Radon diffusion through polymer membranes used in the solar neutrino experiment Borexino

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Abstract

We have measured the radon diffusion, solubility and permeability coefficients of various foils being of interest for the Borexino experiment. The applied methods and instrumentation are described and the mathematical model for diffusion of Rn, including its decay, is outlined. A very strong influence of water on the Rn diffusion through nylon foils was found. The rather low Rn permeability for dry nylon foil (mean value is equal to 3.35×10^{-12} cm^2/s) increases by more than two orders of magnitude if the foil is immersed in water. No significant influence compared to dry nylon has been observed if the foil was surrounded by pseudocumene. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The radon-222 (Rn) permeability of various polymer foils of interest in the solar neutrino experiment Borexino [1] was studied. The experiment, located in the underground Gran Sasso laboratories, will use a large volume of liquid scintillator for neutrinos detection. The primary aim is to measure the contribution of ^{7}Be-neutrinos to the solar neutrino flux. The Standard Solar Model flux of ^{7}Be-neutrinos would correspond to about 43 events/day in a fiducial volume of 100 metric tons. In case of conversion into other neutrino flavors, the count rate will be even smaller. The expected small count rate sets strong limits on the radio-impurities of the Borexino detector.

The detector has a shell structure as shown in Fig. 1. At the center, the scintillator is enclosed in a nylon containment vessel of 8.5 m diameter and 0.125 mm wall thickness. The scintillator is surrounded by a buffer region that consists of two sections: the inner buffer region and the outer buffer region. This two sections are separated by another amorphous nylon foil (0.1 mm thick) as a Rn barrier. A 13.7-m diameter stainless-steel sphere, on which 2000, 20 cm in diameter photo-tubes with light concentrators are mounted, encloses the outer buffer. The space between the stainless-steel sphere and the outer tank (not shown in Fig. 1) is filled with purified water. The water serves as a shield against the external gamma-radiation. The buffer liquid (pseudocumene – PC) shields the scintillator enclosed in the inner

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Nylon scintillator vessel, nylon 6
H = 0.125mm, A = 226.8m²

Rn barrier, nylon 6
H = 0.1mm, A = 484.9m²

Outer buffer section

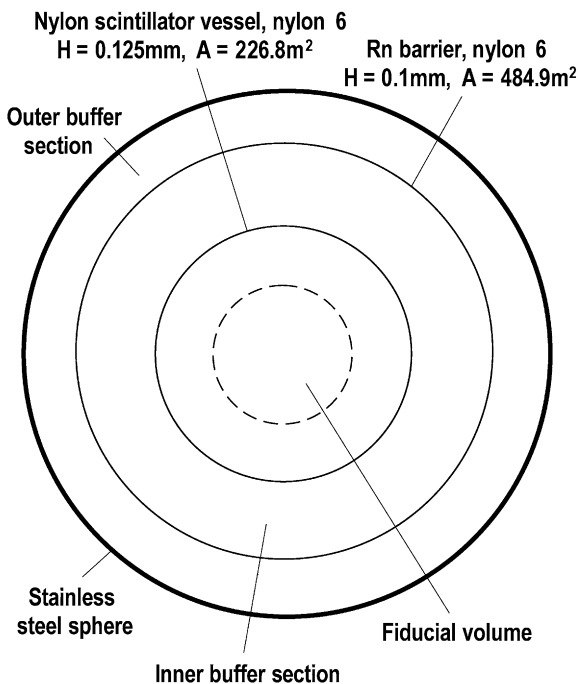Stainless steel sphere

Inner buffer section

Fiducial volume

Fig. 1. A schematic view of the Borexino detector, showing the stainless-steel sphere, the radon barrier and the inner nylon vessel.

vessel (IV) mainly against gamma rays from radio-impurities of the photomultipliers. The Rn barrier in the buffer at a distance of about 1.5 m from the IV keeps the Rn emanating from the photomultiplier and other components of the outer buffer region away from the inner buffer region. Thus, the scintillator (PC with the fluorescent dye PPO) is shielded by 1.5 m of pure PC against the gamma radiation of the Rn-progenies in the outer buffer. The nylon foil of the IV serves as an additional barrier against the residual Rn diffusing through the Rn barrier and the buffer liquid.

Borexino is an extreme low-background detector with radiopurity requirements for the liquid scintillator as low as 10^{-16} g/g in U and Th. This corresponds to a tolerable ^{222}Rn concentration of about 1 μBq/m³. With the "Counting Test Facility" (CTF) it was demonstrated that the required radiopurity in Th/U and ^{14}C can be achieved [2]. In contrast to Borexino, the CTF consists only of the scintillator containing vessel (2.1 m in diameter), 100 phototubes surrounding it at an open

structure and an outer tank (11 m in diameter and 10 m high) filled with high-purity water. The nylon foil of the scintillator containment vessel, here directly exposed to water, has a thickness of 0.5 mm. In the upgraded version of the CTF (CTF II) a 0.1 mm thick second nylon bag will be installed in front of the phototubes as a Rn barrier protection for the inner water shield next to the scintillator.

In this contribution we present methods developed to measure Rn permeability through different types of nylon and Kalrez exposed to dry gas, water, pseudocumene or a combination of these substances as they occur in Borexino and the CTF, respectively.

The aim of the investigations was to extract diffusion and solubility constants of Rn from these measurements, so that the background counting rate of the scintillator caused by Rn diffused into and trough the nylon walls can be estimated. Thus created data base helps to choose the proper type and adequate thickness of nylon foils.

2. Mathematical model of radon diffusion through a polymer membrane

Our diffusion model includes Rn decay inside the investigated membrane and Rn decay and production of short-lived radioactive progenies in the active volume of the detector. The model is tailored for applying scintillation-type Rn detectors which are sensitive to α particles emitted by ^{222}Rn, ^{218}Po and ^{214}Po.

