APPLICATION OF TWO-MEMBRANE SYSTEM TO MEASURE SUBDIFFUSION COEFFICIENTS*

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Comparing the experimental results to theoretical functions, we estimate the subdiffusion coefficient of PEG2000 in agarose gel. The experiment was performed with the two-membrane system where thin membranes separated homogeneous solution of PEG2000 for pure solvent at an initial moment. The theoretical function was found by solving analytically the subdiffusion equation.

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1. Introduction

The subdiffusion is a transport process where the mean square displacement of a Brownian particle is a power function of time [1]

$$\left\langle \Delta x^2(t) \right\rangle = \frac{2D_\alpha}{\Gamma(1+\alpha)}\, t^\alpha \,, \tag{1}$$

where D_α is the subdiffusion coefficient measured in the units $\mathrm{m}^2/\mathrm{s}^\alpha$ and α is a subdiffusion parameter which obeys $0 < \alpha < 1$. The case of $\alpha = 1$ corresponds to the normal diffusion. The subdiffusion occurs in a medium where a mobility of the particle is strongly hindered due to the internal structure of the medium, as for example in porous media or gels [1, 2]. The subdiffusion is described by the equation [1]

$$\frac{\partial C(x,t)}{\partial t} = D_\alpha \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2 C(x,t)}{\partial x^2} \,, \tag{2}$$

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where $C(x,t)$ denotes the concentration of transported substance. The Riemann–Liouville fractional time derivative is defined for $\alpha > 0$ as

$$\frac{\partial^\alpha f(t)}{\partial t^\alpha} = \frac{1}{\Gamma(n-\alpha)} \frac{\partial^n}{\partial t^n} \int_0^t dt' \frac{f(t')}{(t-t')^{1+\alpha-n}}\,, \tag{3}$$

where the integer number n fulfills the relation $n-1 < \alpha \leq n$.

Till now, there were only a few methods to extract the subdiffusion coefficient from experimental data [2, 3]. We mention here the method of measuring time evolution of near membrane layers in the one membrane system [2], and the study of [3] where the subdiffusion coefficient was determined experimentally for the first time — the interdiffusion of heavy and light water in a porous medium was observed by means of nuclear magnetic resonance.

In our paper we exploit the system in which the homogeneous solution of substance under study is divided into three parts by two thin membranes. At the initial moment the substance is present only in the middle part of the system whereas the external parts contain only the pure solvent. We experimentally measure the concentrations in the middle part of the system and next we compare the experimental data with the solutions of the subdiffusion equation where D_α and the parameters of membrane permeability λ_1 and λ_2 are the fit parameters.

2. Experiment

The measurement has been conducted in a membrane system, shown in Fig. 1. The membrane system under study is a cell with three glass cuvettes separated by horizontally located membranes. Initially, we fill the lower and upper cuvettes with the agarose hydrogel solvent while in the middle

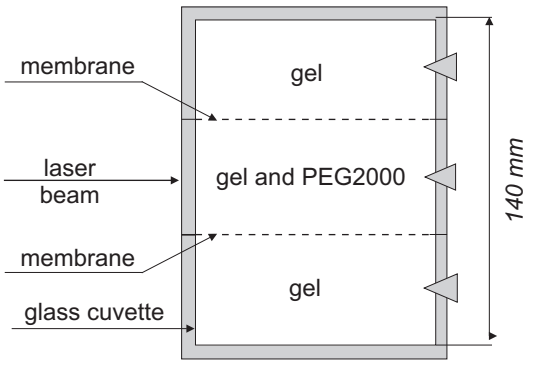

Fig. 1. Experimental setup. Detailed description is in the text.

