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Near-surface structure of Nafion in deuterated water

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The swelling of a polymer ion-exchange membrane Nafion in water with various heavy isotope contents (D_2O) was studied by photoluminescent UV spectroscopy. The photoluminescence arises because of the presence of sulfonic groups attached to the ends of the perfluorovinyl ether groups that form the tetrafluoroethylene (Teflon) backbone of Nafion. The width of the colloidal region, which is formed near the membrane surface as a result of the outgrowth of Nafion microfibers toward the bulk liquid, varies non-monotonically with D_2O content, displaying a narrow maximum in the low concentration region. A significant insight into the unexpected isotopic effects revealed in swelling Nafion in deuterated water is provided. Mainly, the polymer swelling is very sensitive to small changes (on the order of several tens of parts per million) in the content of deuterium, which, for instance, can help in understanding the isotopic effects in living tissues. *Published by AIP Publishing.*
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I. INTRODUCTION

Studies of proton exchange membranes used in hydrogen energy have proliferated over the last decade. This is not surprising. The perfluorinated polymer membrane NafionTM from DuPont (USA) finds increasing use in fuel cells due to its high thermal, mechanical, and chemical stability, as well as high proton conductivity. A recent review¹ claims that the number of publications on Nafion has grown to 5400 over the past 13 years. About half of these publications are devoted to the use of Nafion in hydrogen fuel cells.

Among these, some interest has focused on swelling near the surface of Nafion, from which external micron-sized particles are pushed out. This near-surface region was called the exclusion zone (EZ), see the monograph² and references therein. The size of the EZ can amount to *hundreds of microns*, and under certain experimental conditions this structure does not change for several days. The size of the EZ in heavy water is slightly less than in ordinary water.³ In Ref. 4, an attempt to understand this peculiar exclusion zone was made by the study of the radiation absorption of the EZ, when the pump radiation was directed parallel to the surface of Nafion so that grazing incidence geometry was achieved. In the experiment,⁴ the beam of a laser diode with a wavelength of 270 nm was shifted toward the Nafion plate, submerged in the cell with water, in a plane, normal to the Nafion surface. The absorptivity and the spectrum of the luminescence normal to the optical pump axis were measured. The absorptivity of the irradiated region increases as the pump beam approaches the

Nafion surface. In addition, the intensity and spectral characteristics of the photoluminescence are controlled by the distance between the Nafion surface and the optical pump axis. In Ref. 4, the observed effect was attributed to a special phase state of water in the volume of the EZ. If true this would be very important, indeed a game changer. It is reminiscent of the well-known and still unexplained studies^{5–8} on stable bulk suspensions of heavily dialyzed latex spheres; the spheres can be hundreds of nanometers apart. Our work shows that the effects with Nafion are different from the propositions of Refs. 2–4 and have a more mundane origin.

Some remarks, germane to the issue, are these: It is known⁹ that one of the maxima of the absorptivity of both dry and swollen in water Nafion occurs at a wavelength of 270 nm. It is also known (see, for example, Ref. 10) that water does not absorb in this spectral region. Furthermore, the usual consensus reliably established in numerous experiments (see the monograph¹¹ and references therein) would be that the solid-state substrate can change the structure or order of the adjacent liquid only up to a distance of 2–3–4 monolayers. If that unremarkable situation obtains here also, then the effect in the exclusion zone observed in Refs. 2–4 would be related to the presence of Nafion particles or nanostructures in the EZ volume rather than to some new state of water. As follows from the results of Ref. 4, these particles are, therefore, present in the bulk water at distances up to 400 μm from the membrane surface. In further support, we note that when optical radiation interacts with matter and a complex

molecular system is irradiated inside the absorption band, quantum transitions are stimulated in a longer wave range; i.e., luminescence should arise. This also accounts for the results of Ref. 4.

Polymeric structures are comprehensively investigated by a number of spectroscopic techniques, which cover a wide spectral range from THz¹² to UV.^{13–17} We now proceed to a detailed account of our experiments. To study the physical nature of the exclusion zone of Nafion, we have developed an original instrument for laser diagnostics of the near-surface structure of Nafion in water on the basis of photoluminescent UV spectroscopy. The method involves fiber optics, see Refs. 18 and 19. Here, this technique is used to study Nafion N117 (membrane thickness equal to 175 μm) at room temperature (22 °C) soaked in water, with a deuterium content varying from 3 to 10⁶ ppm. This range includes all possible concentrations of deuterium in water; in ordinary (natural) water, the deuterium content, according to the Standard Mean Ocean Water (SMOW), is 157 ± 1 ppm.²⁰ Our interest in Nafion swelling in deuterated water derives from the studies of Ref. 3, according to which an effect of water isotopic composition on the size of the exclusion zone could be expected. In addition, in our previous work²¹ an isotopic effect has already been explored in the process of soaking Nafion in deuterated water. This study used Fourier transform infrared spectrometry in the near-IR range. We might then anticipate some correlations of the results of IR spectrometry and photoluminescence spectroscopy in the near-UV range. The experimental scheme for luminescent spectroscopy developed here for swollen Nafion studies has a number of similarities with the setup described in Ref. 4.

II. PROPERTIES OF MATERIALS

In the experiments, we used samples of deuterium depleted water (DDW); deuterium content ≤ 3 ppm (Sigma-Aldrich, USA). In addition, samples of deionized ordinary water Milli-Q (specific resistance 18 M Ω ·cm at 25 °C) as well as samples of D₂O (Cambridge Isotope laboratories, UK) were used; the deuterium content is 99.9 at. %, i.e., $\sim 10^6$ ppm. Samples of water with different deuterium contents were prepared by proportional volumetric mixing of D₂O and DDW. In the liquid samples thus obtained, the Nafion plates (DuPont, USA, plate thickness $d = 175$ μm) were soaked. Finally, we investigated solutions of Nafion in isopropyl alcohol (Sigma-Aldrich, USA) and aqueous solutions of polymer heparin [C₁₂H₁₉NO₂₀S₃]_n (Sigma-Aldrich, USA, weight content 58 mg/ml) and chondroitin sulfate [C₁₄H₂₁NO₁₅S]_n (Belmedpreparaty, Belarus, mass content of 100 mg/ml) since the molecular structure of heparin and chondroitin sulfate, like Nafion, also contains sulfonic groups SO₃H.

