambda - 196)^2},$$

$$\gamma(\lambda) = \frac{C_1}{\alpha_1 + (\lambda - \lambda_1)^2} + \frac{C_2}{\alpha_2 + (\lambda - \lambda_2)^2}.$$ (2)

Here the term $\frac{\ln 10}{d} \left[ \log \frac{1}{1 - K \cdot \lambda^{-4}} \right]$ stands for the contribution from Rayleigh scattering (the technique to correct the optical density for the background scattering is described in detail, for example, in Ref. [47]), while the term $\frac{C_{196}}{\alpha_{196} + (\lambda - 196)^2}$ implies the contribution from the Lorentz absorption contour at the wavelength 196 nm. The term $\gamma(\lambda)$ is the sum of Lorentz contours, which approximate the Nafion absorptivity in the middle/near UV and visible region; this term is of special interest to us. Here, $K, C_0, C_{196}, \alpha_{196}$ and $C_1, C_2, \alpha_1, \alpha_2$ served as fitting parameters. After finding the values of these parameters, the dependence of $\gamma(\lambda)$ can be plotted (see Figure 2).
As follows from the graphs, one can distinguish two absorption bands centered at $\lambda_1 = 232$ and $\lambda_2 = 268$ nm; hereinafter, we refer to them as "$\lambda_1$-band" and "$\lambda_2$-band", respectively. Note that the centers of these bands are very close to those obtained in [46]. It is also seen that the absorption coefficient $\gamma$ decreases upon soaking in water. This is obviously due to the formation of the porous structure upon soaking and the decrease in the volume number density of the absorbing polymer particles. Indeed, we can express the absorption coefficient as

$$\gamma = \sigma_{abs} \cdot \langle n_{Naf} \rangle,$$

where $\sigma_{abs}$ is the absorption cross-section (which is implied to be constant), and $\langle n_{Naf} \rangle$ is the value of volume number density of the Nafion particles, averaged over the sample thickness.

According to the laws of the light – substance interaction, the luminescence from Nafion can be excited upon irradiating at a wavelength, belonging to one of the absorption bands. Since the absorptivity of water near $\lambda = 200$ nm rapidly grows with decreasing the wavelength, approaching to the vacuum UV region, the use of the optical pump at the wavelength from the $\lambda_1$-band is not reasonable, while using the pump at the wavelength from the $\lambda_2$-band looks more preferable. Specifically, we used the fourth harmonic of the single-mode pulsed-periodic YAG:Nd$^{3+}$- laser manufactured by the group of companies "Laser Compact", Russia, model DTL-382QT, $\lambda = 266$ nm, pulse repetition frequency was 3 kHz, pulse-width was 5 ns, averaged pulse energy was 4 μJ, the frequency multiplying was performed with BBO crystal. The radiation at this wavelength falls in the center of the $\lambda_2$-band; the spectral line of this laser is shown in figure 3 a. This one and the following spectral patterns were obtained with the help of a FSD-8 mini-spectrometer, see below. In addition, we use CW radiation of a laser diode with the average power of 50 mW at a wavelength of $\lambda = 369$ nm, which is related the edge of the $\lambda_2$-band; this spectral line is shown in figure 3 b.
Figure 3. Spectral lines of the pump radiation for excitation of luminescence from Nafion; case a is related to the fourth harmonic of YAG: Nd<sup>3+</sup>- laser, and case b is related to the CW laser diode.

In figure 4 we show the spectrum of luminescence from dry Nafion excited at wavelengths \( \lambda = 266 \) and 369 nm. As follows from the graphs, the dependences obtained for both wavelengths are completely identical. In the case of pumping at wavelength \( \lambda = 266 \) nm, the luminescence spectrum is slightly red-shifted; the physical nature of this shift is beyond the scope of this study. It is also seen that for both pump wavelengths, the spectral luminescence maximum corresponds to \( \lambda = 508 \) nm; we hereinafter study the luminescence at this wavelength.

Figure 4. Luminescence spectra from dry Nafion, irradiated at wavelengths \( \lambda = 266 \) and 369 nm.

In figure 5 we show the temporal dynamics of the luminescence intensity from the dry Nafion at wavelength \( \lambda = 508 \) nm for the pumps at \( \lambda = 266 \) and 369 nm. As is seen, Nafion's luminescent state eventually decays upon irradiating at wavelength \( \lambda = 266 \) nm, while CW irradiation at wavelength \( \lambda = 369 \) nm does not lead to a decrease in the luminescence signal; the nature of the luminescent state degradation with irradiation at wavelength \( \lambda = 266 \) nm is outside the scope of this work. Since the aim of our experiments is non-invasive diagnostics of swelling Nafion in water with different deuterium content, irradiation at wavelength \( \lambda = 266 \) nm, obviously, is not suitable, i.e. the most optimum pump wavelength is \( \lambda = 369 \) nm. It is well to say that the spectral minimum of water absorptivity also corresponds to \( \approx 370 \) nm; see, e.g., [48].
Figure 5. Dependence of the luminescence signal at a wavelength of $\lambda = 508$ nm on the irradiation time for the pump wavelength $\lambda = 266$ nm (blue curve), and $\lambda = 369$ nm (red curve).

3.2. Experimental setup for investigation of luminescence from Nafion.

The schematic of the experimental setup is shown in Figure 6. The probing radiation of CW laser diode (1) (optical pump) at wavelength $\lambda = 369$ nm was input to the multimode optical quartz fiber (2) with a core diameter $\varnothing = 100$ μm and numeric aperture $NA = n_0 \sin \alpha = 0.3$, where $n_0 = 1$ is the refractive index of air, $\alpha$ is the divergence angle of the optical beam at the fiber output in the air. This fiber was fixed in the hole, centered at the bottom of a cylindrical cell (3) made of stainless steel; the direction of the pump radiation set the optical axis of the system. The cell was thermally stabilized at room temperature ($T = 23$ °C) with a liquid thermostat (accuracy of stabilization was ± 0.1 °C) and filled with liquid samples. First, we investigated solutions of Nafion in pure isopropyl alcohol, which in some experiments were diluted with water, having different deuterium content. Besides, aqueous solutions of heparin and chondroitin sulfate were investigated.