cuvette there is an aqueous gel solution of transported substance. Then, the substance diffuses from the middle cuvette to the exterior ones through the membranes. Since the concentration gradients are in the vertical direction only, the diffusion is expected to be one-dimensional (along the axis x). The substance concentration is measured by means of the laser interferometric method [4, 5]. The output of a 15 mW He–Ne laser is spatially filtered and split into two beams. The first beam goes through the membrane system parallel to the membrane surface while the second reference beam 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 from middle cuvette across the top and bottom membranes to the outside cuvettes. We note that measurement does not disturb the system under study. The experimental set-up is described in detail in the previous papers [4–6]. Here we only mention that it consists of the cuvette with membrane, the Mach–Zehnder interferometer including the He–Ne laser, TV–CCD camera, and the computerized data acquisition system. For each measurement we prepared two gel samples: the pure gel 2% (w/v) water solution of agarose and the same gel dripped by the solute of polyethylene glycol 2000 (PEG). PEG2000 is a polymer of general formula [HO-$(CH_2$-$CH_2)_n$-O] where $n \cong 40$. The concentration of solutes in the gel was fixed to be 0.0075 mol/dm^3. The three cuvette of the membrane system were then filled with the samples and the processes of the solute transport through membranes started. The agarose gel water solvent was prepared by dissolving agarose powder (Sigma) in 90° C water. All experiments were performed at room temperature $(22 \pm 0.5)^\circ$ C. The agarose gels are assumed to be inert to the solute at our experimental conditions. The polymer membranes (which are of the thickness $20\,\mu$ m) were needed for two reasons. It initially separated the homogenous solute gel solution in one cuvette from the pure gels in another ones. It also precisely fixed the geometry of the whole system. At the beginning of the experiment the cuvettes were pressed to each other in close contact so that the diffusion across membranes was initiated. The change of solute concentration in the middle cuvette during the experiment involves variation in the refractive index of the gel solution. The interferograms provide quantitative measurements of the solution refractive index within the membrane system. The measurement of the refractive index of the gelled solutions containing different concentration of the solute under study enabled us to calculate the values of the concentration at different distances from the membranes and at different times inside of the middle cuvette. If the solution in the observation cell is homogeneous, the fringes are straight, parallel, and evenly

spaced. The solute concentration at x is determined by deflection of fringes $d(x,t)$ from their straight line run. Since the relation between the concentration $C(x,t)$ and the refraction coefficient $n(x,t)$ is assumed to be linear, we have:

$$C(x,t) = C_0 \pm \frac{ald(x,t)}{hf}\,, \tag{4}$$

where C_0 is the initial substance concentration in middle cuvette of the membrane system, a is the proportionality factor between the concentration, and the refraction index, l is the wavelength of the laser light, h denotes the distance between the fringes in the area where they run parallel, f is the thickness of the solution layer in the measurement cuvette.

3. Theory

The system under consideration is assumed to be homogeneous in a plane perpendicular to the x axis, thus it is effectively one-dimensional. The system has three parts with two infinitely thin partially permeable membranes located at $x = x_1$ and $x = x_2$ (see Fig. 2). The walls divide the system into three homogeneous parts which in the following will be denoted as 1 for $x < x_1$, M for $x_1 < x < x_2$ and 2 for $x > x_2$.

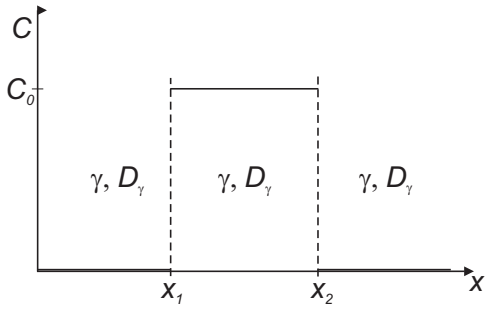

Fig. 2. The schematic view of the system under consideration at an initial moment.

