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Time evolution of near membrane layers

K. Dworecki[1,a], T. Kosztołowicz[1,b], St. Mrówczyński[1,2,c], and S. Wąsik[1]
[1] Institute of Physics, Pedagogical University, ul. Konopnickiej 15, PL 25-406 Kielce, Poland
[2] Sołtan Institute for Nuclear Studies, ul. Hoża 69, PL 00-681 Warsaw, Poland

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Abstract. The near membrane layer is a region where the concentration of the substance transported across the membrane is significantly decreased. Its thickness is defined as a length over which the concentration drops k times with k being an arbitrary large number. The time evolution of such a layer is studied experimentally by means of the laser interferometric method. It is shown that within the experimental errors the thickness of the near membrane layer grows in time for any k as $a\sqrt{t}$ with the coefficient a being independent of the initial concentration and the membrane permeability. Time evolution of the near membrane layers is also analyzed theoretically. The regularities found experimentally are naturally described within the model which has been earlier developed by one of us. In particular, a scales as $\mathrm{erfc}^{-1}(1/k)$.

PACS. 66.10.Cb Diffusion and thermal diffusion – 82.65.Fr Film and membrane processes: ion exchange, dialysis, osmosis, electroosmosis

1 Introduction

The transport in membrane systems is of great interest in several fields of technology [1], where the membranes are used as filters, and biophysics [2], where the membrane transport plays a crucial role in the cell physiology. The diffusion in a membrane system is also interesting by itself as a nontrivial stochastic problem. While the time-dependent concentration profiles of the substance transported across the membrane give a detailed description of the macroscopic substance motion, we are often interested only in the regions with a sufficiently large concentration. Such a situation occurs when the phenomenon under consideration strongly depends on the concentration. For example, the hydrodynamic stability in the membrane systems studied in [3] is controlled by the Rayleigh number, which in turn depends on the transported substance concentration [4]. Therefore, it is sometimes convenient to introduce the so-called *near membrane layer* (NML) where the substance concentration drops k times, with k being an arbitrary large number [5]. NML can be also treated as a useful representation of the measured concentration profiles which is less sensitive to the experimental inaccuracies. In this paper we study NML experimentally and theoretically.

Our experimental investigation is carried out by means the laser interferometric method. The laser light is spilt into two beams. The first one goes through the membrane system parallelly to the membrane surface while the second, reference one goes directly to the light detecting system. The interferograms, which appear due to the interference of the two beams, are controlled by the refraction coefficient of the solute which in turn depends on the substance concentration. The analysis of the interferograms allows one to reconstruct the time-dependent concentration profiles of the substance transported across the membrane. Further one can find how NML evolves in time. We show that the time evolution of the NML thickness manifests surprisingly simple regularities.

The time dependence can be studied using the Smoluchowski (diffusion) equation. However, one has to impose two boundary conditions at the membrane surface. The first one is provided by the substance current conservation but there is *no* obvious choice of the second condition. When the membrane has a finite thickness, the diffusive transport within the membrane is often described by the Smoluchowski equation as well [6]. The diffusion constant however differs from that one which is in the regions outside the membrane. Then, one assumes [6] that the ratio of the concentrations at both sides of each of the membrane surfaces equals a constant which is a free parameter. We find this approach as not very satisfactory. Since a real membrane is not homogeneous and its internal structure is rather complicated, using the diffusion equation inside the membrane is rather questionable. The boundary condition, which fixes the concentration ratios, is introduced without physical justification. When the membrane thickness goes to zero, the membrane selectivity vanishes entirely, and, consequently, the approach is hardly useful for very thin membranes. In the series of papers [7–9],

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[a] e-mail: `dworecki@pu.kielce.pl`
[b] e-mail: `tkoszt@pu.kielce.pl`
[c] e-mail: `mrow@fuw.edu.pl`

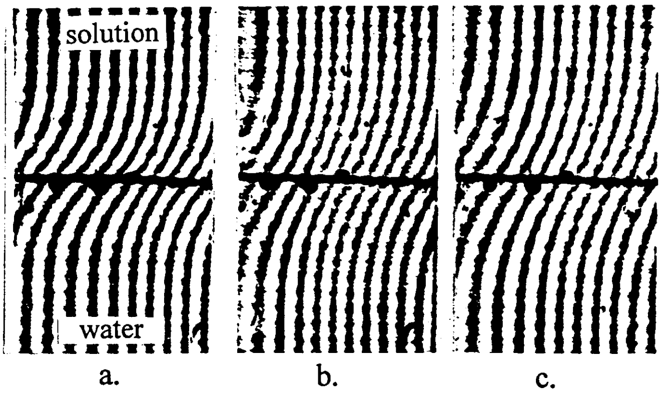

Fig. 1. The interferograms which are analyzed to obtain the concentration profiles. There is initially uniform ethanol solution of the concentration 125 mol/m^3 in the upper part of the measurement cuvette. The interferograms are taken at several values of time: (a) 240 s, (b) 600 s, and (c) 1200 s.