The case of Rn diffusion through a membrane is considered. One face $x = H$, of a membrane is kept at a constant concentration C_1. If the diffusion is small, we can assume that the concentration at the other face, $x = 0$, is also constant and equal to zero. H is the thickness of the membrane. The membrane is initially at zero concentration. All above conditions can be combined in the following form:

$$w = 0, \quad x = 0, \quad t \geq 0$$
$$w = C_1, \quad x = H, \quad t \geq 0$$
$$w = 0, \quad 0 < x < H, \quad t = 0 \tag{1}$$

where $w = w(x, t)$ is the concentration of the diffusing substance. If the diffusing substance does not

decay, the diffusion process can be described by a simple equation:

$$\frac{\partial w}{\partial t} = D\frac{\partial^2 w}{\partial x^2} \tag{2}$$

where D is the diffusion constant (we assume that this coefficient is isotropic and constant during the measurements). The solution of above equation with initial conditions (1) can be found by the method of the Laplace transformation. If we express this solution in the form of series, we obtain

$$w = \frac{C_1 x}{H} + \frac{2C_1}{\pi}\sum_{n=1}^{\infty}\frac{\cos n\pi}{n}\sin\frac{nx\pi}{H}\,e^{-Dn^2\pi^2 t/H^2}. \tag{3}$$

If the diffusing substance decays and its decay constant is λ_0, then the equation for diffusion becomes

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2} - \lambda_0 u \tag{4}$$

where $u = u(x,t)$ is the concentration of the diffusing substance. Danckwerts [3] showed, that there is a relation between the solution of the simple diffusion Eq. (2) and the equation that involves decay of diffused substance. If $w(x,t)$ is a solution of Eq. (2), then the solution of Eq. (4) for the same boundary conditions is

$$u = \lambda_0\int_0^t w\,e^{-\lambda_0 t'}\,\mathrm{d}t' + w\,e^{-\lambda_0 t}. \tag{5}$$

Substituting expression (3) in (5) gives, after integration

$$u = \frac{xC_1}{H} + \frac{2C_1}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi x}{H}$$
$$\times\left[\frac{\lambda_0}{\beta} + \left(1 - \frac{\lambda_0}{\beta}\right)e^{-\beta t}\right] \tag{6}$$

where $\beta = Dn^2\pi^2/H^2 + \lambda_0$. The above equation describes how the Rn concentration changes inside the membrane with time.

If we assume that there is a linear relationship between an external concentration of diffusing substance and the corresponding concentration within the membrane, it follows that $C_1 = SC_1'$ where C_1' is the external concentration in equilibrium
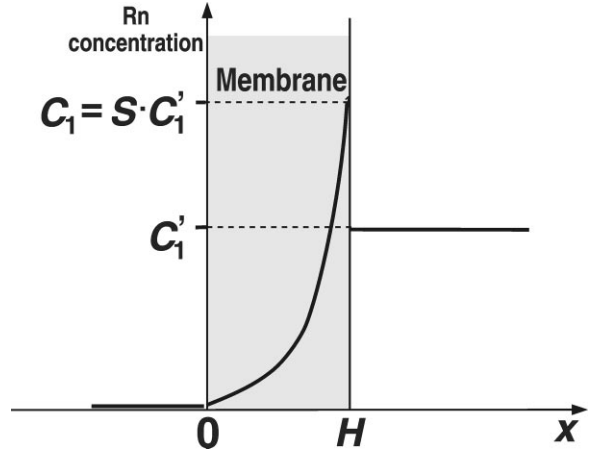

Fig. 2. The radon concentration inside and outside of the membrane for the case $S > 1$.

with the internal concentration C_1, and S is the solubility. If there is the same gas on both sides of the membrane, the solubility is identical on both sides. The Rn concentration inside and outside of the membrane for the case of $S > 1$, is shown in Fig. 2.

The rate, at which radon emerges from unit area of the face $x = 0$ of the membrane is given by $D(\partial u/\partial x)_{x=0}$. Using Eq. (6) we obtain the following expression for the rate:

$$D\frac{\partial u}{\partial x}\bigg|_{x=0} = \frac{DSC_1'}{H} + \frac{2DSC_1'}{H}\sum_{n=1}^{\infty}(-1)^n$$
$$\times\left[\frac{\lambda_0}{\beta} + \left(1 - \frac{\lambda_0}{\beta}\right)e^{-\beta t}\right]. \tag{7}$$

In our experiment we can measure the Rn concentration on both sides of the membrane. As already mentioned, the Rn concentration is kept constant on one side of the membrane. This is achieved by using a special Rn source. In order to obtain the Rn concentration on the other side of the membrane, the decay of Rn in the gas volume on that side must also be taken into account. The Rn concentration is measured with ZnS(Ag) scintillation chambers. This type of detector register α particles emitted by ^{222}Rn and its short-lived progenies (^{218}Po, ^{214}Po). To describe the process of Rn accumulation on the far side of the

membrane (taking into account the decay of Rn and its progenies) the following set of differential equations has to be solved:

$$\frac{dy_0}{dt} = -\lambda_0 y_0 + A D \frac{\partial u}{\partial x}\bigg|_{x=0}$$

$$\frac{dy_1}{dt} = -\lambda_1 y_1 + \lambda_0 y_0$$

$$\frac{dy_2}{dt} = -\lambda_2 y_2 + \lambda_1 y_1$$

$$\frac{dy_3}{dt} = -\lambda_3 y_3 + \lambda_2 y_2$$

$$\frac{dy_4}{dt} = -\lambda_4 y_4 + \lambda_3 y_3$$

$$\frac{dy_5}{dt} = -\lambda_5 y_5 + \lambda_4 y_4 \tag{8}$$

where λ_0, λ_1, λ_2, λ_3, λ_4, λ_5 are the decay constants and y_0, y_1, y_2, y_3, y_4, y_5 are the numbers of atoms (in the detector volume) of ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po, and ^{210}Pb, respectively. A is the surface area of the membrane. In our calculation we assume that at $t = 0$ the number of Rn atoms and its progenies was equal to zero ($y_0 = y_1 = y_2 = y_3 = y_4 = y_5 = 0$). Since the scintillation chambers measure the total alpha decay rate of Rn and its progenies a relation between the solution of Eq. (8) and the registered count rates of both detectors has to be found. This is possible in the form of their counting rate ratio. If the count rate of the detector that monitors the constant Rn concentration C'_1 is n_1, and the count rate of the other detector is n_2, and if the active volumes V_d and the counting efficiencies of both detectors are equal, the ratio n_2/n_1 can be expressed by

$$\frac{n_2}{n_1} = \frac{\lambda_0 y_0 + \lambda_1 y_1 + \lambda_4 y_4}{3 \lambda_0 C'_1 V_d}. \tag{9}$$

Assuming radioactive equilibrium between Rn and its progenies, Eq. (9) can be rewritten as

$$\frac{n_2}{n_1} = \frac{\lambda_0 y_0}{\lambda_0 C'_1 V_d} = \frac{y_0}{C'_1 V_d} \tag{10}$$