In addition, we studied the regimes of swelling Nafion in water with different deuterium content. In these experiments, the pump beam illuminated a square Nafion plate (4) with a side $h = 4$ mm and thickness $d = 175$ μm; the plate was placed in parallel to the optical axis, i.e. the experiment was performed in the grazing-incidence pumping geometry. The luminescence emission was reflected from the walls of the cylindrical cell (Nafion is transparent in the visible range), and turned out to be focused along the optical axis; the focusing resulted in a significant gain in the intensity of the measured signal. The emission of luminescence was input to the receiving multimode optical fiber (5), analogous to the fiber (2); this fiber was also centered at the bottom of the cell. The luminescence signal was then fed to the FSD-8 minispectrometer (6), and processed by a computer (7). In some cases, the Nafion plate was shifted away from the optical axis with a stepper (8).
The necessity for preliminary experiments with aqueous solutions of heparin and chondroitin sulfate was dictated by the fact that these substances, like Nafion, have the terminal sulfonic group $\text{SO}_3\text{H}$. In the case of Nafion, the terminal sulfonic group is "anchored" to the perfluorovinyl ether group, which is the Teflon base. As was obtained in our preliminary experiments, if Teflon is irradiated at wavelength $\lambda = 369 \text{ nm}$, luminescence does not occur in the whole spectral range under study. Thus, the hypothesis naturally arises that the luminescence is excited due to the presence of the sulfonic groups. To make sure this assumption is valid, we carried out experiments with solutions of Nafion in isopropyl alcohol and aqueous solutions of heparin and chondroitin sulfate; it was verified beforehand that there is no luminescence signal from pure isopropyl alcohol and water upon irradiating at wavelength $\lambda = 369 \text{ nm}$. To prepare the solution of Nafion, a plate of Nafion with the size of 6 cm$^2$ was subjected to soaking in 35 ml of isopropyl alcohol for 22 hours, which resulted in a slight dissolving of the Nafion plate. Then the remainder of the Nafion plate was removed from the liquid, and the luminescence from the solution of Nafion was studied. In figure 7 we show the luminescence spectra from the solution of Nafion in isopropyl alcohol, and aqueous solutions of heparin and chondroitin sulfate.
As follows from the graphs in figure 7, the spectra of Nafion, heparin and chondroitin sulfate are completely identical in their form, and have a pronounced peak at $\lambda = 508$ nm. At the same time, the spectral maximum in the Nafion solution is red-shifted compare to aqueous solutions of heparin and chondroitin sulfate; the reason for that shift is still unclear for us. We believe that the qualitative similarity of these spectra is a direct proof that in all three samples the sulfonic groups SO$_3$H are the centers of luminescence.

The luminescence signal (measured in arbitrary units, a. u.) can be expressed in the form

$$ P = A + k \cdot I_{pump} \cdot n_{Naf} \cdot \sigma_{lum} \cdot V, $$

where $I_{pump}$ is the pump intensity, $n_{Naf}$ is the volume number density of the luminescence centers (the sulfonic groups); this value obviously coincides the volume number density of the Nafion particles. Besides, $A$ is the intensity of noise of the measuring device, $A = 20 - 270$ a. u., $k$ is the transfer coefficient of the measuring device, $\sigma_{lum}$ is the luminescence cross-section, and $V$ is the luminescent volume, which is determined by the cross-section of the pump beam and the height of the Nafion plate. It is seen that product $I_{pump} \cdot n_{Naf} \cdot \sigma_{lum} \cdot V \equiv W$ has the sense of the luminescence power. For the transfer coefficient $k$ we have the approximation

$$ k = \begin{cases} k_0 = \text{const}, & W > W_{thr}, \\ 0, & W \leq W_{thr}, \end{cases} $$

where $W_{thr}$ is the threshold luminescence power; at $W \leq W_{thr}$ the sensitivity of our measuring device is zero. It is clear that $W_{thr} \sim (n_{Naf})_{thr}$, where $(n_{Naf})_{thr}$ is the threshold volume number density of luminescing centers. Figure 8 gives the dependence of the luminescence signal $P$ on the content of Nafion in the solution of isopropyl alcohol; the zero abscissa point corresponds to pure isopropyl alcohol. We note that the precise values along the abscissa axis are not known; we conventionally assumed that the Nafion content in the initial solution (immediately after removal the remainder of the Nafion plate) is 100 a. u.; it is the maximum abscissa value. The dependence within the rectilinear portion is approximated by formula

$$ P = -237 + 16 \cdot n_{Naf}. $$

The graph in figure 8 is consistent with equation (3) only providing that the value of $\sigma_{lum}$ is a constant.

![Figure 8. Dependence of the luminescence signal on the content of Nafion in isopropyl alcohol solution.](image)

As it will be shown below, the value of signal $P$ decreases while Nafion is soaked in water with different deuterium content. This may be due to either a decrease in the value of $\sigma_{lum}$ (an isotope effect in quenching the luminescence), or a decrease in the volume number density of Nafion particles $n_{Naf}$ upon soaking. To estimate the contribution of possible quenching of the luminescence by deuterium atoms, the following experiment was carried out. Luminescence from the solution of Nafion in isopropyl alcohol was studied upon diluting with protium, natural and deuterium water. The
corresponding graphs are given in figure 9; here the volume content of isopropyl alcohol is scaled along the abscissa axis. The zero abscissa point corresponds to luminescence from pure water. As follows from the graphs, the behavior of $P$ within the experimental error is the same for all liquids, i.e. the isotopic effects in quenching the luminescence can be ignored.

Experiments on the study of luminescence from Nafion were carried out by using two alternative protocols. In the first protocol, a plate of dry Nafion was placed in the empty cell in such a way that the pump radiation (optical axis) was directed along the Nafion surface (such spatial arrangement of the Nafion plate and the optical axis was found from the maximum of the luminescence signal), and then the test liquid was poured into the cell; the moment of filling the cell with liquid served as the start for the time counting. In the experiments on this protocol, the luminescence signal $P$ was measured as a function of the time $t$ of soaking the polymer in water with different deuterium content.