one of us has developed the approach which is also based on the Smoluchowski equation. The boundary condition is well motivated and the membrane can be treated as an infinitely thin wall characterized by the permeability coefficient. The time dependence of NML can be easily derived and, as we show here, it naturally describes the experimental data.

The paper is organized as follows. In Section 2 we present the experimental procedure with the results on the concentration profiles and the near membrane layers. Section 3 is devoted to theoretical considerations. The solution of the Smoluchowski equation is found and the time dependence of the NML thickness is derived. The predictions of our theoretical model are compared with the experimental data. We summarize our study in Section 4.

2 Experiment

The membrane system under study is the cuvette of two chambers separated by the horizontally located membrane. Initially, we fill the upper (lower) chamber with the aqueous solution of the ethanol while in the lower (upper) one there is pure water. Then, the ethanol diffuses to the lower (upper) chamber. Since the concentration gradients are in the vertical direction only, the diffusion is expected to be one dimensional (along the axis x). In other words, the ethanol concentrations are assumed to be uniform in the planes parallel to the membrane.

As already mentioned, we employ the laser interferometric method to measure the time-dependent concentration profiles in the membrane system. Let us note that the measurement does not disturb the system under study. The experimental set-up is described in [10,11]; here we only mention that it consists of the measurement cuvette with the membrane, the Mach-Zehnder interferometer [12] including the He-Ne laser, TV-CCD camera, and the computerized data acquisition system.

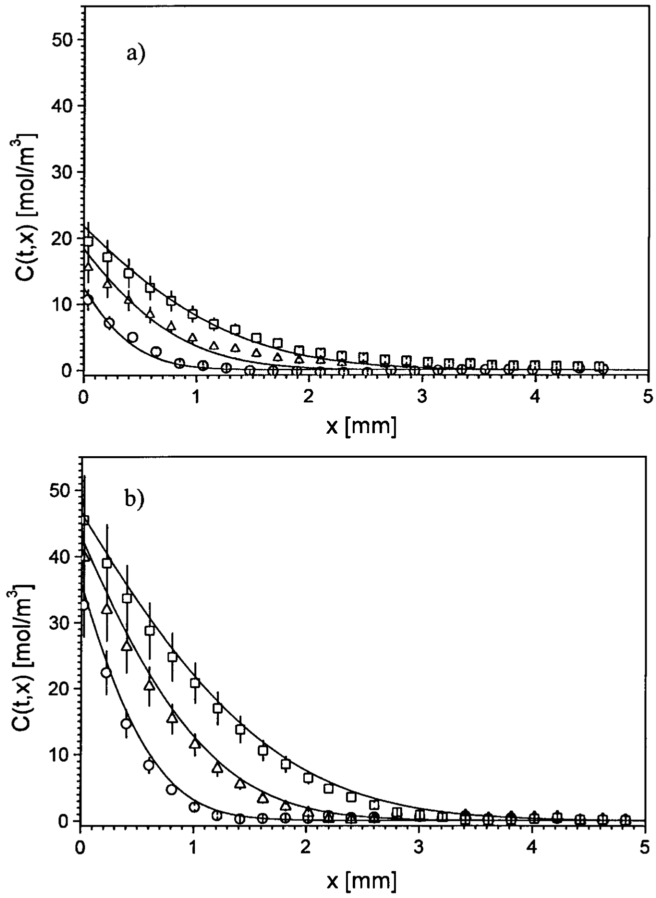

Fig. 2. The concentration profiles for $C_0 = 125$ mol/m^3 taken at several values of time: ○ 240 s, △ 600 s, and □ 1200 s. The permeability of the membrane from (a) is significantly smaller than that from (b). The solid lines represent the Smoluchowski equation solution with $D = 0.76 \cdot 10^{-9}$ m^2/s and $\delta = 0.51$ for (a) and $\delta = 0.11$ for (b). The theoretical curves are shifted to the left in (a) and (b) by 0.3 mm (see text).