III. PRELIMINARY EXPERIMENTS

A. Optimal wavelength selection for optical pumping

The absorption spectra of dry Nafion and Nafion swelled for 1, 10, and 24 h in natural water, purified by the Milli-Q technique, were measured using a Cary 100 UV-Vis

spectrophotometer (Varian, Inc., Australia). The measured absorption spectra corrected for Rayleigh scattering (a correction technique in similar problems is considered in detail, for example, in Ref. 22) display three absorption bands centered at $\lambda_1 = 196$, $\lambda_2 = 232$, and $\lambda_3 = 268$ nm. The results agree with the data of Ref. 9.

Luminescence can be excited provided that the pump radiation falls within one of the absorption bands of the substance under study. In this case, the pump radiation should not be absorbed in water; otherwise this radiation will be substantially attenuated even before the membrane is irradiated. Since water absorbs near the bands λ_1 and λ_2 due to the proximity to the vacuum UV, it makes no sense to use pumping in this range. We used the fourth harmonic of a single-mode pulsed-periodic YAG: Nd³⁺ laser (“Laser Compact.” Russia, model DTL-382QT) with the wavelength $\lambda = 266$ nm, pulse repetition rate 3 kHz, pulse width 5 ns, average pulse energy 4 μJ ; frequency multiplication was performed with a β -barium borate (BBO) crystal. In addition, we used a continuous wave laser diode at a wavelength of $\lambda = 369$ nm with an average power of 50 mW; the radiation at this wavelength belongs to the long-wavelength edge of the λ_3 -band.

In Fig. 1, we show the luminescence spectrum of dry Nafion under irradiation at wavelengths $\lambda = 266$ and 369 nm. The accumulation time (exposure time) for each measurement of the spectrum was 8 s. The experimental scatter was due to fluctuations in the pump intensity. It can be seen that the dependences obtained are identical. When pumped at a wavelength of $\lambda = 266$ nm, the luminescence spectrum is red-shifted; the elucidation of the nature of this shift is beyond the scope of this paper. It is also seen that the spectral maximum for both pump wavelengths corresponds to $\lambda = 508$ nm.

Figure 2 shows the time dynamics of the luminescence signal P from the dry Nafion for pumping at $\lambda = 266$ and 369 nm; the instrumental error is the same for both curves, and the experimental points are connected by segments. It can be seen that the luminescence state is destroyed with time under irradiation at a wavelength of $\lambda = 266$ nm. This is due to local heating and degradation of the polymer. At the same time, irradiation at a wavelength of $\lambda = 369$ nm does not lead to a decrease in the level of luminescence. Thus, the most

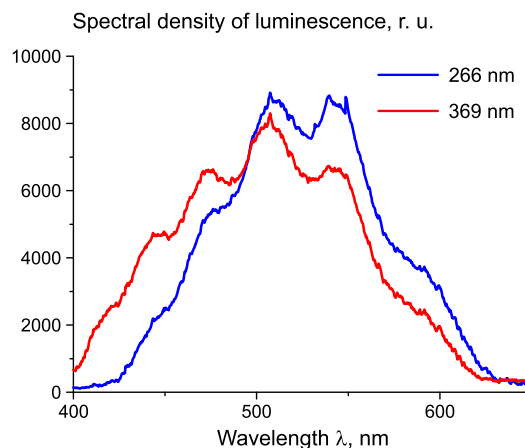


FIG. 1. Luminescence spectra of dry Nafion irradiated at the wavelengths $\lambda = 266$ nm (blue line) and 369 nm (red line).

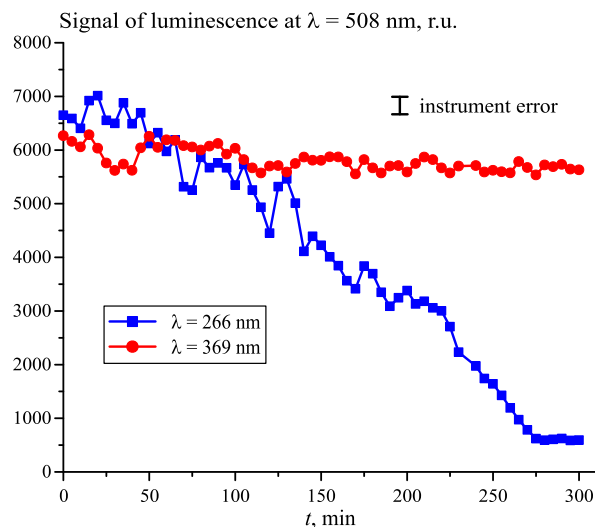


FIG. 2. Time dependence of the luminescence signal P in the spectral maximum ($\lambda = 508$ nm) for irradiation at $\lambda = 266$ nm (blue line) and $\lambda = 369$ nm (red line).

optimal pump wavelength is $\lambda = 369$ nm. We note that the spectral minimum of the absorption coefficient in water also corresponds to $\lambda = 370$ nm, see, for example, Ref. 10.

B. The elucidation of the physical nature of luminescence

The Nafion structure consists of the tetrafluoroethylene (Teflon) backbone with terminal sulfonic groups SO_3H . Preliminary spectroscopic observations showed that Teflon, irradiated at $\lambda = 369$ nm, does not luminesce in the spectral range studied. It is therefore reasonable to assume that the role of luminescent centers is played by sulfonic groups.