Above assumption is fulfilled if the time, after which Rn reaches equilibrium with its progenies (about

three hours) is short in comparison to the total measurement time (from several dozen to several hundred hours). The set of differential equations (8) can be reduced to the first equation which, after being solved gives just y_0. This equation can be rewritten in the following form:

$$\frac{dy_0}{dt} + y_0 \lambda_0 = \frac{ADSC'_1}{H} + \frac{2ADSC'_1}{H} \sum_{n=1}^{\infty} (-1)^n$$

$$\times \left[\frac{\lambda_0}{\beta} + \left(1 - \frac{\lambda_0}{\beta} \right) e^{-\beta t} \right] \tag{11}$$

where $\beta = (Dn^2\pi^2/H^2) + \lambda_0$. The analytical solution of above equation is

$$y_0(t) = \frac{ADSC'_1}{H\lambda_0} \left[1 - e^{-\lambda_0 t} + 2 \sum_{n=1}^{\infty} (-1)^n \frac{\lambda_0}{\beta} \right.$$

$$\left. \times (1 - e^{-\beta t}) \right] \tag{12}$$

where D and S are the diffusion and solubility coefficients of Rn in the foil, A is the surface area of the foil (through which Rn diffuses) and H is the thickness of the foil. In some cases it is interesting to know the relative count rate n_2/n_1 after equilibrium between Rn diffused through the membrane and Rn decay in the active volume of the detector is established. For $t \to \infty$ expression (12) can be reduced to the form

$$y_0(t \to \infty) = \frac{ADSC'_1}{H\lambda_0} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \right.$$

$$\left. \times \frac{\lambda_0 H^2}{\lambda_0 H^2 + Dn^2\pi^2} \right]. \tag{13}$$

Finally, expression for the asymptotic value of the relative count rate n_2/n_1 (Eq. (10)) can be written as follows:

$$\frac{n_2}{n_1}(t \to \infty) = \frac{ADS}{H\lambda_0 V_d} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \right.$$

$$\left. \times \frac{\lambda_0 H^2}{\lambda_0 H^2 + Dn^2\pi^2} \right]. \tag{14}$$

Fig. 3 presents calculated dependences of the asymptotic value of the relative count rate as
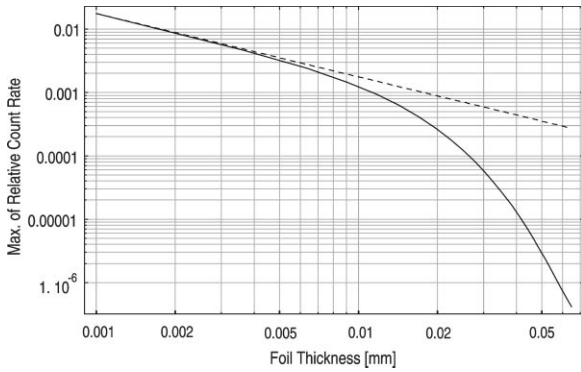
Fig. 3. The dependence of the asymptotic value ($t \to \infty$) of the relative count rate on the foil thickness ($D = 1.1 \times 10^{-12}$ cm^2/s, $S = 5.5$). Dotted line corresponds to the thin foil approximation (without Rn decay inside the investigated foil).

a function of the foil thickness. For the shown example the following diffusion and solubility constants have been assumed: $D = 1.1 \times 10^{-12}$ cm^2/s and $S = 5.5$. The dependence calculated on the basis of the Eq. (14) is presented as a solid line. The dotted line corresponds to the thin foil approximation, calculated on basis of the following equation:

$$\frac{n_2}{n_1} = \frac{ADS}{H\lambda_0 V_d}. \tag{15}$$

It is clear (see Fig. 3) that this approximation can be used only if the foil is thinner than 0.001 cm. In the other case Eq. (14) has to be employed, because the Rn decay inside of the membrane can no longer be neglected.

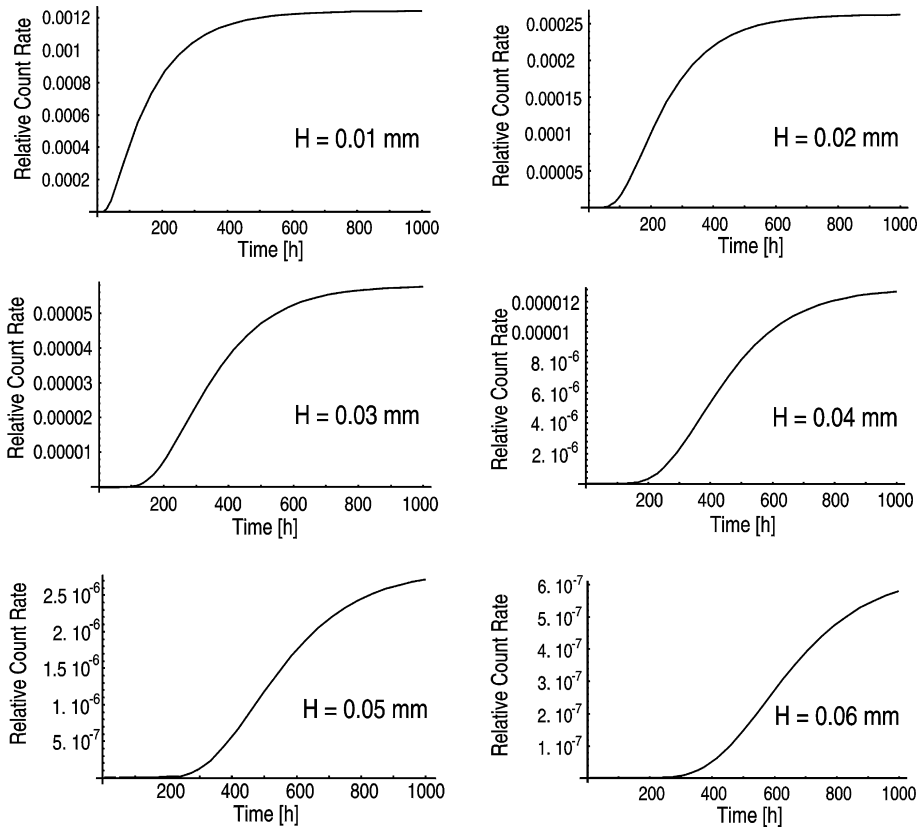In Fig. 4 it is demonstrated in which way the time dependence of the count rate changes with

Fig. 4. The dependence of the relative count rate on time for the 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 mm thick foils ($D = 1.1 \times 10^{-12}$ cm^2/s, $S = 5.5$).

increasing foil thickness. These profiles have been calculated for foils of 0.01 to 0.06 mm thickness using the same coefficients, D and S, as above.