![Figure 9. The luminescence signal upon diluting the solution of Nafion in isopropanol with protium, natural and deuterium water.](image)

The second experimental protocol included soaking of the Nafion plate in the cell with water, having different deuterium content, for 30 minutes (the choice for this particular time of swelling will be substantiated later). In this experiment the Nafion plate was initially mounted in the cell filled with a liquid sample in such a way that the pump radiation "slid" over the plate surface in the grazing-incidence geometry, and after 30 min of soaking the plate was shifted from the optical axis by a step 25 μm with the help of the stepper; the number of the steps was determined by decreasing the luminescence signal up to zero level. Thus, in this experiment, the luminescence signal $P$ was investigated as a function of the distance $x$ between the Nafion interface and the optical axis; the time of a single measurement in that experiment amounted to several seconds. Note that in figure 6 we schematically illustrate the setup of the experiment by the second protocol.

In the experiments by the second protocol, it is necessary to take into account the spatial profile of the pump intensity $I_{\text{pump}}(x)$ and the spatial distribution $n_{\text{Naf}}(x)$ of the volume number density of the Nafion particles, so we rewrite equation (3) in the form

$$P(x) = A + \int_{-\infty}^{\infty} G(x-x_1) \cdot n_{\text{Naf}}(x_1) \, dx_1,$$

where a symmetric kernel of this integral equation $G(x-x_1)$ is the apparatus function of the measurement setup; all dimensional constant factors in (3) enter the kernel $G(x-x_1)$. Our goal is to obtain an explicit expression for $G(x-x_1)$, and then to find the distributions of $n_{\text{Naf}}(x)$, when Nafion is soaked in water with different deuterium content.
An example of solving equation (6) for dry Nafion is shown in figure 10; the value $x = 0$ corresponds to the Nafion interface. In the case of dry Nafion the distribution $n_{dry}(x)$ is conveniently approximated by two Heaviside functions $\theta(x)$ in the form

$$n_{dry}(x) = B \cdot [\theta(x + d) - \theta(x)], \quad (7)$$

where $d = 175 \, \mu m$ is the thickness of the Nafion plate, $n_0$ is dimensional constant. Assuming that the pump radiation at the output from the optical fiber diverges, and the profile $I_{pump}(x)$ is a Gaussian function, it is natural to set the kernel $G(x)$ as

$$G(x) = G_0 \exp \left(-\frac{x^2}{2a^2}\right), \quad (8)$$

where $G_0$ is another dimensional constant, and $a$ is the sought width of the Gaussian profile.

The left-hand side of equation (6) can be represented in the form

$$P(x) = A + G_0 \alpha \sqrt{\pi} \frac{1}{2} \left[ \text{erf} \left( \frac{x + d}{\sqrt{2a^2}} \right) - \text{erf} \left( \frac{x}{\sqrt{2a^2}} \right) \right]; \quad (8)$$

here, the second term is the integral convolution of the Gaussian and Heaviside functions. Minimizing the discrepancy functional between the theoretical curve $P(x)$ and experimental points for dry Nafion (see the theoretic curve in Figure 10), we find that $a = 84 \, \mu m$, which is very close to the core diameter of the optical fiber ($\phi = 100 \, \mu m$), $G_0 \alpha = 7.56 \times 10^3$ a.u., and $A = 124$ a.u. Note that within the framework of this approach, the value of $n_{Na}(x)$ is scaled in a.u. (similar to the signal $P(x)$), in contrast to equation (3), where this value has a dimension of cm$^{-3}$. Note also that the value of $A = 124$ a.u. corresponds approximately to the average level of the noise intensity of the measuring device. Concluding this section, the results of measuring $n_{Na}$ should be considered as averaging over an area with a size of about 84 μm.

In the case of Nafion plate, immersed in water, the pumping beam divergence decreases due to water refraction in accordance with the formula $NA = n_w \sin(\alpha_w)$, where $n_w = 1.33$ is the refractive index of water, $\alpha_w$ is the divergence angle of the optical beam at the fiber output in water. Since the relative arrangement of the optical fiber and the Nafion plate is constant, the relation between the parameters of the Gaussian function for Nafion in water and dry Nafion is $a_w = a (\tan(\alpha_w)/\tan(\alpha))$, where $\alpha = \arcsin(NA)$, $\alpha_w = \arcsin(NA/n_w)$; thus we obtain $a_w = 62 \, \mu m$. 

Figure 10. Dependence of $P(x)$ for dry Nafion. Black open circles are the experimental points, red curve is theoretic approximation for the experimental dependence, blue curve is spatial distribution of $n_{Na}(x)$. 

In the case of Nafion plate, immersed in water, the pumping beam divergence decreases due to water refraction in accordance with the formula $NA = n_w \sin(\alpha_w)$, where $n_w = 1.33$ is the refractive index of water, $\alpha_w$ is the divergence angle of the optical beam at the fiber output in water. Since the relative arrangement of the optical fiber and the Nafion plate is constant, the relation between the parameters of the Gaussian function for Nafion in water and dry Nafion is $a_w = a (\tan(\alpha_w)/\tan(\alpha))$, where $\alpha = \arcsin(NA)$, $\alpha_w = \arcsin(NA/n_w)$; thus we obtain $a_w = 62 \, \mu m$. 

Figure 10. Dependence of $P(x)$ for dry Nafion. Black open circles are the experimental points, red curve is theoretic approximation for the experimental dependence, blue curve is spatial distribution of $n_{Na}(x)$. 