We choose the initial condition as

$$C(x,0) = \begin{cases} 0\,, & x < x_1\,, \\ C_0\,, & x_1 < x < x_2\,, \\ 0\,, & x > x_2\,. \end{cases} \tag{5}$$

The boundary conditions demand the constant ratio of the concentrations at two sides of the membrane

$$\frac{C_1(x_1^-,t)}{C_M(x_1^+,t)} = \lambda_1\,, \qquad \frac{C_2(x_2^+,t)}{C_M(x_2^-,t)} = \lambda_2\,, \tag{6}$$

the dimensionless parameters λ_1 and λ_2 control the permeability of the membranes. These boundary conditions are supplemented by the equations expressing the continuity of the fluxes at the membrane surfaces

$$J_1(x_1^-,t) = J_M(x_1^+,t)\,, \qquad J_M(x_2^-,t) = J_2(x_2^+,t)\,. \tag{7}$$

The boundary conditions (6) and (7) were already used to model the (sub)-diffusion in membrane system [7].

The concentration profile $C(x,t)$ of the system is found by solving Eq. (2) with the initial conditions (5) and boundary ones (6) and (7) by means of the Green's function and Laplace transform. The solution for the middle part M of the system reads

$$\begin{aligned}
C_M(x,t) &= C_0 - \frac{C_0}{2}\left[f_{-1,\gamma/2}\left(t;\frac{x-x_1}{\sqrt{D_\gamma}}\right) + f_{-1,\gamma/2}\left(t;\frac{x_2-x}{\sqrt{D_\gamma}}\right)\right] \\
&+ C_0\sum_{i=0}^{\infty}\left(\frac{(1-\lambda_1)(1-\lambda_2)}{(1+\lambda_1)(1+\lambda_2)}\right)^i\left\{\frac{1-\lambda_1}{2(1+\lambda_1)}f_{-1,\gamma/2}\left(t;\frac{2di+(x-x_1)}{\sqrt{D_\gamma}}\right)\right. \\
&+ \frac{1-\lambda_2}{2(1+\lambda_2)}f_{-1,\gamma/2}\left(t;\frac{2di+(x_2-x)}{\sqrt{D_\gamma}}\right) \\
&- \frac{\lambda_1(1-\lambda_2)}{(1+\lambda_1)(1+\lambda_2)}f_{-1,\gamma/2}\left(t;\frac{2di+(2x_2-x_1-x)}{\sqrt{D_\gamma}}\right) \\
&- \frac{\lambda_2(1-\lambda_1)}{(1+\lambda_1)(1+\lambda_2)}f_{-1,\gamma/2}\left(t;\frac{2di+(x_2-2x_1+x)}{\sqrt{D_\gamma}}\right) \\
&- \frac{(1-\lambda_1)(1-\lambda_2)}{2(1+\lambda_1)(1+\lambda_2)}\left[f_{-1,\gamma/2}\left(t;\frac{2d(i+1)+(x-x_1)}{\sqrt{D_\gamma}}\right)\right. \\
&\left.\left.+f_{-1,\gamma/2}\left(t;\frac{2d(i+1)+(x_2-x)}{\sqrt{D_\gamma}}\right)\right]\right\}.
\end{aligned} \tag{8}$$

4. Comparison of experimental and theoretical functions

In Fig. 3 we present the experimentally measured concentrations in the middle part of the system. The theoretical functions, which also show there, are calculated for $C_0 = 0.0075\,\mathrm{mol/dm^3}$, $D_\alpha = 2.55\times10^{-10}\,\mathrm{m^2/s^{0.86}}$ and $\alpha = 0.86$. The subdiffusion parameter α was found analyzing the time evolution of the near membrane layer by means of the method presented in [2]. As we mention above D_α and $\lambda_{1,2}$ were treated as fit parameters.