In the following measurements we employ this diffusion model to deduce the diffusion constant and the Rn solubility. They are evaluated from the profiles fitted to the experimental data by the least squares method.

3. Experimental equipment

The diffusion, solubility and permeability coefficients of polymers for Rn are not generally available in the literature. Some efforts have been made to select a suitable material to serve as a Rn barrier [4], to discriminate between different Rn isotopes [5] or to investigate the permeability characteristics of membranes to ^{222}Rn (or ^{220}Rn) [6–10]. The method presented here enables the study of diffusion and solubility of ^{222}Rn in membranes and thus leads to the fundamental constant – the diffusion coefficient [9]. The used apparatus, of which a schematic view is shown in Fig. 5, consists of two similar scintillation Rn detectors, a Rn reservoir and a Rn source. The quartz windows between the active volumes of the detectors and of the photomultipliers are covered by ZnS(Ag) on the opposite side of the PMTs to form the sensitive surfaces of the scintillation chambers. The light generated in the ZnS(Ag) by alpha particles (emitted by Rn and its progenies) is detected by photomultipliers.

Compared to the previous measurements [10] the apparatus was modified by introducing a continuous Rn supply instead of using a single Rn spike. The Rn source consist of 100 cm^3 of ^{226}Ra-solution (18.5 kBq) enclosed in a silicon rubber pipe, which is placed in a vessel of 4.6 l vol. More than 80% of Rn generated in the solution diffuses through the silicon walls of the pipe into the 4.6 l gas (dry nitrogen) vol. Rn together with nitrogen is circulated by means of a pump in the hermetically sealed system of Rn source, drying column $(Mg(ClO_4)_2)$ and Rn reservoir. Both detector chambers have similar active volumes of about $V_d = 28$ cm^3. The active volume of the first detector is separated from the Rn reservoir by a paper
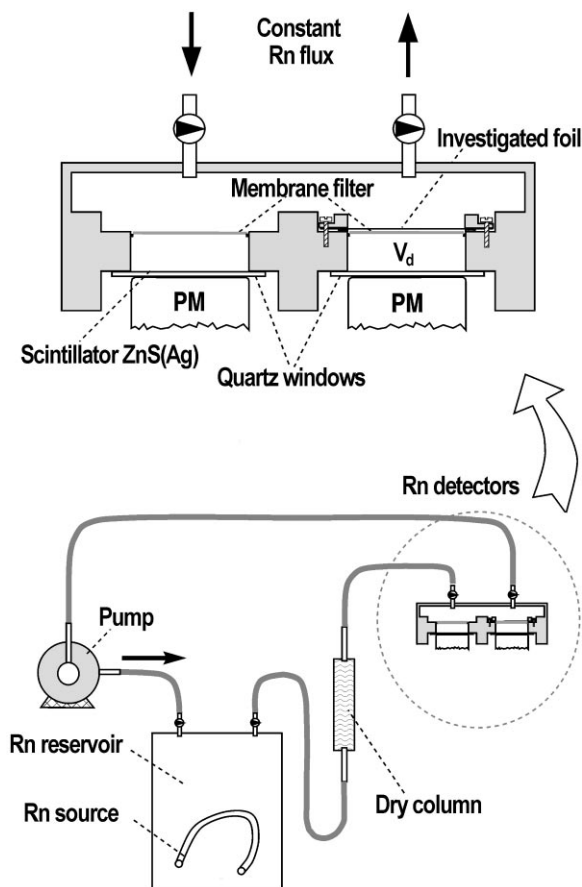

Fig. 5. A schematic view of the apparatus for the measurement of the diffusion and solubility coefficients in membranes.

filter to assure the same Rn concentration as in the reservoir. The count rate n_1 of this detector (corrected for background) is proportional to the Rn concentration C_1' in the reservoir when equilibrium with the progenies is reached. The active volume of the second detector is separated from the reservoir by the membrane to be investigated. The membrane is carefully sealed with a special metal gasket (generally In). The gasket is the most critical part in measurements of low Rn permeability since small leaks could falsify the results. The surface area of the membrane through which Rn diffuses corresponds to $A = 22.9$ cm^2. The count rate of the second detector n_2 (also background corrected) is proportional to the total amount of Rn diffused through the investigated membrane.

The relative efficiency of both detectors has been determined with membrane filter on both sides, so that the active volumes had the same Rn concentration.

The count rate of the first detector n_1, increases during about 3 h after Rn was introduced into the reservoir ($V = 255$ cm^3), due to the growth of Rn-daughters. The Rn concentration C_1' in the reservoir is kept constant over the whole measuring period. The Rn concentration C_2' in the active volume of the second detector and its count rate n_2 (generated by Rn and its short-lived alpha-emitting progeny) starts to increase after a certain time-period depending on the material type and thickness of the membrane. The ratio n_2/n_1 registered as a function of time[1] ($n_2/n_1 = C_2'/C_1' = C_2/C_1$) contains the desired information.

For background determination, as well as for the calibration and the measurements itself, the whole system (active volumes, Rn source and Rn reservoir) was filled with dry nitrogen. The first measurement was made using the dry 0.15 mm nylon C38F foil. The dependence of the relative count rate on time for this foil is shown in Fig. 6. It is obvious that the permeability was too low to be detectable. This measurement characterizes the sensitivity of our apparatus. From it we can draw the following conclusions:

- The gasket system used for the sealing of the foil is Rn-tight if the ratio of C_2/C_1 stays in the range above 10^{-5}–10^{-6}.
- The diffusion coefficient of the 0.15 mm nylon C38F foil is lower than 2.2×10^{-13} cm^2/s.
- The Rn permeability of the 0.15 mm thick nylon foil is lower than 6.5×10^{-13} cm^2/s, assuming that after 20 days of measurement the signal was not larger than the background. It should be noted here, that the permeability cannot be simply a product of the diffusion and solubility coefficients. For a membrane with a very low Rn permeability, Rn decay during its diffusion through the foil can no longer be neglected and strongly depends on the thickness of the foil. In such situation the effective permeability must be considered (see Eq. (17)).
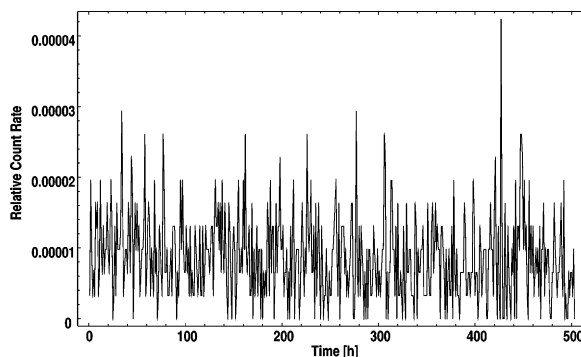
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[1] n_1 is the average value.