In the case of Nafion plate, immersed in water, the pumping beam divergence decreases due to water refraction in accordance with the formula $NA = n_w \sin(\alpha_w)$, where $n_w = 1.33$ is the refractive index of water, $\alpha_w$ is the divergence angle of the optical beam at the fiber output in water. Since the relative arrangement of the optical fiber and the Nafion plate is constant, the relation between the parameters of the Gaussian function for Nafion in water and dry Nafion is $a_w = a (\tan(\alpha_w)/\tan(\alpha))$, where $\alpha = \arcsin(NA)$, $\alpha_w = \arcsin(NA/n_w)$; thus we obtain $a_w = 62 \, \mu m$. 

Figure 10. Dependence of $P(x)$ for dry Nafion. Black open circles are the experimental points, red curve is theoretic approximation for the experimental dependence, blue curve is spatial distribution of $n_{Na}(x)$.
3.3. Temporal dynamics of Nafion swelling in water with different deuterium content.

In this section, the results of measuring $n_{\text{Naf}}$ by the first experimental protocol are shown: the laser beam is directed along the interface of Nafion subjected to swelling in water. We can define the size of near-surface area, where the value of $n_{\text{Naf}}$ varies upon swelling, as $l \approx a_w \approx 62 \, \mu\text{m}$. This area consists of a thin near-surface volume of the membrane and a liquid layer adjacent to the membrane; according to our model (see below), the polymer fibers effectively "grow out" from the interface toward the liquid bulk, and the near-surface liquid layer is being filled with such fibers. Before describing the experimental results, obtained by the first measurement protocol, it is necessary to note an important feature in the dynamics of luminescence: immediately after immersing the Nafion sample in the liquid the luminescence signal from the Nafion interface increases, but upon soaking this signal eventually drops to a certain stationary level. This situation is shown in Figure 11; the luminescence signal increases approximately twice in the entire spectral range upon soaking the plate of dry Nafion in natural water for 30 sec.

![Figure 11. An increase in the luminescence intensity the after immersing Nafion in natural water.](chart)

The reason for the sharp increase of luminescence after immersing Nafion in a liquid can be explained in the frame of the model put forward in [12]. As was shown in this work, the bundles of polymer particles in dry Nafion are mainly oriented along the surface, but when Nafion is immersed in water, these bundles rotate so as to be oriented across the surface. This effect has a direct relation to our experimental results. Basically, we observe the luminescence of terminal sulfonic groups at the Nafion-water interface; these groups are anchored to the ends of the polymer fibers, and when Nafion is immersed in water, the density of these groups at the interface substantially should increase compare to dry Nafion.

In figure 12 we show a typical example of the experimental dependence of the luminescence signal $P(t)$; the dependence is given for the deuterium content $C = 500$ ppm.

The experimental dependences for all liquids are presented on a semi-logarithmic scale: log $P(t)$, see figure 13. As follows from the graphs, the luminescence signal $P$ decays exponentially, and we can distinguish three dynamic regimes characterized by the decay times $\tau_1$, $\tau_2$ and $\tau_3$:

\[
P(t) = \begin{cases} 
C_1 \exp\left(-t/\tau_1\right), & 0 \leq t \leq t_1 \\
C_2 \exp\left(-t/\tau_2\right), & t_1 \leq t \leq t_2, \\
C_3 \exp\left(-t/\tau_3\right), & t > t_2
\end{cases}
\]
where \( t_1, t_2 \) and \( t_3 \) are the moments of the appearance of the first, second and third crossovers on the graphs of Figure 13.

Figure 12. A typical example of the dependence \( P(t) \); Nafion was soaked in water with a deuterium content \( C = 500 \text{ ppm} \).

As follows from the graphs, \( \tau_3 \gg \tau_1, \tau_2 \); we put \( \tau_1 \sim \infty \). Yet the times \( \tau_1 \) and \( \tau_2 \) can be found from the corresponding tangents of the slope in the graphs. It can be seen that the sets \((\tau_1, \tau_2, \tau_3)\) and \((t_1, t_2, t_3)\) are controlled by the deuterium content.

Assuming that dependence of the luminescence signal \( P \) on \( n_{Naf} \) is linear, which is described by formula (5), one can find the ratio \((n_{Naf})_0/(n_{Naf})_i\), where \((n_{Naf})_0\) is the volume number density of Nafion particles at the moment of time \( t = 0 \), while \((n_{Naf})_i\) is the volume number density of Nafion particles at the moments of time \( t_1 \) and \( t_2 \), corresponding to the first and second crossovers in Figure 13, \( i = 1, 2 \). The values of \((n_{Naf})_0\) and \((n_{Naf})_i\), scaled in arbitrary units, can be found as the abscissas of the function in formula (5) at the corresponding values of \( P_0 \) and \( P_i \), where \( P_0 = P_{l=0} \), \( P_i = P_{l=0}^i \). The ratio \((n_{Naf})_0/(n_{Naf})_i\) vs log \( C \) is plotted in figure 14. As follows from this graph, this ratio behaves non-monotonically with the deuterium content. We note that the attenuation of luminescence after a certain soaking time is reversible: after drying of swollen Nafion (the samples were dried for two days in a drying cabinet), the luminescence signal was completely restored up to the level of dry Nafion.
Figure 13. Dependence of log $P(t)$ for liquids with different deuterium content.
Figure 14. Dependence of the ratio of initial and final volume number densities of Nafion particles upon soaking in liquid with different deuterium content.

Figure 15 shows the time intervals $t_1$ and $t_2 - t_1$ between the crossover points in figure 13 vs the deuterium content.

Figure 15. Time intervals between the crossover points in the graphs Figure 13 vs the deuterium content.