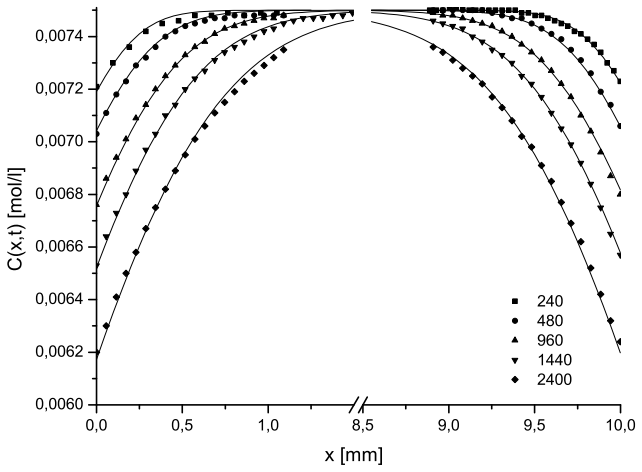

Fig. 3. The concentrations profiles for the times given in the legend. Symbols represent the experimental data, continuous lines represent the theoretical functions.

However, the parameter $\lambda_{1,2}$ appears to be a function of time. For the time interval $(0, 2400)$ s the function of $\lambda_{1,2}$ can be approximate by the linear functions (Fig. 4) and read as $\lambda_1(t) = 7.98 \times 10^{-5}t + 0.028$ and $\lambda_2(t) = 7.90 \times 10^{-5}t + 0.023$.

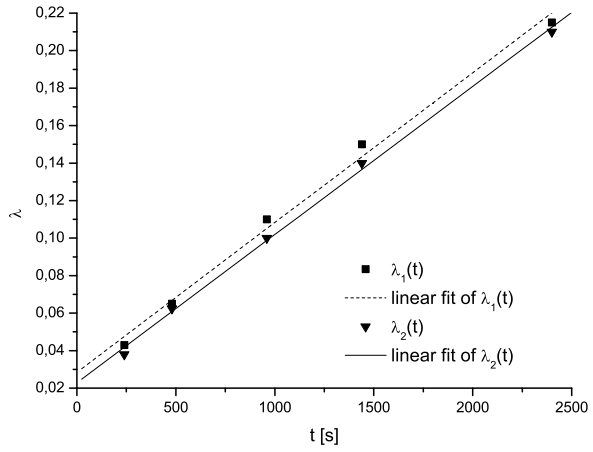

Fig. 4. Time dependence of λ_1 and λ_2.

5. Final remarks

We have obtained the subdiffusion coefficient of PEG2000 in 2% agarose gel equal to 2.55×10^{-10} m^2/s$^{0.86}$. We have estimated the error of the fitted parameters as 10% (as well as in the study presented in [2]). The order of this coefficient is in agreement with the orders of subdiffusion coefficients for glucose and sucrose in agarose gel [2]. The experimental data are well described by the solution of the Eq. (2) with the boundary conditions (6) and (7) where λ_1 and λ_2 are assumed to be constant. To obtain satisfactory fit, it was needed to assume that the parameters λ_1 and λ_2 linearly grow with time. We explain this fact observing that the permeability of the membranes increase in time due to the decrease of the concentration near the membranes. We add that the theoretical model of transport in the two-membrane system where the permeability of the membrane changes with time will be discussed elsewhere [8].

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REFERENCES

[1] R. Metzler, J. Klafter, *Phys. Rep.* **339**, 1 (2000); *J. Phys.* **A37**, R161 (2004).

[2] T. Kosztołowicz, K. Dworecki, S. Mrówczyński, *Phys. Rev. Lett.* **94**, 170602 (2005); *Phys. Rev.* **E71**, 041105 (2005).

[3] A. Klemm, R. Metzler, R. Kimmich, *Phys. Rev.* **E65**, 021112 (2002).

[4] K. Dworecki, *J. Biol. Phys.* **21**, 37 (1995).

[5] K. Dworecki, S. Wąsik, A. Slęzak, *Physica A* **326**, 360 (2003).

[6] K. Dworecki, *Physica A* **359**, 24 (2006).

[7] C. Hoogervorst, J. de Goede, J. Versluijs, J. Smit, *J. Phys. Chem.* **82**, 1318 (1978).

[8] T. Kosztołowicz, K.D. Lewandowska, K. Dworecki, in preparation.