The interferograms are sensitive to the variation of the refraction coefficient within the membrane system and consequently to the concentration gradients. When the solute is uniform the interference fringes are straight and they bend when the concentration gradient appears. The example of the interference images is shown in Figure 1. The substance concentration at x is determined by the deviation d of the fringes from their straight line run. Since the relation between the concentration C and the refraction coefficient is assumed to be linear, we have

$$C(t,x) = C_0 + \alpha \frac{\lambda d(t,x)}{hf} ,$$

where C_0 is the initial substance concentration; α is the proportionality constant between the concentration and the refraction index, $\alpha = 3.19 \cdot 10^5$ mol/m^3 for the ethanol aqueous solution; λ is the wavelength of the laser light; h denotes the distance between the fringes in the field where they are straight lines; f is the thickness of the solution layer in the measurement cuvette. Recording the interferograms with a given time step one can reconstruct the time-dependent concentration profiles.

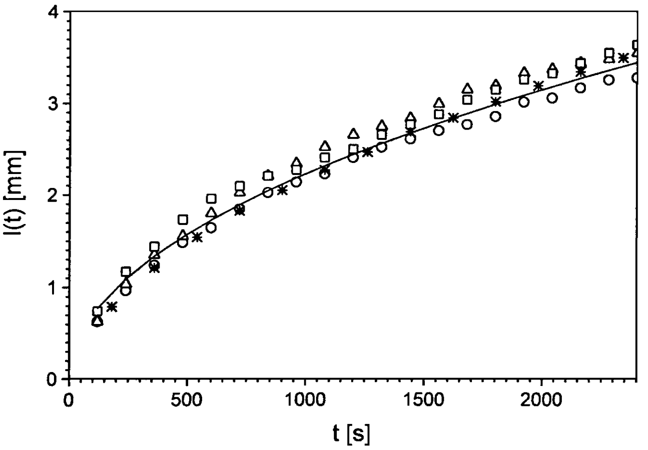

Fig. 3. Time evolution of the near membrane layer for $k = 12.5$ and several values of the initial ethanol concentrations: ○ 125 mol/m^3, △ 250 mol/m^3, □ 500 mol/m^3, and ⋆ 750 mol/m^3. The solid line represents $l(t) = a\sqrt{t}$ with $a = 6.8 \cdot 10^{-5}$ m/s$^{1/2}$.

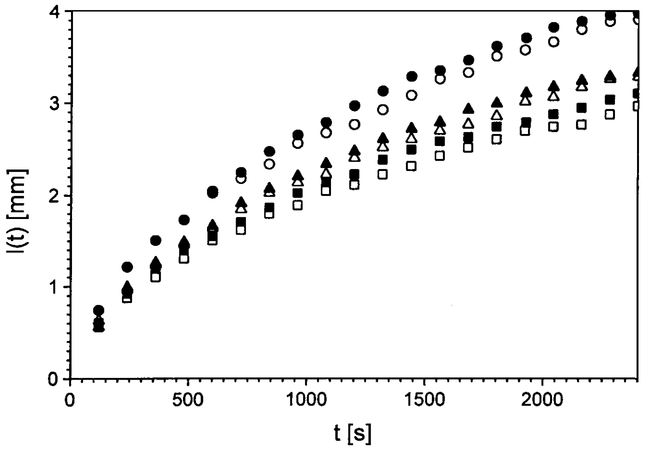

Fig. 4. Time evolution of the near membrane layer for two membranes of different permeabilities and three values of k. The filled (open) symbols correspond to the more (less) permeable membrane; □, △ and ○ refer to k equal to, respectively, 8.33, 12.5 and 33.3. The initial concentration is 125 mol/m^3.

Since the specific weight of the ethanol is significantly lower than that of water, one observes the alcohol convective motion when the ethanol is initially in the lower chamber [11]. To deal with a diffusive regime we have further studied only the configuration with the ethanol being initially in the upper chamber.

We have measured the profiles for several values of the initial ethanol concentration and for two cellulose membranes of different permeabilities. The membrane thickness is, respectively, 0.17 mm and 0.01 mm. In Figure 2 we present the concentration profiles taken at different moments of time. Repeating several times the measurements at the same conditions we tasted the stability of our results. While the shape of the concentration profiles has appeared to be rather stable, the absolute normalization has varied by about 15%. The error bars shown in Figure 2 just correspond to this uncertainty.