Fig. 6. The dependence of the relative count rate on time for the 0.15 mm nylon membrane.

The described apparatus allows also to study the influence of liquids on the Rn permeability of the investigated membranes by placing a layer of this liquid onto the surface of the membrane foil. The diffusion of Rn (dissolved in this liquid) through the foil can thus be measured. We have used this procedure to test the Rn permeability of various polymers with water and pseudocumene on one side of the foil.

However, in Borexino the Rn barrier and the IV foil will be in contact with liquids on both sides. The permeability in such conditions can be extracted from the above measurements only with some difficulty and uncertainty. Therefore, another apparatus was built to simulate the real conditions. As shown in Fig. 7, it consists of a diffusion chamber with liquids on both sides of the investigated foil and of two circulating loops which are interconnected. Rn emanated from the same ^{226}Ra-solution containing tube, as described above, is circulated through a Rn exchange chamber, where the Rn loaded gas is in contact with a liquid (in our case either water or PC). This liquid is circulated in the second loop through one side (source side) of the diffusion chamber. Rn is taken up by this solution according to the relative solubilities in both phases. The membrane foil separates the source side from the liquid (PC) on the other side. The Rn concentration in the circulating liquid (source side) is measured by vacuum transferring of an aliquot into a bubbler extractor and by flushing Rn with nitrogen into a 0.7 l Lucas chamber. The Rn diffused
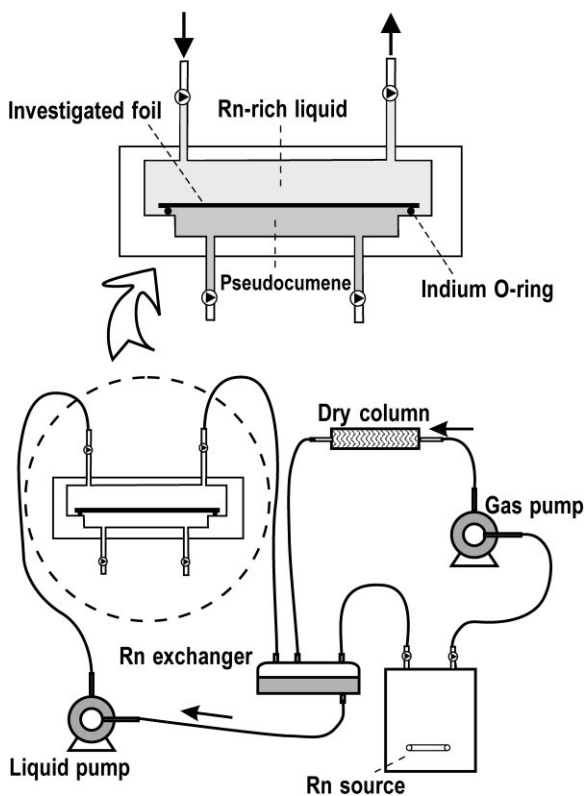
Fig. 7. A schematic view of the apparatus for the measurement of the Rn effective permeability in membranes of polymer placed in liquid environment.

through the membrane into PC (second part of the diffusion chamber) is extracted by flushing with nitrogen direct into the same Lucas chamber. C_1^* is the Rn concentration in the liquid at the source side and C_2^* is the diffused fraction dissolved in PC. The effective permeability of Rn can be evaluated by aid of the following equation, assuming that equilibrium has been reached (which is the case after about 20 days):

$$P_{\text{eff}} = \frac{\lambda_0 a H}{(C_1^* - C_2^*)A} \tag{16}$$

where a is the activity of Rn which has diffused through the foil and $A = 41.2 \text{ cm}^2$ is the surface area of the membrane. Unfortunately, in this experiment it is not possible to measure the D and S coefficients. With the calculated P_{eff} for the thickness H it is possible to calculate P'_{eff} for another

thickness H', using the following equation:

$$P_{\text{eff}} = DS \frac{d_l H}{\sinh(d_l H)} \tag{17}$$

where d_l is the inverse of the Rn diffusion length in foil ($1/d_l = d_e = \sqrt{D/\lambda_0}$).

4. Measurements of radon diffusion and solubility constants in membranes of polymers

By using the described apparatuses in Chapter 3 (Figs. 5 and 7) the diffusion and solubility coefficients of different nylon (C38F, nylon 6 [colorless uni-axially oriented] and nylon 6 [light blue, heat stabilized]) foils and one Kalrez (compound 4079) foil have been examined under various conditions. Kalrez may be used to seal the photomultipliers mounting on the stainless steel sphere of the Borexino detector. For this purpose its Rn permeability has to be checked.

4.1. Investigation of dry foils and foils with thin liquid film on one side

Measurements described in this subsection were done by using the apparatus which is shown in Fig. 5.

At the beginning we investigated two similar 0.015 mm thick nylon 6 foils under the same experimental conditions (temperature of $(17.3 \pm 0.8)°C$, and under dry nitrogen atmosphere) to test the reproducibility of the method. Fig. 8 depicts the measured ratio n_2/n_1 versus time for the first foil. The theoretical curve fitted to the experimental data is also shown. The insert in Fig. 8 shows the time dependence of the count rate n_1. The values of obtained D and S coefficients are given in Table 1, Pos. 1 and 2. Both measurements were in good agreement with each other (see Chapter 5).

The measurement of the Kalrez foil of the thickness of 0.28 mm was started under dry condition, then, after 59 h, a thin layer of PC was placed on top of the foil and the measurement was continued. In this way we could test the influence of PC on the Rn permeability through Kalrez and the impact of PC with its high Rn solubility on the diffusion
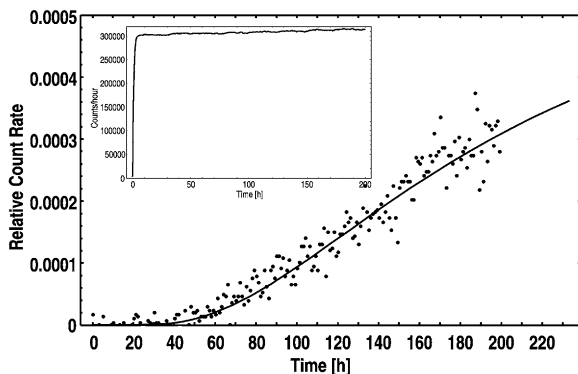
Fig. 8. The dependence of the relative count rate on time for the first 0.015 mm dry nylon 6 foil. The solid line – last-square fit to experimental data ($D = 1.17 \times 10^{-12}$ cm^2/s, $S = 6.0$). In the upper-left corner the count rate n_1 is shown.

process. The registered relative count rate versus time is shown in Fig. 9. The deduced values for the D and S coefficients are summarized in Table 1, Pos. 3 and 10 and are discussed in the next chapter.