To verify this assumption, we measured the luminescence from aqueous solutions of heparin and chondroitin sulfate, as well as from a solution of Nafion in isopropanol, because of the presence of the sulfonic group SO_3H in the molecular structure of heparin, chondroitin sulfate, and Nafion; in the same graph, we show the results of the excitation of luminescence upon irradiation of the surface of a Teflon plate immersed in water. To prepare Nafion solutions in isopropanol, the Nafion plate with a size of 6 cm^2 and a thickness of $175\text{ }\mu\text{m}$ was soaked in isopropanol for 22 h and partially dissolved; the residue of the plate was subsequently removed from the liquid. The spectra are shown in Fig. 3; luminescence from water and isopropyl alcohol upon irradiation at $\lambda = 369$ nm is absent. It can be seen that the luminescence spectra of solutions of Nafion, heparin, and chondroitin sulfate are qualitatively similar in shape. However, the spectrum of the Nafion solution is red-shifted due to the displacement of the electron density of the sulfonic group toward the fluorocarbon chain. This leads to the appearance of a dipole structure and a Stark shift. The qualitative similarity of the spectra is explicit confirmation that the sulfonic groups SO_3H serve as luminescence centers in all three samples.

Hereinbelow, we investigate solutions with various concentrations; for each solution, the experimental points and the calculated confidence intervals were determined by

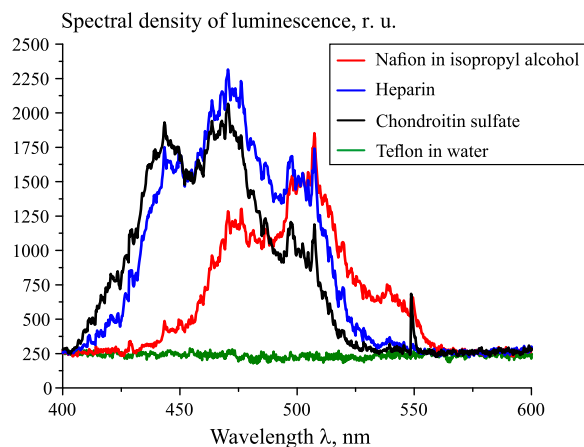


FIG. 3. Spectral fluorescence intensities of Nafion solution in isopropanol (red line), aqueous solution of heparin (blue line), aqueous solution of chondroitin sulfate (black line), and Teflon in water (green line) with pumping at $\lambda = 369$ nm.

averaging over 10 measurements. Figure 4 illustrates the dependence of the luminescence signal P from the Nafion solution in isopropanol at a wavelength of $\lambda = 508$ nm (the spectral maximum of the luminescence); the zero abscissa corresponds to pure isopropanol. The concentration of the solution in this particular case is not known to us; we consider (conditionally) that the concentration is 100 a.u. immediately after removal of the Nafion plate from the solution, and then the solution was diluted proportionally with isopropyl alcohol.

The rectilinear segment (Fig. 4) can be approximated by the following formula:

$$P = -237 + 16 n_{\text{Naf}}, \quad (1)$$

where n_{Naf} is the volume number density of the luminescence centers, i.e., terminal sulfonic groups. Since these groups are attached to polymeric chains, n_{Naf} can be associated with the volume number density of Nafion particles. The dependence obtained can be represented as

$$P = A + k I_{\text{pump}} \sigma_{\text{lum}} n_{\text{Naf}} V, \quad (2)$$

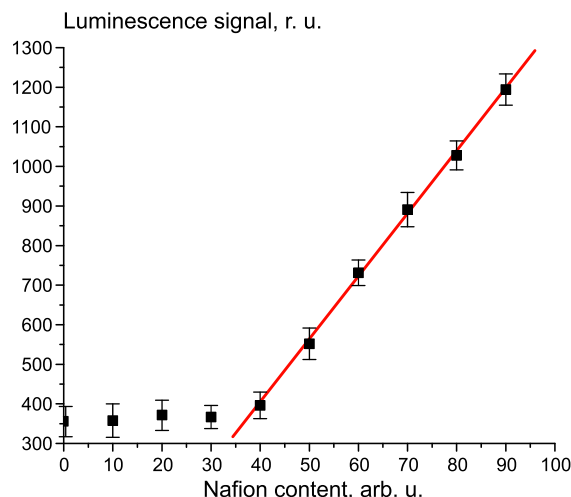


FIG. 4. Dependence of the luminescence signal P on the content of Nafion in isopropanol solution.

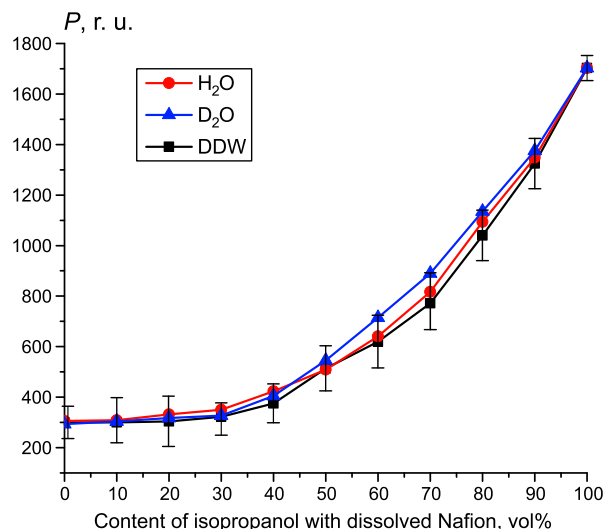


FIG. 5. Luminescence signal P when Nafion solution in isopropanol is diluted with DDW (black curve), natural water (red curve), and D_2O (blue curve).

where I_{pump} is the pump intensity, $A = 20\text{--}270$ r.u. corresponds to the spectral density of the minispectrometer noise and stray-light illumination, k is the transfer coefficient of the setup, V is the luminescence volume, and σ_{lum} is the luminescence cross section (it is obvious that the spectral maximum of σ_{lum} corresponds to $\lambda = 508$ nm). It follows from Fig. 4 that $\sigma_{\text{lum}} = \text{const}$. The dimensional constants included in Eq. (2) are taken into account by the factor k ,

$$k = \begin{cases} k_0 = \text{const}, & W > W_{\text{thr}} \\ 0, & W \leq W_{\text{thr}}, \end{cases} \quad (3)$$

where W_{thr} is the threshold (detection limit) of luminescence power, $W \equiv I_{\text{pump}} \sigma_{\text{lum}} n_{\text{Naf}} V$.