Having the profiles one can define the near membrane layer (NML). When the substance diffuses across the membrane into the pure solvent, the thickness l of NML is defined as a length over which the concentration decreases k times, *i.e.*

$$C(t, x = 0) = kC(t, x = l) \;, \qquad (1)$$

with $x = 0$ being the membrane position[1].

Since k is an arbitrary number we have found the thickness of NML from the earlier obtained concentration profiles for three values of k: 8.33, 12.5 and 33.3. As already mentioned, our concentration profile measurements suffer from the absolute normalization uncertainty of about 15%. However, this uncertainty does *not* influence the NML thickness because the absolute normalization coefficient

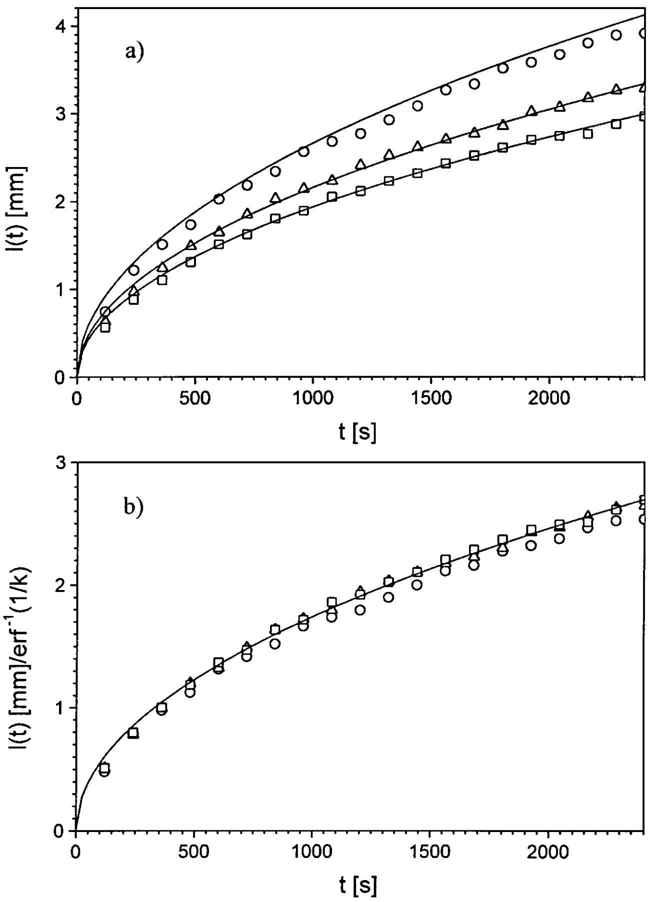

Fig. 5. The k-dependence of the near membrane layers. The data in (b) are those from (a) rescaled by a factor $\mathrm{erfc}^{-1}(1/k)$. □, △ and ○ refer to k equal to, respectively, 8.33, 12.5 and 33.3. The initial concentration is 125 mol/m^3. The solid lines in (a) represent $l(t) = a\sqrt{t}$ with a equal to, respectively, $8.4 \cdot 10^{-5}$ m/s$^{1/2}$, $6.8 \cdot 10^{-5}$ m/s$^{1/2}$ and $6.1 \cdot 10^{-5}$ m/s$^{1/2}$. The line in (b) corresponds to $2\sqrt{Dt}$ with $D = 0.76 \cdot 10^{-9}$ m^2/s.

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[1] If the substance diffuses to the region of the nonzero initial concentration C_0, the definition (1) is generalized as $C(t, 0) - C_0 = k\big[C(t, l) - C_0\big]$. This form can be applied to the layers on both sides of the membrane.

drops out entirely in the NML defintion (1). Therefore, the estimated errors of the data points shown in Figures 3, 4 and 5 are comparable to the size of the data point symbols. As seen in Figures 3, 4 and 5, NMLs manifest the remarkable properties. The NML thickness appears to be independent, within the experimental errors, of the initial concentration (Fig. 3) and of the membrane permeability (Fig. 4). As shown in Figures 3 and 5, the thickness grows in time as $\sqrt{t}$. In the next section we will discuss the NML thickness from the theoretical point of view.