In succeeding measurements, nylon 6 and C38F foils of different thickness and under different conditions were examined in the following configurations:

- To examine the influence of water on the Rn permeability through nylon, several measurements were made using wet nylon foils. The foils were immersed in water for 3 h–6 days prior to the measurements and a thin layer (about 4 mm) of water was placed on top of the wet foil during the measurement. A high humidity was maintained on the opposite side of the foil (100% humidity was kept inside of the active volume of the detector). Results of the measurements are given in Table 1, Pos. 4–8.
- The influence of PC on the Rn diffusion through nylon exposed to PC before the measurement was examined in a similar way. The nylon 6, 0.015 mm foil was first immersed in pseudocumene, mounted in the apparatus and a thin layer of PC was placed on top of the nylon foil during the measurement, whereas the other side was exposed to PC vapour. During the test a maximum partial PC vapour pressure was kept

inside the active volume of the detector. Results of the measurement are presented in Table 1, Pos. 9.

It was also tried to simulate a possible filling procedure of the Borexino detector. In this scenario the detector would be filled first with water for a short period and then the water is replaced by PC. The main open question was if water that is adsorbed by the IV material in the first step would remain also during the presence of PC. Two different tests have been performed; in one case Rn was circulated over the PC with dry nitrogen (water molecules have a chance to diffuse out of the wet nylon, diffuse through the PC layer and can be adsorbed in the drying column) and in the other case the nitrogen had 100% humidity. In the first case, a 0.18 mm thick nylon C38F foil was immersed in water 6 weeks before the measurement. The foil was then mounted, according to the configuration presented in Fig. 10, covered with a layer of PC and dry nitrogen with Rn was circulated above the PC layer. To avoid drying of the foil high humidity was maintained inside the active volume of the detector. Results of the measurement obtained in a two weeks run are presented in Table 2, Pos. 1 and in Fig. 10.

In the other case another C38F nylon foil ($H = 0.15$ mm) was immersed in water during 3 days before the measurement was started. Here a thin layer of water was placed on top of the foil. After 10 days the water was replaced by PC and the measurement was continued with a wet circulating nitrogen (with Rn). In contrast to the first case there is no possibility that the water adsorbed in the foil can escape. The results of the investigation are given in Table 2, Pos. 2.

4.2. Investigation of foils with liquids on both sides

Two measurements were also carried out using the second apparatus described in Chapter 3 (see Fig. 7). In the first measurement water was used as the circulating liquid (source side) and PC on the other side ([H$_2$O/foil/PC] configuration). The examined foil, nylon C38F of the thickness $H = 0.15$ mm, was left in the diffusion chamber for 5 months, so that changes in the structure of the

Table 1
The diffusion, solubility and effective permeability coefficients obtained for the foils under different conditions using the apparatus shown in Fig. 5. The permeability was calculated according to the formula (17)

Pos.	Nylon type thickness, conditions	Solubility S	Diffusion coeff. D [cm^2/s]	P_{eff} [cm^2/s] (calculated)
Dry foils				
1	Nylon 6, 0.015 mm, colourless, uniaxially oriented	5.0 ± 0.5	$(1.0 \pm 0.2) \times 10^{-12}$	$(2.8 \pm 1.3) \times 10^{-12}$
2	Nylon 6, 0.015 mm, colourless, uniaxially oriented	6.0 ± 0.7	$(1.17 \pm 0.3) \times 10^{-12}$	$(3.9 \times 2.1) \times 10^{-12}$
3	Kalrez, 0.28 mm, compound 4079	12.1 ± 2.8	$(1.2 \pm 0.3) \times 10^{-9}$	$(1.2 \pm 0.5) \times 10^{-8}$
Nylon with thin water film on the one side and 100% humidity on the other				
4	C38F, 0.646 mm, in H$_2$O, 6 weeks before the test	0.55 ± 0.2	$(1.5 \pm 0.6) \times 10^{-9}$	$(3.3 \pm 1.8) \times 10^{-10}$
5	C38F, 0.151 mm, in H$_2$O, 15 d before the test	0.8 ± 0.3	$(1.2 \pm 0.4) \times 10^{-9}$	$(9.0 \pm 3.1) \times 10^{-10}$
6	Nylon 6, 0.015 mm, colourless, uniaxially oriented, in H$_2$O, 3 d before the test	0.7 ± 0.3	$(1.3 \pm 0.5) \times 10^{-9}$	$(9.1 \pm 3.6) \times 10^{-10}$
7	Nylon 6, 0.025 mm, light blue, heat stabilised, in H$_2$O, 3 d before the test	1.3 ± 0.4	$(0.3 \pm 0.1) \times 10^{-9}$	$(3.9 \times 1.9) \times 10^{-10}$
8	Nylon 6, 0.035 mm, uniaxially oriented, in H$_2$O, 3 h before the test	1.4 ± 0.4	$(0.4 \pm 0.1) \times 10^{-9}$	$(5.5 \pm 2.1) \times 10^{-10}$
Nylon with thin PC film on the one side and PC vapours on the other side				
9	Nylon 6, 0.015 mm, colourless, uniaxially oriented, in PC, 5 d before the test	1.0 ± 0.4	$(2.5 \pm 1.2) \times 10^{-12}$	$(1.9 \pm 0.9) \times 10^{-12}$
10	Kalrez, 0.28 mm, compound 4079 dry before the test	11.7 ± 2.5	$(1.2 \pm 0.3) \times 10^{-9}$	$(1.1 \pm 0.5) \times 10^{-8}$

polymer chains caused by the two liquids (water and PC) certainly had reached equilibrium. Thereafter, the Rn-circulating loop and the water circulating loop of the source side were turned on for 21 days and the Rn concentration in water ($C_1^{H_2O}$) and in the PC (C_2^{PC}) was measured subsequently. The mean values of the Rn concentration in water and in PC are