As will be shown below, the value of P depends on the deuterium content, which can arise due to isotopic quenching of the luminescence, i.e., decrease in σ_{lum} , as well as due to a change in n_{Naf} . In order to estimate the contribution of a possible luminescence quenching by deuterium atoms, we performed the following experiment. Nafion solution in isopropyl alcohol was diluted by volume with water with deuterium content $C = 3$ ppm (DDW), natural water ($C = 157$ ppm), and heavy water ($C = 10^6$ ppm). The corresponding graphs are shown in Fig. 5; for convenience of perception, the experimental errors (approximately the same for the liquids studied in this experiment) are indicated only for DDW. The volume content of isopropyl alcohol is plotted along the abscissa axis, and the zero abscissa corresponds to pure water. It is seen that the behavior of P is the same for all liquids, within experimental error. Therefore, the isotopic effects of luminescence quenching can be ignored.

IV. LASER LUMINESCENCE DIAGNOSTICS OF NAFION IN LIQUIDS

The scheme of the experimental setup is shown in Fig. 6.

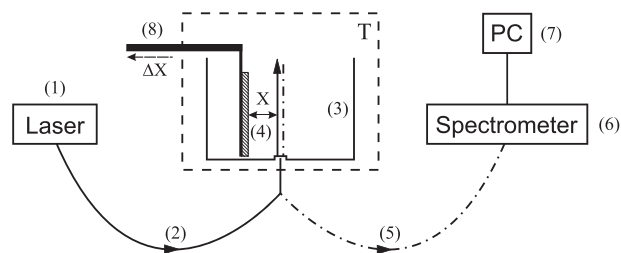


FIG. 6. Schematic of the experimental setup for laser luminescence spectroscopy. (1)—Source of optical pumping; (2)—multimode quartz optical fiber for the pumping radiation transfer; (3)—cylindrical cell; (4)—Nafion plate; (5)—optical fiber for the luminescence radiation; (6)—minispectrometer; (7)—computer; (8)—stepper.

The probing radiation of continuous wave laser diode (1) (optical pumping) at a wavelength $\lambda = 369$ nm was introduced into the multimode quartz optical fiber (2) with a diameter $\varnothing = 100$ μm and a numerical aperture $NA = m_0 \sin \alpha = 0.3$, where $m_0 = 1$ is the refractive index of air, α is the angle of beam divergence at the exit end of the fiber in air. The fiber was fixed in a hole located in the center of the bottom of a cylindrical cell (3) made of stainless steel; the direction of the pump beam sets the optical axis of the experimental setup. The cell was thermostabilized at room temperature ($T = 23$ °C) with a liquid thermostat (accurate to ± 0.1 °C) and filled with water with different deuterium contents. We studied the swelling of a square Nafion plate (4) with a side $h = 4$ mm and a thickness $d = 175$ μm . The vertical edges of the Nafion plate were rigidly fixed with two vertical parallel clamps in parallel to the optical axis; i.e., the experiments were carried out at grazing incidence; no additional substrate for fixation the plate was used. The size of the clamps was much less than the width of the Nafion plate; i.e., for the central region of the plate along the vertical direction (this region was subject to irradiation by the incident light), the approximation of the free boundary was realized. Upon immersing in water, the Nafion plate bended along the vertical axis. However, such bending led only to an effective shift of the Nafion-water boundary (this shift amounted to about 1 mm) but did not result in a change in the incident angle of the pump radiation. The luminescence radiation was reflected from the internal faces of the cell (Nafion is transparent in the visible range) and collected along the optical axis of the cell. This resulted in a significant gain in luminescence intensity. The luminescence signal was received by a quartz fiber (5), fixed at the center of the cell and transferred to the FSD-8 minispectrometer (6). The duration of a single measurement was 7–8 s. The experimental data were accumulated by using a computer (7). After a 30-min soaking in the same cell filled with deuterated water, the Nafion plate was irradiated in the same geometry of grazing incidence. Furthermore, the plate was displaced parallel to the optical axis by means of a stepper motor (8) in 25 μm steps. The required number of steps was determined by the decay of the luminescence signal P to zero; i.e., luminescence was investigated as a function of the distance x between the Nafion surface and the optical axis. The reference point $x = 0$ was determined from the condition of the maximum luminescence signal; i.e., the precise position of the Nafion–water boundary was, generally speaking, unknown to us. We only can claim that

this position is determined accurate to the micrometer screw step.

V. THEORETICAL FRAMEWORK OF MEASUREMENT TECHNIQUE

For a correct interpretation of the results, it is necessary to take into account the spatial profiles of the pump intensity $I_{\text{pump}}(x)$ and the spatial distribution of the volume number density of Nafion particles $n_{\text{Naf}}(x)$; i.e., Eq. (2) must be rewritten in the following form:

$$P(x) = A + \int_{-\infty}^{+\infty} G(x - x_1) \cdot n_{\text{Naf}}(x_1) dx_1, \quad (4)$$

where the symmetric kernel of this integral equation $G(x - x_1)$ is the apparatus function of the experimental setup; all the dimensional factors in Eq. (2) are included in 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 $n_{\text{Naf}}(x)$ upon the soaking of Nafion in water with different deuterium contents.

An example of a solution to Eq. (4) for dry Nafion is shown in Fig. 7; the value $x = 0$ corresponds to the boundary of dry Nafion. In this case, the distribution $n_{\text{Naf}}(x)$ can be approximated by two Heaviside functions $\theta(x)$ as

$$n_{\text{Naf}}(x) = n_0 \cdot [\theta(x + d) - \theta(x)], \quad (5)$$

where $d = 175 \mu\text{m}$ is the thickness of the Nafion plate and n_0 is a dimensional constant. Assuming that the pump radiation at the fiber output is divergent and the profile $I_{\text{pump}}(x)$ is described by a Gaussian function, we take $G(x) = G_0 \exp\left[-\frac{x^2}{2a^2}\right]$, where G_0 is some dimensional constant and the parameter a is the width of Gaussian profile, which we seek.