As follows from figures 13 and 14, for natural water ($C = 157$ ppm, log $C = 2.2$), the first crossover occurs at time $t_1 = 52$ min, and the value of $n_{\text{NaOH}}$ decreases approximately twice. In this connection it is interesting to compare the results for natural water presented in Figs. 14 and 2; recall that in Figure 2 we show the results of measuring the Nafion absorption coefficient $\gamma = \sigma_{\text{abs}} \cdot \langle n_{\text{NaOH}} \rangle$ upon soaking in natural water (see comments to figure 2). As is seen in figure 2, the absorption coefficient (i.e. the value of $\langle n_{\text{NaOH}} \rangle$) decreases only slightly after one hour of swelling compared with dry Nafion; the ratio of intensities in the spectral maximum at wavelength $\lambda = 266$ nm for dry Nafion (red curve) and for Nafion, soaked in natural water for an hour (green curve), is about 1.33. This discrepancy, in our opinion, is due to the fact that the value of $\langle n_{\text{NaOH}} \rangle$ is the result of averaging over the sample thickness, while in the experiments on luminescence we deal with the local value of $n_{\text{NaOH}}$, here the locality is
understood as averaging over the near-surface area with size \( a_w = 62 \ \mu m \), where the value of \( n_{Na} \) changes most effectively upon swelling; note, that in our particular case the sample thickness \( d = 175 \ \mu m \) is close to the size \( a_w \). Obviously, in the process of swelling the distribution of \( n_{Na}(x) \) in the depth of the membrane is no longer described by the Heaviside function, see equation (7); however, our experimental technique does not allow us to obtain the relevant form of such a distribution.

Dependences of the decay times \( \tau_1 \) and \( \tau_2 \) on the deuterium content are shown in Figure 16. As follows from the graphs in Figs. 15 and 16, both the characteristic times of the relaxation processes \( \tau_1 \) and \( \tau_2 \), and the durations of these processes depend on the deuterium content. In addition, the conditions \( \tau_1 > t_1 \) and \( \tau_2 > t_2 - t_1 \) are met for all liquid samples. We introduce here the degree of completion of the relaxation process \( \sigma_i = 1 - (\tau_i - \Delta t_i)/\tau_i \), \( i = 1, 2 \), \( \Delta t_1 \equiv t_1 \), \( \Delta t_2 \equiv t_2 - t_1 \). The relaxation process with the characteristic time \( \tau_i \) has a capability of being completed provided that \( \tau_i \sim \Delta t_i \); in this case \( \sigma_i \approx 1 \). At the same time, for \( \tau_i >> \Delta t_i \) the relaxation process is obviously not completed (\( \sigma_i \approx 0 \)). In figure 17 we give the dependence of \( \sigma_i \) on the deuterium content. As follows from the graphs, the first relaxation process can be considered as completed only for protium and deuterium water (points with extreme values on the abscissa axis). It is also seen that a certain correlation in the behavior of \( \sigma_1 \) and \( \sigma_2 \) is realized only in the range 90 - 300 ppm (1.9 < \log C < 2.5); this range includes natural water.

![Figure 16. Dependences of characteristic \( \tau_1 \) and \( \tau_2 \) on the deuterium content.](image-url)
Figure 17. Dependence of the values of $\sigma$ on the deuterium content.

3.4. Spatial characteristics of the swollen Nafion in water with different deuterium content.

This section is devoted to experimental studies, performed by the second experimental protocol. As was noted above, before carrying out the experiments, the Nafion plate was soaked for a certain time in the test fluid; the choice of this time was dictated from the following considerations. As was shown, there are two moments of time $t_1$ and $t_2$; for the time $t < t_1$ the first relaxation process with the characteristic time $\tau_1$ develops. Thus, to study the spatial characteristics of Nafion swelling during the first relaxation process, the soaking time $t'$ should meet the condition $t' \leq (t_1)_{\text{min}}$, where $(t_1)_{\text{min}}$ is the minimum time $t_1$ for all the samples studied; we can choose the time $t' = 30$ minutes. Yet to study the spatial characteristics of Nafion during the second relaxation process, the soaking time $t''$ for all liquid samples must meet the condition $t_1 \leq t'' \leq t_2$; this condition is not satisfied for all deuterium concentrations (for example, $t_1_{\log C>3} > t_2_{\log C<2.75}$, see Figure 15). Therefore, the spatial characteristics of Nafion, which can be manifested during the second relaxation process, have not been studied.

In figure 18 we show the experimental dependences for $P(x)$ (black circles) together with the corresponding theoretic dependences for $P(x)$ (red curves), and for $n_{\text{Naf}}(x)$ (blue curve) for various deuterium content; the problem of finding the theoretical dependences $P(x)$ and $n_{\text{Naf}}(x)$ was solved within the framework of the algorithm, described in the comments to eqns. (6) - (8). We seek the distribution function for $n_{\text{Naf}}(x)$ in the form

$$n_{\text{Naf}}(x) = B \left[ n^{(0)}(x - \xi) + \theta(x - \xi) \cdot b \exp\left(-q(x - \xi)^2\right) \right], \quad (10)$$

where, as earlier, $\theta(x)$ is Heaviside function, $d = 175$ $\mu$m is the thickness of the Nafion plate, $n^{(0)}(x) = \theta(x + d) - \theta(x)$ is the normalized volume number density of the Nafion particles inside the plate, the fitting parameter $\xi$ stands for the shift of the Nafion boundary in water relative to the Nafion boundary in air due to deformation of the plate interface upon swelling, the fitting parameter $q$ is the reciprocal of the dispersion of the Gaussian distribution, the amplitude fitting parameters $B$ and $b$ are not important for us. As before, the search for the fitting parameters was carried out by minimizing the discrepancy functional between the theoretical and experimental values of the function $P(x)$. Substituting (10) in (6), we find after integrating the function $P(x)$ in the form
\( P(x) = A + G_0 B \frac{a_w \sqrt{\pi}}{\sqrt{2}} \left\{ \frac{\text{erf} \left( \frac{x + d - \xi}{\sqrt{2a_w^2}} \right) - \text{erf} \left( \frac{x - \xi}{\sqrt{2a_w^2}} \right)}{\sqrt{2a_w^2} b + 1} \right\} \)

where, as earlier, \( a_w = 62 \mu m \), \( A \) is average level of the noise intensity of the measuring device, \( G_0 \) is a certain dimension factor. We note that the key points, which allowed us to solve this problem, were taking into account the decrease in the divergence of the optical pump beam in water as compared with the divergence in air (see the comments to Figure 10), and taking into account the Nafion boundary shift upon swelling. Note that in the final graphs, shown in Figure 17, the shift \( \xi \) of the Nafion boundary in the distribution of \( n_{\text{Naf}}(x) \) is aligned to the point \( x = 0 \), which, in our opinion, improves the presentation quality. We also note that when the deuterium content is \( C = 3 \) ppm, the distribution of the experimental dependence \( P(x) \) is narrower than in the case of dry Nafion, see Figure 10. This is obviously due to the fact that at such deuterium content the polymer fibers outgrowing, resulting in an effective broadening of the distribution of \( n_{\text{Naf}}(x) \), is very small, and the effect of decreasing the divergence of the pump beam in liquid could prevail, see the comment to Figure 10.