$$C_1^{H_2O} = (0.761 \pm 0.019) \text{ Bq/cm}^3$$

$$C_2^{PC} = (0.166 \pm 0.022) \text{ Bq/cm}^3.$$

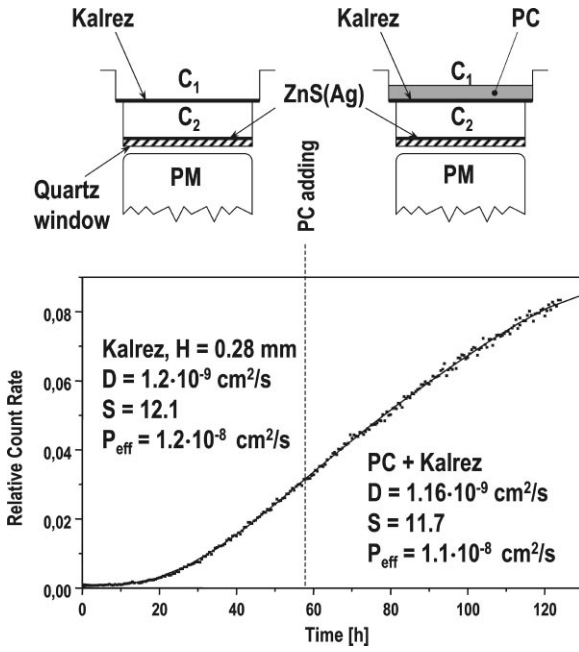The measured Rn activity diffused through the foil into PC corresponds to $a = (2.79 \pm 0.09)$ Bq, the

Fig. 9. The relative count rate versus time for the Kalrez foil. The solid line – last squares fit to the experimental data.
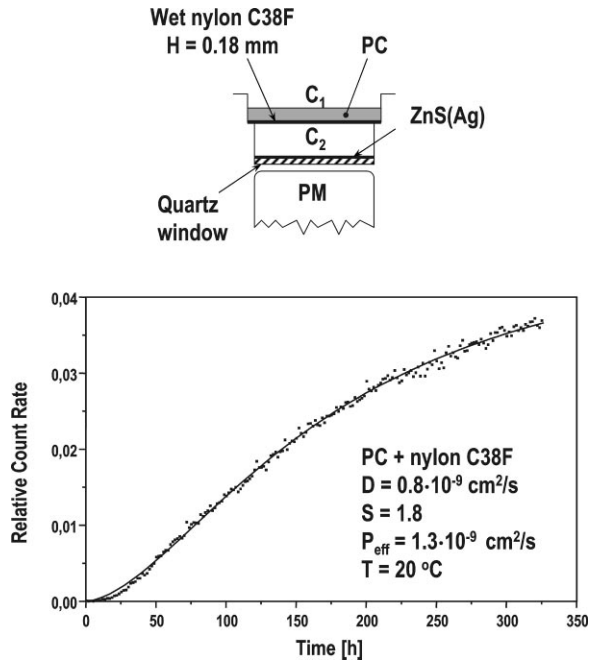

Fig. 10. The relative Rn concentration versus time registered for the [PC/wet nylon C38F/100% humidity air] configuration and dry circulating gas.

foil surface area was $A = 41.2$ cm^2 and the mass of the PC was $m_{PC} = 15$ g.

The second measurement was performed with PC as the circulating liquid ([PC/foil/PC] configuration). The nylon 6 foil of the thickness $H = 0.015$ mm was 12 days in contact with PC before the loops were turned on for 20 days. Subsequently the following Rn concentrations were measured:

$$C_1^{PC} = (14.9 \pm 1.3) \text{ Bq/cm}^3$$

$$C_2^{PC} = (0.0058 \pm 0.0009) \text{ Bq/cm}^3$$

where C_1^{PC} is the Rn concentration in the circulating PC. The diffused Rn activity into PC was $a = (0.098 \pm 0.003)$ Bq, m_{PC} and the foil surface area were identical to above. The effective permeability calculated according to Eq. (16) from both measurements is given in Table 3.

Table 2
The diffusion, solubility and effective permeability coefficients obtained using the apparatus shown in Fig. 5 when the possible filling procedure of the Borexino detector was simulated (water replacing by PC). The permeability was calculated according to Eq. (17)

Pos.	Nylon type, thickness, conditions	Solubility S	Diffusion coeff. D [cm^2/s]	Permeability P_{eff} [cm^2/s]
1	C38F, 0.18 mm in H$_2$O, 6 weeks before dry circulating gas	1.8 ± 0.5	$(0.8 \pm 0.2) \times 10^{-9}$	$(1.3 \pm 0.5) \times 10^{-9}$
2	C38F, 0.15 mm H$_2$O $\rightarrow$ PC, wet circulating gas	0.5 ± 0.2	$(1.7 \pm 0.4) \times 10^{-9}$	$(0.8 \pm 0.3) \times 10^{-9}$

Table 3
The Rn permeability through foils obtained using apparatus presented in Fig. 7 and according to Eq. (16)

Pos.	Nylon type, thickness, conditions	P_{eff} if C_1 in liquid is used	P_{eff} if C_1 in gas above liquid is used
1	H_2O/C38F, 0.15 mm/PC	$(3.6 \pm 0.7) \times 10^{-9}$ cm²/s	$(1.0 \pm 0.3) \times 10^{-9}$ cm²/s
2	PC/Nylon 6, 0.015 mm/PC	$(5.0 \pm 0.6) \times 10^{-13}$ cm²/s	$(5.7 \pm 0.6) \times 10^{-12}$ cm²/s

5. Results and discussion

In Table 1 the results obtained with the first experimental setup (Fig. 5) are summarized. In the last column the effective permeabilities calculated according to Eq. (17) are given.

A clear Rn diffusion through dry nylon was observed only for the thinnest available nylon 6 foil (0.015 mm thick). The two independent measurements are given in Pos. 1 and 2. The reproducilibity of the measurements is satisfactory.

The values of the Rn solubility and diffusion coefficient achieved for the two nylon C38F foils with $H = 0.646$ and 0.151 mm with a thin water film are in good agreement within 1σ (Pos. 4 and 5). S and D measured for wet nylon 6, $H = 0.015$ mm (colourless, uni-axially oriented) are (Pos. 6) very similar to the results for the wet nylon C38F (Pos. 4 and 5). The difference S and D between the nylon 6 foils (Pos. 7 and 8) can originate from their different structures. There is a clear effect of water on nylon diffusion properties. In the presence of water the diffusion coefficient increases by more than two orders of magnitude. The observed short-term effect is due to fact, that water molecules break the hydrogen bonds between nylon molecules and saturate the bonds. According to our tests, nylon C38F absorbs about 10% (by weight) of water. Rn can diffuse through the changed nylon more easily.