Performing the integration in Eq. (4), we arrive at the following formula:

$$P(x) = A + G_0 n_0 \frac{a\sqrt{\pi}}{2} \left[\text{erf}\left(\frac{x+d}{\sqrt{2}a}\right) - \text{erf}\left(\frac{x}{\sqrt{2}a}\right) \right]. \quad (6)$$

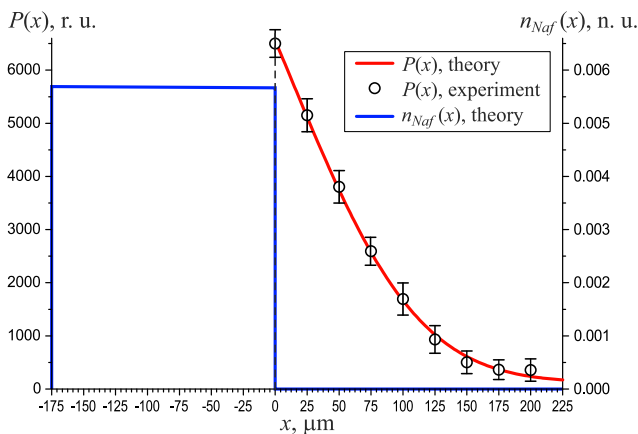


FIG. 7. Dependence of $P(x)$ for dry Nafion. Circles are experimental points, the red curve is the theoretical approximation of the experimental dependence, and the blue line is the normalized distribution of $n_{\text{Naf}}(x)$.

Here $A = 124$ r.u. is the average noise level of the setup and the second term represents the integral convolution of Gaussian and Heaviside functions. Minimizing the discrepancy functional between the theoretical curve $P(x)$ and the experimental points (see Fig. 7), we obtain $a = 84 \mu\text{m}$; hereinafter, $n_{\text{Naf}}(x)$ is normalized to the integral value.

When Nafion is submerged in water, the divergence of the pump beam decreases compared to the divergence in air in accordance with the formula $NA = m \cdot \sin \alpha$, where $NA = 0.3$ is the numerical aperture of the optical fiber, m is the refractive index of water, and α is the divergence angle of the pump beam at the fiber output. For the Gaussian function in water, we have $G(x) = G_0 \exp\left[-\frac{x^2}{2a_w^2}\right]$, where $a_w = a(\tan \alpha_w / \tan \alpha)$, $\alpha = \arcsin(NA)$, $\alpha_w = \arcsin(NA/m_w)$, $m_w = 1.33$ is the refractive index of water, which means that $a_w = 62 \mu\text{m}$.

The effective broadening of the $P(x)$ distributions obtained for all liquid samples (see Sec. VI) compared to the distribution $P(x)$ for dry Nafion suggests that when Nafion is soaked in water, some polymer fibers grow out into the bulk of the liquid. In theoretical analysis, we do not take into account that fiber outgrowth develops on both sides of the Nafion plate along the abscissa axis. This phenomenon is controlled by the deuterium content. This is remarkable. The relative hydration of sulphonic and fluoride groups that set the intrinsic curvature (and self-assembly) of the polymer is determined by competitive adsorption of deuterium. Clearly deuterium “wins out” over water molecules. The polymer fibers are attached at one end to the membrane surface; i.e., no complete separation and escape into the liquid bulk occurs. For a quantitative modelling of the process, see Ref. 23.

To find the spatial distribution of $n_{\text{Naf}}(x)$ (blue curves), an inverse problem was solved using the following algorithm. We seek the function $n_{\text{Naf}}(x)$ in the following form:

$$n_{\text{Naf}}(x) = B \left[n^{(0)}(x - \xi) + \theta(x - \xi) \cdot b \exp(-q(x - \xi)^2) \right], \quad (7)$$

where, as earlier, $\theta(x)$ is the Heaviside function. In our simple model, we represent the residual “solid” Nafion plate as an equivalent rectangle of fixed thickness $d = 175 \mu\text{m}$, thereby, the density inside the plate is considered to be proportional to $n^{(0)}(x) = \theta(x + d) - \theta(x)$. Meanwhile, the effective density of the plate is decreased upon soaking. The fitting parameter ξ stands for the uncertainty in the value of shift of the Nafion–water boundary (this shift occurs upon immersing in water) and does not exceed $\sim 30 \mu\text{m}$. For all the investigated liquids, this uncertainty is close to the micrometric screw step ($25 \mu\text{m}$). The search for fitting parameters (ξ , q , B , b) was performed through minimization of the discrepancy functional between the theoretical and experimental values of the function $P(x)$. The greatest practical interest in this model is the value of the q , which denotes the reciprocal of the variance of the Gaussian function, corresponding to the half-width of the Gaussian distribution $b \exp(-q(x - \xi)^2)$. Substituting Eq. (7) into Eq. (4) and integrating, we obtain the function $P(x)$ in the following form:

$$P(x) = A + G_0 B \frac{a_w \sqrt{\pi}}{\sqrt{2}} \cdot \left(\left[\operatorname{erf} \left(\frac{x + d - \xi}{\sqrt{2a_w^2}} \right) - \operatorname{erf} \left(\frac{x - \xi}{\sqrt{2a_w^2}} \right) \right] + \left[\frac{b}{\sqrt{2a_w^2 q + 1}} \left[1 - \operatorname{erf} \left(\frac{-x + \xi}{\sqrt{2a_w^2} \sqrt{2a_w^2 q + 1}} \right) \right] \exp \left(-\frac{q(x - \xi)^2}{2a_w^2 q + 1} \right) \right] \right). \quad (8)$$

VI. SPATIAL DISTRIBUTION OF NAFION PARTICLES IN THE NEAR-SURFACE REGION

In Fig. 8, we give the experimental $P(x)$ dependences (black circles) and the corresponding theoretical $P(x)$ curves (red) for different deuterium concentrations. The blue curves are reconstructed spatial distributions of Nafion density $n_{\text{Naf}}(x)$ in accordance with the parametric model described in Sec. V. Since the mass of Nafion particles is conserved when soaking, the dependences of $n_{\text{Naf}}(x)$ are normalized to the integral value.