In Figure 19 we present the dependence of the spatial scale \( L_0 = (2q)^{1/2} \), which is a half-width of the Gaussian distribution of \( n_{\text{Naf}}(x) \) in the bulk liquid, see equation (10). The error in this graph corresponds to 25 \( \mu m \), which is the step size of the micrometer screw. As follows from the graph, the quantity \( L_0 \) behaves non-monotonically depending on the deuterium content. It is important to note that equation (6) is related to the class of Fredholm integral equations of the first kind [4]. It is known that such equations have a unique solution, but this solution is unstable with respect to small deviations of the left-hand member of this equation, i.e., the function \( P(x) \), which is the result of our measurements. In other words, the problem of finding a solution to this equation is the so-called ill-defined problem. Thus, the question of conformity between the theoretical solution \( n_{\text{Naf}}(x) \) and the real distribution of the Nafion density in water inevitably arises. It is very important for us that, according to the results of study [13] the EZ size (the size of area, from where colloid micron-sized particles are pushed out) in natural water (\( \log C = 2.2 \)) is approximately equal to 200 − 220 \( \mu m \). It is thus straightforward to assume that the EZ is just the area, containing the grown out polymer fibers; the size of that area is about 300 \( \mu m \), see Figure 19. In the framework of this assumption, we can claim that the theoretical function \( n_{\text{Naf}}(x) \), expressed by Equation (10), has a physical meaning. Our further measurements showed that the size of \( L_0 \) does not change when the Nafion samples are being soaked for the times \( t > t' = 30 \) minutes, i.e. the outgrowth of polymer fibers towards the bulk liquid is most likely not associated with diffusion kinetics. Indeed, the outgrown polymer fibers are anchored to the Nafion interface, so these should be basically immobile. Furthermore, the outgrown fibers and the interface are negatively charged in accordance with Equation (1); thus the process of outgrowing should be essentially accelerated in repulsive electrostatic field. However, the temporal dynamics of such outgrowth was not studied.
Figure 18. Dependence of $P(x)$ for Nafion, swollen in water with various deuterium content. Black open circles are the experimental points, red curve is theoretic approximation for the experimental dependence, blue curve is spatial distribution of $\rho_{Naf}(x)$. 
4. Discussion of the results.

As shown above, there are three relaxation regimes of swelling with characteristic times $\tau_1$, $\tau_2$, and $\tau_3$; the times $\tau_1$ and $\tau_2$ strongly depend on the deuterium content, while the time $\tau_3 \gg \tau_1$, $\tau_2$; we put $\tau_3 \sim \infty$. The time intervals, for which the regimes with times $\tau_1$, and $\tau_2$ are developed, also depend on the deuterium content. To interpret these results, it is necessary to mention the work [11], where experiments on the measurement of ionic conductivity, as well as on SANS and SAXS in the process of swelling Nafion in natural water (deuterium content $C = 157$ ppm, log $C = 2.2$), were described. In accordance with the model developed in [11], as the Nafion is being soaked in natural water, the following regimes are realized in the near-surface layer of the membrane. First, the dry membrane is characterized by the presence of isolated spherical ionic clusters with a diameter of about 15 Å, while an inter-cluster distance is $\sim 27$ Å. The swelling induces a modification of the ionic cluster structure, which become spherical water pools with the ionic groups at the polymer-water interface; those pools were termed as ionic domains. The water pool diameter is $\sim 20$ Å, while the inter-aggregate distance is $\sim 30$ Å, thus the water pools are still isolated from one another. At growing the water content, the water pools diameter increases from 20 to 40 Å, while the inter-pool distance increase is not substantial, which leads to percolation. For water volume fraction larger than 0.2, the large increase in the ionic conductivity indicates a percolation of the ionic domains: the structure of spherical ionic domains, connected with water channels, is formed. 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.

In our opinion, the dynamic regimes of Nafion swelling, observed in our experiments, can be qualitatively explained on the basis of the model, put forward in [11]. Namely, the first relaxation regime can be associated with the formation of ionic domains with subsequent percolation; this mode is terminated by the dynamic phase transition of the structural inversion (the first crossover, the point $t_1$ in Figure 13). In accordance with the red color curve in Figure 14, the volume number density of Nafion particles (more precisely, the volume number density of the luminescent sulfonic groups) for natural water decreases by half. In other words, during the time $t_1$ the volume fraction of water inside the membrane increases up to 0.5, which agrees with the results of [11]. With further swelling, this mode is replaced by the formation of aqueous suspension of rod-like Nafion particles, which corresponds to the second crossover (the point $t_2$ in Figure 13). According to the blue curve in Figure 14, at this moment of time the volume number density of Nafion particles decreases approximately four-fold, which corresponds to the volume fraction of water inside the membrane of about 0.75; this also agrees with the model [11]. A more detailed analysis requires that the nonlinear kinetic equation
describing the nonlinear diffusion of water molecules into the polymer membrane solution to be solved with taking into account the isotopic effects.