The Rn solubility in nylon 6, $H = 0.015$ mm with a thin PC film (Pos. 9) is lower than in dry nylon 6. A possible explanation could be that PC molecules diffuse into the nylon foil, partially occupy volume between the polymer chains and thus reduces the Rn solubility. The Rn diffusion coefficients in this two cases are consistent within 1σ. PC does not affect Rn diffusion through nylon remarkable.

The Rn solubility in Kalrez is high in both cases (dry and with PC on top of the foil (Pos. 3 and 10)).

The presence of PC does not influence the Rn solubility and the Rn diffusion coefficient in Kalrez. Fig. 9 shows the experimental arrangement and the measured counting rate ratio.

In Table 2 the results of the filling scenario simulation are presented. In case of wet nylon C38F with a thin PC layer on top the Rn solubility is a little bit higher (Pos. 1) than for the same wet nylon without PC (Table 1, Pos. 5), but still consistent within 2σ. The Rn diffusion coefficients are constant within 1σ. In the case of nylon C38F with a thin layer of water on top, which was later replaced by PC (wet circulating gas above – Pos. 2) the obtained results are similar to the case with dry atmosphere (Pos. 1) and consistent within 2σ. As a consequence, we conclude that structure changes caused by once absorbed water in C38F foil which is later surrounded by PC remain for a much longer time, than the measuring time (two weeks). This makes one discussed filling scenario less favorable.

Table 3 gives the results obtained with the second apparatus. The effective permeability of Rn through foils surrounded on both sides with liquids can be calculated on the basis of Eq. (16). In the first measurement (water as a circulating liquid) the investigated foil was nylon C38F of the thickness $H = 0.15$ mm in the configuration $[H_2O$/foil/PC]. After calculations (using $C_1^{H_2O}$ and C_2^{PC}, see Chapter 4.2) we obtained the following effective permeability:

$$P_{\text{eff}}^{H_2O} = (3.6 \pm 0.7) \times 10^{-9} \text{ cm}^2/\text{s}.$$

In order to compare this value with data of Table 1, e.g. with Pos. 5, we have to take into account the Rn solubility in water $S^{H_2O} = 0.33$ and in PC, $S^{PC} = 11.5$ and have to divide the Rn concentration in water and in PC by them. As results for the 0.15 mm foil, we obtained $P_{\text{eff}}^{s,H_2O} = (1.0 \pm 0.3) \times 10^{-9}$ cm²/s. Furthermore we

have to apply the Eq. (17) to obtain the $[H_2O/foil/H_2O$-vapour] version (for the 0.15 mm thick foil) of $P_{eff}^{0.15} = (0.9 \pm 0.3) \times 10^{-9}$ cm^2/s, where D and S are taken from Table 1, Pos. 4 for nylon C38F of the thickness $H = 0.151$ mm. The comparison of the both values, P_{eff}^{s,H_2O} and $P_{eff}^{0.15}$ shows almost agreement. Additionally, we note good agreement of the two permeability values for wet nylon C38F covered by a thin layer of PC (Table 2, Pos. 2). However, it does not prove that diffusion and solubility coefficients are equal in these cases because P_{eff}^{s,H_2O} for the configuration $[H_2O/foil/PC]$ was calculated directly from the experiment but was not obtained as a product of measured D and S values.

In the second measurement (PC as a circulating liquid) we investigated the foil nylon 6 of the thickness $H = 0.015$ mm in the [PC/foil/PC] configuration. The calculated (Eq. (16)), effective permeability of Rn through this membrane results in

$$P_{eff}^{PC} = (5.0 \pm 0.6) \times 10^{-13} \text{ cm}^2/\text{s}.$$

This can be compared with the value $P_{eff}^{0.015} = (1.9 \pm 0.9) \times 10^{-12}$ cm^2/s (Table 1, Pos. 8) for the [PC/foil/PC-vapours] configuration, obtained by the set up in Fig. 5.

The comparison is correct if we consider the Rn solubility in PC. According to Ref. [11] this solubility is equal to $S^{PC} = 11.5 \pm 1.8$. For equivalent experimental conditions we have to divide the measured Rn concentration in PC, C_1^{PC} and C_2^{PC} by S^{PC}. In this case, the effective permeability $P_{eff}^{s,PC} = (5.7 \pm 0.6) \times 10^{-12}$ cm^2/s (calculated using Eq. (16) and $C_1^* = C_1^{PC}/S^{PC}$ and $C_2^* = C_2^{PC}/S^{PC}$) can be compared with $P_{eff}^{0.015} = (1.9 \pm 0.9) \times 10^{-12}$ cm^2/s (Table 1, Pos. 8).

From these measurements and calculations it follows that for the same nylon 6 of the thickness $H = 0.015$ mm in comparable experimental conditions ([PC/foil/PC-vapours] and [PC/foil/PC-liquid] configurations)values of P_{eff} are obtained which differ by a factor of about 3. Since we have no clear explanation for this difference, we recommend to use $P_{eff}^{s,PC}$ for future calculations because it was obtained under conditions which better match the experimental conditions in Borexino.

Our measurements of dry nylon 6 (Table 1, Pos. 1) can also be compared with the result of Müller [8] of Ultramid B (nylon-BASF): $S = 3.0 \pm 1.6$, $D = (0.43 \pm 0.22) \times 10^{-10}$ cm^2/s and $P = (1.3 \pm 0.95) \times 10^{-10}$ cm^2/s. The two order of magnitude difference between permeabilities can be caused by differences in the materials structure and in the measurement conditions as well. Additionally, the permeability of Müller was simply calculated as the product of the solubility and the diffusion coefficient.

L. Cadonati of Princeton University has performed permeability measurements on partly identical membrane foil with another method [12].

6. Conclusions

The applied method enables to measure diffusion (and effective permeability) coefficients down to 10^{-12} cm^2/s. For the first time a polymer with an extremely low Rn permeability was found. The mean Rn solubility and diffusion coefficient obtained for dry nylon 6 are 5.5 and 1.1×10^{-12} cm^2/s, respectively. It was demonstrated that nylon membranes are potentially suitable as highly effective Rn barriers. Different scenarios occuring in the Borexino experiment and its pilot experiment (CTF) have been investigated. The most outstanding finding was that water alters the structure of nylon to such an extend that the effective permeability for Rn increases by more than two orders of magnitude. No influence of PC on the Rn permeability has been observed compared to the dry case. The latter is true also for foils made from the elastomer Kalrez.

Acknowledgements

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