Upon soaking, the height of the equivalent rectangle, representing the effective density of the residual Nafion plate, naturally decreases; which is explained by the appearance of nano-channels, filled with water, inside the membrane. It is highly possible that the outgrowth of Nafion fibers toward the liquid bulk is accompanied by an effective reduction in the size d of the original plate. To verify this, it is necessary to measure the spatial distribution $n_{\text{Naf}}(x)$ both to the right and to the left of the plate, and also inside the plate. However, the design of the experimental setup does not allow us to do this. Of course, one can expect that there should appear a density gradient in the near-surface layer of the plate; i.e., the distribution of density of Nafion particles inside the plate is no more uniform. However, a reliable determination of this non-uniformity is beyond our measuring capabilities. For this reason, the inhomogeneous density distribution inside the Nafion plate is replaced by a homogeneous distribution with an effective value that turns out to be lower than that of a dry Nafion plate (Fig. 8). This approach is justified by the fact that we mainly are interested in a new colloidal phase of Nafion particles, which arises during the soaking and extends into the volume of the liquid by hundreds of microns.

Figure 9 shows the dependence of the quantity $L_0 = (2q)^{-1/2}$; L_0 is measured from the solid boundary $x = 0$, and the experimental points are connected by segments. As follows from the graph, the quantity L_0 depends non-monotonically on the deuterium content. We note that Eq. (4) belongs to the class Fredholm integral equations of the first kind.²⁴ It is known that these equations have a unique solution. But this solution is unstable with respect to small deviations of the theoretical curve $P(x)$, which approximates the experimental values. The solution of such an equation is an ill-posed problem. Thus, a question arises about the consistency between the distribution obtained for $n_{\text{Naf}}(x)$ in the bulk liquid and that from the left part of Eq. (4), which can be measured. It is important that the effect of exclusion zone formation in water with deuterium content $C = 157$ ppm (Refs. 2–4) implies that the characteristic size of the region, from which the colloidal

particles are pushed out, is approximately 200–220 μm . It is logical to assume that this area is filled with polymeric fibers that grow out into the volume of water (Ref. 23, see comments above) and cause the EZ formation. Our measurements have shown that L_0 does not change after a soaking time $t > t' = 30$ min; i.e., the outgrowth of polymer fibers into the volume of the liquid cannot be described by diffusion kinetics; however, the temporal dynamics of the outgrowth has not been studied.

In concluding this section, digress briefly to remark on inferences concerning outgrowth vs. time of soaking. We note that in our previous work,²¹ the dependence of the Nafion transmission coefficient in the 1.85–2.2 μm spectral range was studied via Fourier transform IR-spectroscopy. Having been soaked for a certain time in water samples with different deuterium contents, Nafion plates were investigated immediately after their removal from the liquid. Nafion is transparent in the spectral range under study, and the absorption is due to water molecules that are present in the pores of Nafion and captured by outgrown polymeric fibers. It was shown that the transmittance spectra of water with deuterium content 3–10⁴ ppm in the Nafion matrix differ substantially from one another, while the spectra of the same water in a cell with a size of 90 μm are practically the same, see Figs. 2 and 3 of Ref. 21. We associate this spectral difference with a confinement effect on water with different deuterium contents, penetrated in nanometer-sized channels within the Nafion matrix and, in turn, captured by Nafion fibers. Various manifestations of this effect for water confined in nanometer pores are described, for example, in Ref. 25. It is clear that the transmittance of the Nafion plate should be inverse to the size L_0 . The dependences of the transmittance in the spectral minimum (related to the wavelength $\lambda = 1.92$ μm) vs. deuterium content for Nafion, soaked in deuterated water for 30 min and three days, are given in Fig. 4 of Ref. 21. It turned out that in both cases the transmittance has a local minimum in the range $10^2 < C < 10^3$ ppm, i.e., in the same range, where L_0 has a local maximum. Spearman rank correlation coefficients ρ between the deuterium content dependences of latter two values were calculated by the following formula:

$$\rho = 1 - \frac{6}{n(n-1)} \sum_{i=1}^n (R_i - S_i)^2,$$

where R_i and S_i are the ranks of x_i and y_i , respectively. Here, the array x_i is the ordinates of the graph in Fig. 9, the array y_i is the ordinates of the transmittance graphs in Fig. 4 of Ref. 21.

Before calculating the coefficients ρ , the corresponding arrays were reduced to the normal form in accordance with