Note that for natural water a number of features are observed. Namely, the ratio \((C_{Na^+})_w/(C_{Na^+})_i\), for \(\log C = 2.2\) has a pronounced minimum for both \(t_1\) and \(t_2\) (see Figure 14). This means that for other deuterium contents, the dynamic regimes, found in Ref. [11], should occur at a higher water content within the membrane. In addition, the values of \(\sigma_1\) and \(\sigma_2\) (the degrees of completion of the first and second relaxation processes with characteristic times \(\tau_1\) and \(\tau_2\)) also have a minimum at this concentration and are approximately equal to 0.25 (see Figure 16). Thus the relaxation processes are far from being completed for natural water. Since these relaxation processes may lead to general destroying the membrane, the membrane is assumed to be most stable at swelling in natural water. Finally, the effect of the outgrowth of the Nafion fibers towards the bulk liquid starts also at \(\log C = 2.2\), see Figure 19. It is well to noted that this effect seems to be parasitic for the low-temperature hydrogen fuel cells with the Nafion membrane, see [2 - 4]. Thus, by varying the content of deuterium, it is possible to achieve the most optimal operating mode of these cells.

In conclusion, the general similarity between the Nafion membrane and the cell membrane should be noted. Namely, the cell membrane is a lipid bilayer, where a glycolipid layer is embedded. This layer is a glycolipoprotein complex and serves to transmit a signal into the cell from environment [50]. Thus, we can talk about a certain analogy between the cell membrane and the Nafion membrane, which is swollen in natural water. Indeed, both of them contain a network of water-filled channels and are surrounded by the polymeric fibers in the bulk water. Our further research will be devoted to the study of the specific effect of \(K^+\) and \(Na^+\) ions at soaking Nafion in solutions with different concentrations of these ions at a fixed deuterium content. As is known [50], the ions \(K^+\) and \(Na^+\) play an important role in the processes of cellular metabolism. We hope that the results of these experiments will help us to understand better the nature of the toxicity of deuterium for living organisms.

References

[1] Mauritz K and Moore R 2004 State of understanding of Nafion Chem. Rev. 104 4535-8
[2] Srinivasan S 1989 Fuel Cells for Extraterrestrial and Terrestrial Applications, J. Electrochem. Soc. 136 41 - 8
[3] Kreuer K D 2001 On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, Journal of Membrane Science 185 29–39.
[4] Heitner-Wirguin C 1996 Recent advances in perfluorinated ionomer membranes: structure properties and applications, Journal of Membrane Science 120 1–33.
[5] Gierke T D, Munn G E and Wilson F C 1981 The morphology in Nafion perfluorinated membrane products, as determined by wide-and small-angle X-ray studies, J. Polym. Sci., Polym. Phys. Ed. 19 1687–704.
[6] Gebel G, Aldebert P and Pineri M 1993 Swelling study of perfluorosulphonated ionomer membranes. Polymer 34 333–9.
[7] Fujimura M,Hashimoto T, and Kawai H 1982 Small-angle x-ray scattering study of perfluorinated ionomer membranes. 2. Models for ionic scattering maximum, Macromolecules 15 136–44.
[8] Dreyfus B, Gebel G, Aldebert P, Pineri M, Escobes M and Thomas M 1990 Distribution of the "micelles" in hydrated perfluorinated ionomer membranes from SANS experiments J. Phys. France 51 1341–54.
[9] Gebel G and Lambard J 1997 Small-angle scattering study of water-swollen per- fluorinated ionomer membranes Macromolecules 30 7914–20
[10] Wodzki R, Narebska A and Nioch W K 1985 Percolation conductivity in Nafion membranes, J.Appl. Polym. Sci. 30 769–80
[11] Gebel G 2000 Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution, Polymer 41 5829–38.
[12] Bass M, Berman A, Singh A, Konovalov O and Freger V 2011 Surface-induced micelle orientation in Nafion films Macromolecules 44 2893–9.

[13] Chai B, Pollack and Solute-Free G H 2010 Interfacial Zones in Polar Liquids. J. Phys. Chem. B 114 5371–5.

[14] Pollack G H 2013 The Fourth Phase of Water; Ebner and Sons Publishers (USA Seattle, WA)

[15] Yip J, Duhamel J, Qiu X P and Winnik F M 2011 Fluorescence studies of a series of monodisperse telechelic alpha, omega-diperylenyl poly(N-isopropylacrylamide)s in ethanol and in water, Can. J. Chem 89 163-72.

[16] Holappa S, Kantenon L, Anderson T,Winnik F M and Tenhu H 2005 Overcharging of polyelectrolyte complexes by the guest polyelectrolyte studied by fluorescence spectroscopy, Langmuir 21 11431-8

[17] Holappa S,Kantenon L, Winnik F M, and Tenhu H 2004 Self-complexation of poly (ethyleneoxide)-block-poly(methacrylic acid) studied by fluorescence spectroscopy. Macromolecules 37 7008-18.

[18] Miyazawa K and Winnik F M 2003 Isothermal titration calorimetry and fluorescence spectroscopy studies of the interactions between surfactants and a phosphorylcholine based polyeutane, Progr. Colloid Polym. Sc. 122 149-56.

[19] Mizusaki M, Morishima Y and Winnik F M 2001 An assessment by fluorescence spectroscopy of the stability of polyanion/positively charged liposome systems in the presence of polycations, Polymer 42 5615-24.

[20] Ponchet-LeGrand C and Winnik F M 2001 Solution properties of hydrophobically-modified copolymers of N-isopropylacrylamide and N-valine amylamide: a study by fluorescence spectroscopy and microcalorimetry, Polymer Journal 33 277-86

[21] Gudkov S V, Astashev M E, Bruskov V I, Kozlov V A, Zakharov S D and Bunkin N F 2014 Self-oscillating Water Chemiluminescence Modes and Reactive Oxygen Species Generation Induced by Laser Irradiation; Effect of the Exclusion Zone Created by Nafion, Entrop 16 6166-85.

[22] Bunkin N F, Gorelik V S,Kozlov V A, Shkirin A V and Suyazov N V 2014 Colloidal Crystal Formation at the “Nafion-Water” Interface, J. Phys. Chem. B 118 3372-7.

[23] Bunkin N F, Gorelik V S, Kozlov V A, Shkirin A V and Suyazov N V 2014 Phase states of water near the surface of a polymer membrane. Phase microscopy and luminescence spectroscopy experiments, JETP 119 924-32.