3 Theory

The concentration profile $C(t,x)$ is expected to satisfy the Smoluchowski equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x} + vC \right) ,$$

where D is the diffusion coefficient and v represents the velocity due to the gravitational force. To keep our theoretical approach as simple as possible, we neglect the second term in the right-hand side of the equation and treat D as a constant. Then, we get

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \; . \tag{2}$$

Since the membrane is treated as an infinitely thin, partially permeable wall one needs two boundary conditions at the wall to solve equation (2). While the first one expresses the substance current conservation and reads

$$J(t, x = 0^-) = J(t, x = 0^+) \; , \tag{3}$$

where $J(t,x) = -D(\partial C/\partial x)$, there is no obvious choice of the second condition.

Let us consider what can be learnt about the missing condition from the experimental regularities discussed in the previous section. The fact that the thickness of the near membrane (1) is independent of C_0 is simply due to the linearity of the diffusion equation (2). The independence from the membrane permeability is much less trivial. One observes that the diffusion constant D is the only dimensional parameter in equations (2,3). Consequently, if D is indeed the only dimensional parameter in the problem, a solution of the diffusion equation (2) depends on x^2/Dt which is the only dimensionless combination of D, x and t. Then, any length, in particular $l(t)$, must be proportional to $\sqrt{t}$ in agreement with the experimental data from Figures 3 and 5. However, the dimensional parameter can be introduced to the problem through the boundary condition. For example, the dimensional membrane permeability parameter κ appears in the condition of the form

$$J(t, x = 0) = \kappa\Big[C(t, x = 0^+) - C(t, x = 0^-)\Big] \; . \tag{4}$$

Then, the solution of the diffusion equation, which satisfies equation (4), depends not only on x^2/Dt but on other dimensionless combinations such as $\kappa t/x$. Consequently, the thickness of the near membrane layer is no longer proportional to $\sqrt{t}$ and is κ-dependent.

We conclude the above dimensional analysis as follows. If one assumes that the near membrane layer is *strictly* independent of the membrane permeability and $l(t)$ is *strictly* proportional to $\sqrt{t}$ the missing boundary condition must be free of a dimensional parameter. Such a condition has been introduced and discussed in the series of papers of one of us [7–9]. It reads

$$J(t, x = 0) = (1 - \delta)\, J^0(t, x = 0) \; , \tag{5}$$

where $J(t,x)$ is the substance current in the membrane system while $J^0(t,x)$ denotes the current in the identical system but with removed membrane; δ is the dimensionless membrane permeability coefficient, $0 \le \delta \le 1$. The boundary condition (5) has been deduced [8] from the Green's functions obtained by means of the generalized method of images. The coefficient δ gives the probability that a diffusing particle will pass the membrane under the condition that it approaches the membrane.

As already mentioned, the solute concentration is initially zero in one chamber of the membrane system and it is finite and uniform in the other one, *i.e.*

$$C(t = 0, x) = \begin{cases} C_0 & \text{for} \quad x < 0 \; , \\ 0 & \text{for} \quad x > 0 \; . \end{cases}$$

The solution of equation (2), which satisfies the boundary conditions (3, 5) and the above initial one, is

$$C(t,x) = C_0\left[1 - \frac{1-\delta}{2}\,\mathrm{erfc}\Big(-\frac{x}{2\sqrt{Dt}}\Big)\right] \qquad \text{for} \;\; x < 0 \; , \tag{6}$$

and

$$C(t,x) = C_0\frac{1-\delta}{2}\,\mathrm{erfc}\Big(\frac{x}{2\sqrt{Dt}}\Big) \qquad \text{for} \;\; x > 0 \; , \tag{7}$$

with $\mathrm{erfc}(x)$ being the complementary error function defined as

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty \mathrm{d}\eta\, e^{-\eta^2} \; .$$

Substituting the solution (7) into the layer thickness definition (1) we get

$$l(t) = a\,\sqrt{t} \; , \tag{8}$$

where the coefficient a depends solely on D and k as

$$a = 2\sqrt{D}\,\mathrm{erfc}^{-1}\Big(\frac{1}{k}\Big) \; . \tag{9}$$

As expected, the relation (8) agrees with the experimental results shown in Figures 3, 4 and 5. Indeed, the dependence on the initial concentration C_0 and the membrane permeability coefficient δ, which is present in the solution (7), drops out entirely in equation (8). One also sees that equation (9) determines the k-dependence of $l(t)$.

In Figure 5 we show that the near membrane layer indeed scales with k as $\mathrm{erfc}^{-1}(1/k)$.