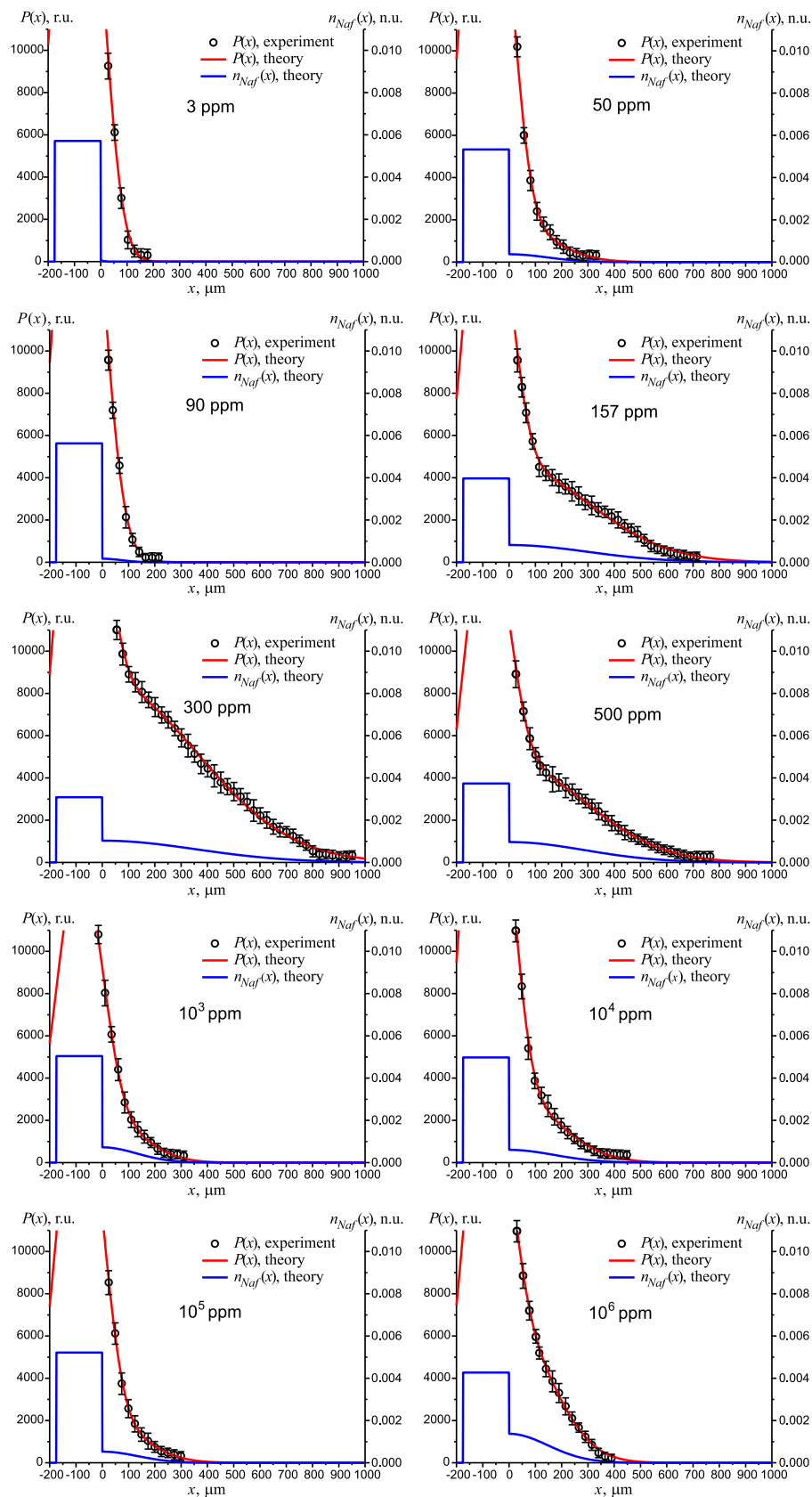


FIG. 8. Dependences of $P(x)$ and $n_{Naf}(x)$ for Nafion swollen in water with different deuterium contents. The black circles are the experimental points $P(x)$, the red curves are the theoretical approximation, and the blue curves are the density distribution $n_{Naf}(x)$.

the algorithm $F(C) = F_0(C) - A \cdot \log(C - 0.75)$, where C is the deuterium content (in ppm), $F_0(C)$ is the initial dependence, $F(C)$ is the corrected dependence, $A \cdot \log(C - 0.75)$ is the background function, and A is a fitting factor, which was chosen

empirically for each dependence. The criterion for the correct choice of this coefficient is the feasibility of the condition $F(C) \approx 0$ at the endpoints, i.e., at $C = 3$ and 10^4 ppm. In addition, the points with abscissas $C = 3$ and 50 ppm were excluded

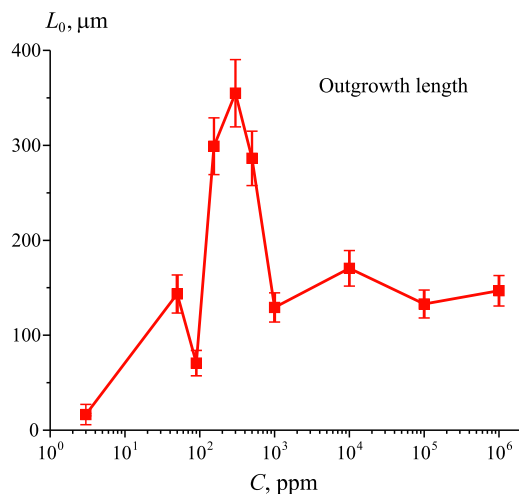


FIG. 9. Variation of the size of the outgrowth area in bulk liquid with deuterium content. The error bars show the uncertainty in the parametrization of experimental data according to the model (Sec. V).

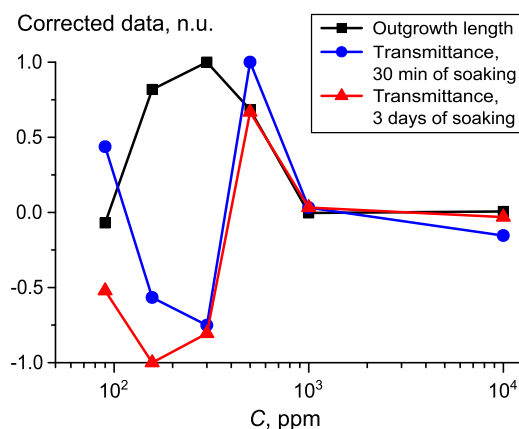


FIG. 10. Dependences of the size of the region of Nafion fibers outgrowth (black curve) and the transmittance for soaking within 30 min (blue curve) and within three days (red curve) vs. the deuterium content, resulted to a normal form.

since we cannot guarantee high accuracy when preparing samples of deuterated water in the considered range of deuterium contents. The values normalized to the maximum are shown in Fig. 10.

For Nafion soaked within 30 min and three days in deuterated water, we have $\rho = -0.66$ and $\rho = -0.43$, respectively, i.e., we are dealing with anticorrelation. It is customary to consider²⁶ that for $0.6 \leq |\rho| \leq 0.79$ we are dealing with “strong” anticorrelation, and for $0.4 \leq |\rho| \leq 0.59$ with “moderate” anticorrelation. This should be expected: with other things being equal, strong anticorrelation should be observed for the same times of soaking.