[24] Pope J C, Sue H, Bremmer T and et al. 2014 High-temperature steam-treatment of PBI, PEEK, and PEKK polymers with H2O and D2O: a solid-state NMR study, Polymer 55 4577-85.

[25] Vinogradova L V, Toeroek G and Lebedev V T 2012 Amphiphilic star-shaped polymer with fullerene (C-60) branching center and its micelle-forming properties in D2O solutions, Rus. J. Appl. Chem. 85 1594 - 9.

[26] Hanykova L, Labuta J and Spevacek J 2006 NMR study of temperature-induced phase separation and polymer-solvent interactions in poly(vinyl methyl ether)/D2O/ethanol solutions, Polymer 47 6107 - 16.

[27] Lakatos I and Lakatos-Szabo J 2004 Diffusion of H+, H2O and D2O in polymer/silicate gels, Col. Surf. A 246(1-3) 19 – 19.

[28] Kujawa P and Winnik F M 2001 Volumetric Studies of aqueous polymer solutions using pressure perturbation calorimetry: a new look at the temperature-induced phase transition of poly-(n-isopropylacrylamide) in water and D2O, Macromolecules 34 4130-4135.

[29] Thomson J F 1963 Biological effects of deuterium. (New York: Pergamon Press) p 133.

[30] Kihara T and McCray J A 1973 Water and cytochrome oxidation-reduction reactions. Biochem. Biophys. Acta. 292(2) 297 - 309.

[31] Lewin S, Williams B A and Potter B J 1970 Some aspects of phenylalanine incorporation in deuterium oxide (D2O) substitution for water (H2O) in polyuridylic acid-directed ribosomal protein biosynthesis. Biochem J. 117(2) 20 - 21.
[32] Gross P R and Harding C V 1961 Blockade of deoxyribonucleic acid synthesis by deuterium oxide. *Science*. **133**(3459) 1131-3.

[33] Strekalova T, Evans M, Chernopiatko A, Couch Y, Costa-Nunes J, Cesuglio R, Chesson L, Vignisse J, Steinbusch H W, Anthony D C, Pomytkin and Lesch K P 2015 Deuterium content of water increases depression susceptibility: the potential role of a serotonin-related mechanism. *Behav. Brain Res* **277** 237-44.

[34] Vasilescu V., Mărgineanu D 1974 The role of water in biological membrane phenomena as revealed by deuterium isotope effects. *Rev. Roum. Physiol*. **11**(2) 167-71

[35] Vasilescu V, Katona E, Popescu A, Zaciuc C and Ganea C 1984 Some Problems Concerning the Role of Water and Protons in the Function of Biological Membranes. in: Membrane Processes. *Molecular Biology and Medical Applications*. ed Gheorghe Benga, Harold Baum and Fred A. Kummerow (New York, Springer) 92-107

[36] Schauf C L and Bullock J O 1979 Modifications of sodium channel gating in Myxicola giant axons by deuterium oxide, temperature, and internal cations. *Biophys J*. Aug 27(2) pp193 -208.

[37] Chernikov A V, Gudkov S V, Shtarkanov I N and Bruskov V I 2007 Oxygen effect in heat mediated damage to DNA, *Biofizika*, **52**(2) 244-51.

[38] Gudkov S V, Bruskov V I, Astashev M E, Chernikov A V, Yaguzhinsky L S and Zakharov S D 2011 Oxygen-dependent auto-oscillations of water luminescence triggered by the 1264 nm radiation., *J. Phys. Chem. B*. Vol. **115**(23) 7693–8.

[39] Den'ko E I 1970 Effect of heavy water (D₂O) on animal and plant cells and on microorganisms. *Usp. Sovrem. Biol*. **70**(1) 41 - 64.

[40] Kushner D J, Baker A and Dunstall T.G 1999 Pharmacological uses and perspectives of heavy water and deuterated compounds. *Can. J. Physiol. Pharmacol* **77**(2) 79 – 88.

[41] Lisitsyn A B, Baryshev M G, Basov A A, Barysheva E V, Bykov I M, Dydkin A S, Tekutskaya E E, Timakov A A, Fedulova L V, Chernukha I M and Dzhimak S S 2014 Influence of deuterium depleted water on the organism of laboratory animals in various functional conditions of nonspecific protective systems. *Biofizika*, **59**(4) 757 – 65.

[42] Rehakova R, Klimentova J, Cebova M, Bart A, Matuskova Z, Labas P and Pechanova O 2016 Effect of deuterium-depleted water on selected cardiometabolic parameters in fructose-treated rats. *Physiol. Res*. **65** S3:S401 - S407.

[43] Wang H, Zhu B, He Z, Fu H, Dai Z, Huang G, Li B, Qin D, Zhang X, Tian L, Fang W and Yang H. 2013 Deuterium-depleted water (DDW) inhibits the proliferation and migration of nasopharyngeal carcinoma cells in vitro. *Biomed Pharmacother* **67** 489 - 96.

[44] Gyöngyi Z, Budán F, Szabó I, Ember I, Kiss I, Krempels K, Somlyai I and Somlyai G 2013 Deuterium depleted water effects on survival of lung cancer patients and expression of Kras, Bcl-2, and Myc genes in mouse lung. *Nutr. Cancer* **65**(2) 240 – 6.

[45] Craig H 1961 Standard reporting concentrations of deuterium and oxygen 18 in natural water, *Science* **133** 1833 - 4

[46] De Almeida S H and Kawano Y 1997 Ultraviolet-visible spectra of Nafion membrane, *Eur. Polym. J.* **33**(8) 1307-11

[47] Owen T 2000 Fundamentals of Modern UV-Visible Spectroscopy: a Primer; *Agilent Technologies*, (Germany : Boeblingen)

[48] http://www1.lsbu.ac.uk/water/water_vibrational_spectrum.html

[49] Bitsadze A V 1995 Integral Equations of First Kind; *World Scientific Publishing Co*. (Singapore :Pte. Ltd.)

[50] Goodsell D S 2009 The Mashinry of Life (New York: Springer).