In our previous studies [10,7] we took the diffusion coefficient from the literature to fit the data. One sees that our formula (8) solely depends on the diffusion coefficient once the k-dependence is eliminated, see Figure 5b. Therefore, D can be obtained directly from our data by means of a single parameter fit. In this way we get $D = 0.76 \cdot 10^{-9}$ m^2/s. The diffusion coefficient is known to be sensitive to the temperature and the ethanol concentration in water. D equals $0.84 \cdot 10^{-9}$ m^2/s at the temperature 283 K and grows to $1.24 \cdot 10^{-9}$ m^2/s at 298 K [13]. The two values correspond to the zero ethanol concentration. Since the diffusion coefficient decreases with the solute concentration our value of D, which is measured at finite concentration and the temperature of about 290 K, seems to be compatible with the mentioned data.

Since the value of D is fixed, there is only one parameter δ to be fitted when the solution (7) is compared with the experimental concentration profiles. The resulting theoretical curves, which are shown in Figure 2, describe the data quite well but a comment is in order here. Our theoretical approach assumes that the membrane is infinitely thin while the membranes which have been used in the measurements are, obviously, of the finite thickness. Further, there is a near membrane dead zone where the concentration measurement is unreliable or even impossible. The dead zone appears due to the imperfection of the cuvette edge and the small deformations of the membrane during the measurements. The latter effect, which is much more important for the thinner membrane, is not very well controlled in our set-up and it leads the substance stirring in the very vicinity of the membrane surface. To take into account all these effects we have shifted the theoretical curves from Figure 2 by 0.3 mm to the left. This is, of course, not a quite satisfactory procedure and in the future studies we intend to resolve the problem in a systematic way. The main objective of this study, however, are not the concentration profiles but the near membrane layers. We have carefully checked that the time dependence of NML is influenced insignificantly when the solution (7) is shifted by 0.3 mm. Thus, the near membrane layers are not only insensitive to the overall normalization error shown in Figure 2 but to the dead zone problem as well.

4 Discussion and summary

The solution of the diffusion equation found with the boundary condition (5) is identical with the solution which satisfies the boundary condition

$$C(t, x = 0^-) = \gamma\, C(t, x = 0^+)\,, \tag{10}$$

where the dimensionless parameter γ, which characterizes the membrane, is related to δ as

$$\gamma = \frac{1-\delta}{1+\delta}\,.$$

Therefore, the formula (8) can be obtained within the boundary condition (10) as well.

Let us mention that the boundary condition (5) applies not only for a pure diffusion. When the convection is present in the system and there is a respective term in equation (2) one easily generalizes equation (5) [7,8] and introduces the parameters which separately determine, as in the Kedem-Katchalsky approach [14], the membrane permeability with respect to the diffusion and to the convection. On the other hand, we see no simple way to generalize equation (10) to distinguish between the diffusive and convective membrane permeability. Therefore, we would like to stress that the equivalence of equations (5) and (10) holds only for a pure diffusion regime.

We have argued that the boundary condition must be free of a dimensional parameter if the near membrane layer is *strictly* independent of the membrane permeability and $l(t)$ is *strictly* proportional to $\sqrt{t}$. Unfortunately, we cannot exclude slight deviations from the regularities. In fact, the small systematic differences between the filled and open symbols seen in Figure 4 might signal the effect. Then, the boundary condition different than (5) or (10) can be consistent with the data as well. We intend to perform a careful study of the issue in future. It will demand an improvement of the experimental procedures and an extensive theoretical analysis. In the very recent paper [15] we have already discussed in detail the boundary condition (4) and explicitly confirmed the results of the dimensional analysis presented here. We plan to confront the condition (4) and some other ones against the data.

At the end let us summarize our study. Using the interferometric method the concentration profiles have been measured for the aqueous solution of the ethanol diffusing across the membrane into pure water. The time evolution of the near membrane layer has been then analyzed. The thickness of the layer, which is defined as a length where the concentration drops k times, appears to grow in time as $a\sqrt{t}$ with the proportionality coefficient a being remarkably independent of the initial ethanol concentration and of the membrane permeability. While the independence of C_0 is the result of the problem linearity, the origin of the cancellation of the membrane permeability is much less trivial. Theoretical analysis performed within the approach proposed by one of us has shown that a depends only on k and the diffusion constant D due to the specific choice of the boundary condition at the membrane. We have used this fact to obtain the numerical value of D fitting the experimental time dependence of the near membrane layer. Then, the experimentally found concentration profiles have been fitted by the solution of the Smoluchowski equation. The membrane permeability coefficient δ is then a single fit parameter.

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