VII. DISCUSSION

The swelling of Nafion in water is very sensitive to the introduction of very small amounts of specific additives. For instance, Garzon *et al.*²⁷ showed that the H_2S admixture even at the level of 10 ppb produced negative effects on performance of a hydrogen fuel cell based on Nafion. It seems logical to assume that the swelling of Nafion in deuterated water is also

controlled by small changes (at least at the level of tens of ppm) in the deuterium content. Molecular-scale structures for interfacial H_2O and HOD inside Nafion pores and channels have been proposed on the basis of classical^{28,29} and quantum chemical (density functional theory, DFT)³⁰ calculations, and their comparison with results of nonlinear optical experiments that probed water at junctions with different phases.^{31–35} For some time, molecular simulations have been applied to investigate aspects of water–ionomer interactions, such as effects of hydration level on ion solvation and transport in Nafion (cf. Refs. 36–39 and references therein) and water confinement on hydrogen bond dynamics.⁴⁰ The prevalence of noncovalent (i.e., hydrogen bonding, dispersion, and electrostatic) forces implies that quantum mechanical simulation is essential in trying to elucidate the operating force fields.

But many body cooperativity of the effects we have observed are such delicate that even the most powerful simulation tools we have available may be unable to pin down the phenomena. One avenue not yet explored is this: It is known that there are very long range forces between long thin conducting polymers. These forces due to quantum mechanical and classical giant dipole fluctuations are strictly non-additive.^{41,42} Their existence is as certain as London-van der Waals or Casimir force. Awareness of their universality is nil, but they do exist. They will operate between DNA molecules, for example. The closest example to our situation with Nafion is the jellyfish. The carapaces of these oldest of all multi-celled animals must be permeated by a dilute network of the same long thin strands of charged polymers that provide their stinging capacity.⁴³ And the water structure of jellyfish is as unknown as similar to that of the Nafion surface. Rather than postulating a new 4th state of water as has reasonably been conjectured by Pollack,² it seems more likely to us that the long range many body inter-polymer forces are the source of the organizing principles behind this water. The same probably holds true for the mysterious structure of water in the polymeric glycocalyxes of the surface layer of blood vessel walls and blood cells including neutrophils, *T* and *B* cells of the immune system, as well as bacteria. And also for the strange undisputed observations of Ise *et al.*^{5–8} on latex sphere suspensions.

Experiments with luminescent spectroscopy have shown that it is possible to distinguish two phases in the Nafion–water system: high-density and low-density (with respect to Nafion content) phases. The high-density phase, which corresponds to a rectangle of width d in the distribution $n_{\text{Naf}}(x)$ (see Fig. 8), can be considered as a solid, albeit non-uniform, polymer matrix, permeated with water-filled nanometer-channels. By virtue of the amphiphilicity of Nafion polymer fibers, the low-density phase can be associated with a colloidal system consisting of Nafion rods formed as a result of a structural inversion; the size of this phase along the abscissa axis reaches hundreds of microns. In this case, we are dealing with a structural phase transition, which is analogous to the phase transition in ternary “oil–amphiphilic surfactant–water” systems, which, as shown in Ref. 44 (see also references therein), leads to the formation of a microemulsion with cylindrical micelles. Thus, the Nafion fibers in the liquid bulk, resulting from the swelling of the polymer matrix in water with

different deuterium contents are structurally analogous to cylindrical micelles; here the role of an amphiphilic surfactant is played by terminal sulfonic groups, and the role of the oil is played by the Teflon backbone.

In our opinion, the fact that the effect of outgrowing of polymer fibers is controlled by the content of deuterium, can be attributed to a specific competitive adsorption of deuterium upon interaction with the polymer matrix within Nafion. The physical adsorption of hydrogen/deuterium in novel nanoporous materials is now under wide investigation both experimentally and theoretically.^{45–50} Special attention is paid to the determination of the absolute/excess adsorption isotherms of hydrogen.^{51–56} In nanopores, the geometrical constraints and additional molecule-surface interactions affect both structural and dynamics properties of hydrogen.^{57–61} In nanopore confinement, the effects are enhanced in comparison with those in the bulk phase due to the very large potential gradients existing within objects of nanoscale dimensions, and as a consequence, the motion of molecules is restricted in some directions.^{52,59} Moreover, the delocalization effects due to the position-momentum uncertainty principle introduce quantum fluctuations in addition to the thermal ones.⁶² We note in conclusion that the question of a possible stabilization of Nafion fibers in water using with deuterium atoms requires special analysis. In any event, it is clear that water in Nafion is in a state quite distinct from the liquid phase and may be expected to have physical properties widely different from those of bulk water.

VIII. CONCLUSIONS

In this work, the near-surface region at the “water-Nafion” boundary was studied as a function of the deuterium content. It is shown that when Nafion is immersed in water, polymer fibers grow out into the volume of the liquid. The polymer fibers are fixed by their ends at the surface of the membrane; i.e., complete separation of polymer particles from the membrane and their subsequent escape to the liquid bulk does not occur. The effect of fiber outgrowth is controlled by the content of deuterium in the liquid and manifests itself to the greatest extent at $10^2 < C < 10^3$ ppm. An independent confirmation for the existence of this effect is the existence of a local minimum of the Nafion transmittance at the wavelength of $1.92\ \mu\text{m}$ in the same region of deuterium contents, and the presence of a strong anticorrelation for the measurements of the outgrowth region size and transmittance. It is important that in the experiments with Fourier transform IR spectrometry, we study samples of the Nafion removed from the liquid; i.e., the contribution of possible structuring of water close to the membrane surface is excluded. We conclude that the results obtained do not conflict with the data of Ref. 4. But these results can be explained by the effects of the polymer fiber outgrowth into the bulk liquid. It is not necessary to require a new phase of bulk water to accommodate the exclusion zone phenomenon.

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